

CRANFIELD UNIVERSITY

Ahmed Muwafaq J. Balakt

Giant Pyroelectric Properties Achieved at a Wide Temperature Range
in Lead-free Sodium Bismuth Titanate-based and Composite Ceramic
Materials

School of Aerospace, Transport and Manufacturing

PhD

Academic Year: 2016 - 2017

Supervisor: Dr. Qi Zhang; Dr. Christopher Shaw
December 2017

CRANFIELD UNIVERSITY

School of Aerospace, Transport and Manufacturing

PhD

Academic Year 2016 - 2017

Ahmed Muwafaq J. Balakt

Giant pyroelectric properties achieved at a Wide Temperature Range
In lead-free Sodium Bismuth Titanate-based and Composite Ceramic
Materials

Supervisor: Dr. Qi Zhang; Dr. Christopher Shaw
December 2017

This thesis is submitted in partial fulfilment of the requirements for
the degree of Doctor of Philosophy

© Cranfield University 2017. All rights reserved. No part of this
publication may be reproduced without the written permission of the
copyright owner.

ABSTRACT

Health and environmental concerns have universally increased in importance during the last several decades. In the material science sphere, researchers are racing to replace poisonous, PZT-based pyroelectric materials with non-hazardous environmentally friendly ones, which simultaneously possess enhanced properties and provide the high performance.

Beside environmental issues, the lower pyroelectric response and narrow operating temperature range have been identified as significant drawbacks of presently used lead-free pyroelectric materials for future diverse advanced industrial applications.

One of the possible, most challenging and highly promising solutions to those industrial problems is utilizing composite ceramic materials (*CCMs*). Those materials combine the best raw materials properties and the sophisticated design. Therefore, they provided better performance compared to the original materials.

The major aim of this systematic study is to investigate and improve the pyroelectric properties of lead-free sodium bismuth titanate modified by barium titanate ceramics, $\text{Na}_{1/2}\text{Bi}_{1/2}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ (*NBT-0.06BT*), at the morphotropic phase boundary (*MPB*) over a wide range of frequencies and temperatures. The secondary goal is to control and lower the first phase transition temperature, termed depolarisation temperature (T_d), to around room temperature (*RT*). Three different techniques were used: (1) modifying the composition by altering A-site element contents; (2) doping the A- and/or B-sites with selective elements; and (3) forming composite pyroelectric ceramic material (*CPCM*).

This study confirms that NBT-0.06BT at the MPB regains its critical composition and is sensitive to any compositional modification. These changes in NBT-0.06BT composition can shift its structure slightly away from the MPB area and will considerably change its pyroelectric properties.

It was found that the pyroelectric properties at RT and T_d were significantly enhanced by tailoring the NBT-0.06BT composition. Likewise, T_d was controlled

and decreased by implementing the same techniques as used to tailor the material composition.

This study succeeded in increasing the range of the pyroelectric coefficient temperature response from one sharp peak at an exact temperature to a broad peak, which extends to around 25 °C with maximum pyroelectric coefficient ($7.10 \times 10^{-4} \text{ C.m}^{-2}.\text{°C}^{-1}$ at 40 °C) by developing CPCM. This significant achievement can expand considerably the range of the pyroelectric working temperature and is, therefore, both useful and valuable for a wide variety of pyroelectric applications.

Keywords:

Electroceramic, Lead-free ceramics $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$, Morphotropic phase boundary (*MPB*), Modified A-site elements of $\text{N}_x\text{B}_y\text{T-}0.06\text{B}_z\text{T}$, A or B site doped NBT-0.06BT, both sites doped NBT-0.06BT, Composite pyroelectric ceramic materials (*CPCM*); Depolarization temperature (T_d), Pyroelectric properties, Figure of merits (*FOMs*).

ACKNOWLEDGEMENTS

First of all, I wish to thank my country Republic of Iraq represented by the Ministry of Higher Education and Scientific Research/ Iraq, which gave me this opportunity to do this PhD research.

I am sincerely thankful to my PhD supervisor Dr. Qi Zhang, for his efforts, encouragement, right advice, and his supporting throughout my PhD study.

I would like also to thanks Dr. Christopher Shaw, my second supervisor, who gives me the technical support and a lot of valuable advices during my PhD work.

I am heartily would like to say a special thanks to my angel Farah Al-Khafaji, my wife, which supports me, provides constant comfort and enables me to carry on and passed all the difficult in our life. Without her great support this PhD study would not achieved. Thus, this work is dedicated to her.

Also, I am kindly would like to thank my sons, Ali, Mustafa, and Mohammed for their patients and endure the burdens of my study journey.

My parents, I would like to express a very special thanks, warm gratitude and respect for their encouragement throughout my life.

I wish to express my appreciation to my family and my friends especially Dr. Shamal Mohammed who give me a good support during my PhD study.

Finally, I would like to say thanks to Dr. Yan Haixue and Mr. Wu Jiyue in Queen Mary University London for collaboration, also to Dr. Quentin Lonne and Mr, Andrew Stallard they provided great help during my PhD work.

TABLE OF CONTENTS

ABSTRACT	i
ACKNOWLEDGEMENTS	iii
LIST OF FIGURES	ix
LIST OF TABLES	xv
LIST OF ABBREVIATIONS.....	xviii
1 Introduction and Literature Review	1
1.1 Background.....	1
1.2 Ferroelectricity and Related Phenomena	3
1.2.1 Dielectric Materials.....	3
1.2.2 Classification of materials based on Symmetry Principle.....	6
1.2.3 Piezoelectric Materials	7
1.2.4 Pyroelectric Materials.....	8
1.2.5 Ferroelectric Materials:	16
1.3 Aim and Objectives.....	37
1.4 Thesis Structure.....	38
1.5 References	41
2 Experimental Procedure and Material Characterisation	61
2.1 Introduction	61
2.2 Synthesis Procedure.....	61
2.2.1 CSSR	62
2.2.2 Preparation of sodium bismuth titanate modified by barium titanate materials and dopants targeting A and B sites	66
2.3 Characterisation Techniques.....	74
2.3.1 X-Ray Diffraction (<i>XRD</i>).....	74
2.3.2 Scanning Electron Microscopy (<i>SEM</i>).....	75
2.3.3 Energy Dispersive analysis (<i>SEM-EDS</i>) or Energy Dispersive X-ray spectroscopy (<i>SEM-EDX</i>)	75
2.3.4 Dielectric Characterisations	75
2.3.5 Pyroelectric Characterisations	76
2.4 References	79
3 Investigation of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ as a potential pyroelectric material.....	81
Abstract.....	81
3.1 Experimental	81
3.2 Results and discussion	81
3.2.1 Microstructure	81
3.2.2 Dielectric properties	85
3.2.3 Pyroelectric properties	91
3.3 Conclusion	93
3.4 References	94

4 Identification of the Morphotropic Phase Boundary Composition in the (1-x)Na _{0.5} Bi _{0.5} TiO ₃ -xBaTiO ₃ , 0.05≤x≤0.08.	99
Abstract.....	99
4.1 Experimental.....	99
4.2 Results and discussion.....	99
4.2.1 Effects of the extra barium titanate (BT) content on microstructure..	99
4.2.2 Effects of the extra barium titanate (BT) content on dielectric properties	103
4.2.3 Effects of extra barium titanate (BT) content on depolarization temperature.....	108
4.2.4 Effects of extra barium titanate (BT) content on pyroelectric properties	113
4.3 Conclusion	118
4.4 References	119
5 Modifying the A-site of the Na _{0.5} Bi _{0.5} TiO ₃ -0.06BaTiO ₃ by changing its elements contents.	127
Abstract.....	127
5.1 The effects of changing the Ba ²⁺ content in the Na _{0.5} Bi _{0.5} TiO ₃ -0.06Ba _{1+x} TiO ₃	127
5.1.1 Experimental	127
5.1.2 Results and discussion	128
5.1.3 Conclusion	138
5.1.4 References.....	138
5.2 Vary the Na _(x) , Bi _(y) , and Ba _(z) contents of the Na _{0.5} Bi _{0.5} TiO ₃ -0.06BaTiO ₃	143
5.2.1 Experimental	143
5.2.2 Results and discussion	143
5.2.3 Conclusion	157
5.2.4 References.....	158
6 Doping A-site of Na _{0.5} Bi _{0.5} TiO ₃ -0.06BaTiO ₃ with xLa, 0.0≤x≤1.0 (%mole). ..	164
Abstract.....	164
6.1 Experimental.....	164
6.2 Results and discussion.....	164
6.2.1 Effects of La ³⁺ on microstructure	164
6.2.2 Effects of La ³⁺ on dielectric properties.....	168
6.2.3 Effects of dopant La ³⁺ on depolarization temperature	172
6.2.4 Effects of La ³⁺ on pyroelectric properties.....	173
6.3 Conclusion	177
6.4 References	178
7 Doping B-site of Na _{0.5} Bi _{0.5} TiO ₃ -0.06BaTiO ₃ with xTa, 0.0 ≤ x ≤ 1.0 (%mole).	185
Abstract.....	185

7.1 Experimental.....	185
7.2 Results and discussion.....	185
7.2.1 Effects of Ta on Microstructure.....	185
7.2.2 Effects of Ta on dielectric properties.....	190
7.2.3 Effects of Ta on depolarization temperature.....	193
7.2.4 Effects of Ta on pyroelectric properties.....	196
7.3 Conclusion.....	202
7.4 References.....	202
8 Co-doping A and B sites of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 with different concentrations of $x\text{La}$ and $y\text{Ta}$	209
Abstract.....	209
8.1 (A) Co-doping A&B sites of NBT - 0.06BT with different concentrations of lanthanum oxide ($x\text{La}_2\text{O}_3$), $0.0 \leq x \leq 1.0$ and tantalum oxide ($y\text{Ta}_2\text{O}_3$) is $y=0.2$	209
8.1.1 Experimental.....	209
8.1.2 Results and discussion.....	210
8.1.3 Conclusion.....	227
8.1.4 References.....	228
8.2 (B) Co-doping A&B sites of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 with lanthanum oxide ($x\text{La}_2\text{O}_3$) is $x=0.5$ and different concentrations of tantalum oxide ($y\text{Ta}_2\text{O}_3$), $0.0 \leq y \leq 1.0$	235
8.2.1 Experimental.....	235
8.2.2 Results and discussion.....	235
8.2.3 Conclusion.....	250
8.2.4 References.....	250
9 Synthesis and Characterisation of the Composite Pyroelectric Ceramic Material (CCPCM) by merging two A-site ((0.2 and 0.5) %La) doped NBT - 0.06BT compositions.....	256
9.1.1 Experimental.....	256
9.1.2 Results and discussion.....	257
9.1.3 Conclusion.....	267
9.1.4 References.....	268
10 Project Overall Discussion.....	275
10.1 Microstructure.....	275
10.2 Dielectric properties.....	279
10.3 Depolarization temperature.....	280
10.4 Pyroelectric properties.....	282
10.5 References.....	284
11 Conclusions and Recommendations for Future Work.....	293
11.1 Conclusions.....	293
11.2 Recommendations for Future work.....	297
APPENDICES.....	298

Appendix A.....	298
-----------------	-----

LIST OF FIGURES

Figure 1-1: Different polarization processes [42].	5
Figure 1-2: The dependant of relative permittivity (ϵ_r) on frequency of alternative electric field showing the contributions of the different types of polarization.	6
Figure 1-3: The relation between the 32 Symmetry Groups.	7
Figure 1-4: Schematic of the relationship between spontaneous polarisation (P_s) and temperature, where, T_c is Curie temperature.	11
Figure 1-5: Schematic of perovskite structure (ABO_3); Grey spheres refer to A-site cations, smaller blue sphere are the B-site cations, and green spheres are oxygen. (a) centrosymmetric, (b and c) non-centrosymmetric [9].	12
Figure 1-6: Schematic of a pyroelectric detector element.	13
Figure 1-7: Schematic of pyroelectric a material detector element connects to the external circuit. (a) At room temperature (dT/dt) = 0. (b) Over increasing temperature (dT/dt) > 0.	15
Figure 1-8: Hysteresis loop for a ferroelectric material. P = polarization; P_s = saturation polarization; P_r = remnant polarization; E = electric field; E_c = coercive field [69].	18
Figure 1-9: Schematic of surface charge, which is associated with spontaneous polarization, (P_s) and depolarization field (E_d).	19
Figure 1-10: The schematic diagram of the six potential deformities of a tetragonal cell at temperature $T \leq T_c$ [9].	20
Figure 1-11: Schematic of domains in the tetragonal material [9].	21
Figure 1-12: (a) TEM image of NBT-0.06BT illustrates the nanometre-sized domains in a virgin state [79]. (b) 180° domains for $BaTiO_3$ [78,88].	22
Figure 1-13: Schematic of polar nanodomains.	23
Figure 1-14: (a) the ideal perovskite structure (cubic) ABX_3 , Grey ball is the A-site ions, blue balls refer to the B-site ions, and oxygen is the green ball [92]. (b) the ions in the periodic table that can occupy A, B, and X sites of the perovskite structure [100].	25
Figure 1-15: The phase diagram of the $PbTiO_3$ - $PbZrTiO_3$ system PZT [3].	27
Figure 1-16: The latest PZT phase diagram [110].	27
Figure 1-17: Schematic of the phase transitions of $BaTiO_3$ with temperature.	29
Figure 1-18: Cubic perovskite phase of $Na_{0.5}Bi_{0.5}TiO_3$ system [9].	31
Figure 1-19: NBT-xBT phase diagram [20].	33

Figure 1-20: The phase diagram of unpoled NBT-xBT [152].	35
Figure 2-1: Schematic of the synthesis steps in the solid-state reaction route [7].	63
Figure 2-2: The synthesis steps of the conventional solid-state reaction route, which was followed in this study.	64
Figure 2-3: The flow chart for the synthesis of the composite pyroelectric ceramic material (<i>CPCM</i>).	65
Figure 2-4: Picture of the samples before sintering.	68
Figure 2-5: Picture of the samples after sintering.	69
Figure 2-6: Schematic of sintering process: (a) three grains before sintering, (b) after sintering [12].	70
Figure 2-7: Schematic of the features of a SPS apparatus [15].	71
Figure 2-8: Schematic of pulsed current flow through powder particles in the SPS method [13].	71
Figure 2-9: Composite pyroelectric ceramic material (<i>CPCM</i>) pellets; (a) before removal of carbon; (b) after removal of carbon.	72
Figure 2-10: Picture of polished samples.	73
Figure 2-11: Samples electroded with silver conductive paint.	74
Figure 2-12: Photo to the device that used to measure the dielectric properties at room temperature and at different frequencies.	76
Figure 2-13: Photo to the device that used to measure the dielectric properties with increase temperature from room upto 150 °C and at different frequencies.	77
Figure 2-14: Schematic of Byer-Roundy pyroelectric rig.	77
Figure 2-15: Photo to the Byer-Roundy pyroelectric rig which used in this study.	78
Figure 3-1: (a) XRD patterns of NBT-0.06BT calcined at different temperature (b) enlargement of [111] peak split into [003] and [021] at 39.0° to 41.0°; (c) enlargement of [200] peak split into [200] and [002] at 43.0° to 48.0°. (*) unknown peak.	83
Figure 3-2: SEM morphology of Samples A to F respectively in this study.	87
Figure 3-3: The energy dispersive analysis (<i>SEM-EDS</i>) of the all samples A to F.	88
Figure 3-4: the relative permittivity of all samples (a) before and (b) after poling process.	90

Figure 3-5: The dielectric loss of all samples where (a) before and (b) after poling process.	91
Figure 4-1: (a) XRD patterns of NBT-xBT calcined at different temperature (b) enlargement of [111] peak split into [003] and [021] at 39.0° to 41.0°; (c) enlargement of [200] peak split into [200] and [002] at 45.5° to 47.5°.....	101
Figure 4-2: SEM surface morphology of the (1-x)NBT-xBT of all samples.....	103
Figure 4-3: The energy dispersive analysis (<i>SEM-EDS</i>) of NBT-xBT, (x=0.05, 0.06, 0.07, and 0.8) Samples A (a), B (b), C (c), and D (d) respectively. .	104
Figure 4-4: the relative permittivity of all samples (a) before and (b) after poling process.	106
Figure 4-5: the dielectric loss of all samples (a) before and (b) after poling process.	107
Figure 4-6: the change of the dielectric properties of the NBT-xBT with increase in temperature, (a) NBT-0.05BT; (b) NBT-0.06BT; (c) NBT-0.07BT and (d) NBT-0.08BT.....	110
Figure 4-7: the change of the $\tan\delta$ with increase in temperature and the depolarization temperature for each sample of NBT-xBT ($0.05 \leq x \leq 0.08$) materials.	111
Figure 4-8: The pyroelectric coefficient for NBT-xBT ($0.05 \leq x \leq 0.08$) and the identifying of the depolarization temperature for Sample C.....	112
Figure 5-1: XRD patterns of NBT-0.06B _(x+1) TiO ₃ ceramics where, (a) x=0.00, 0.01, 0.02, and 0.03; (b) expansion at 2θ from 39.0° to 41.0° and (C) expansion at 2θ from 45.0° to 48.0°.....	130
Figure 5-2: The SEM surface morphology, NBT-0.06B _{1+x} T where, (a) x=0.00; (b) x=0.01; (c) x=0.02; (d) x=0.03.	132
Figure 5-3: The change of the relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) with changing temperature (°C) from RT up to 150°C, for the NBT-0.06B _{1+x} T where $0.0 \leq x \leq 0.03$ from (a) to (d) in three different frequencies (1, 10 and 100) kHz. The identified of the depolarization temperature (T_d) from the dielectric loss lines at 1kHz.....	134
Figure 5-4: (a) XRD patterns of NBT-0.06BT and N _x B _y T-0.06B _z T; (b) enlargement of [111] peak split into [021] and [003] at 39.0° to 41.0°; (c) enlargement of [200] peak split into [200] and [002] at 46.0 to 48.0°.....	145
Figure 5-5: SEM surface morphology of NBT-0.06BT and N _x B _y T-0.06B _z T ceramic compositions.....	148
Figure 5-6: Relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) vs temperature for (a) NBT-0.06BT, (b) N _{0.5} B _{0.5} T-0.06BT, (c) N _{0.5} B _{0.534} T-0.06BT and (d) N _{0.5} B _{0.534} T-0.06B _{1.02} T.	150

Figure 5-7: The identification of the T_d values of all compositions by dielectric method loss tangent ($\tan\delta$) against temperature ($^{\circ}\text{C}$) for NBT-0.06BT and $\text{N}_x\text{B}_y\text{T}$ -0.06 B_zT at 1 kHz.....	151
Figure 5-8: Pyroelectric coefficient (p) vs temperature at different x,y, and z contents of NBT-0.06BT and $\text{N}_x\text{B}_y\text{T}$ -0.06 B_zT ceramics.	152
Figure 6-1: (a) X-ray diffraction patterns of NBT-0.06BT-xLa $0.0 \leq x \leq 1.0$ %; (b) enlargement of splitting [111] peak into [003] and [012] at 39.9° to 41.0° ; (c) enlargement of splitting [200] peak into [200] and [002] at 46.0° to 48.0° . *Unidentified peak.	166
Figure 6-2: SEM morphology of the NBT-0.06BT-xLa $0.0 \leq x \leq 1.0$ (%) ceramics.	167
Figure 6-3: Relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) vs temperature for NBT-0.06BT-xLa. a: $x=0.0\%$; b: $x=0.2\%$; c: $x=0.5\%$ and d: $x=1.0\%$, at three different frequencies (1, 10, and 100) kHz.	170
Figure 6-4: (a) the change of the relative permittivity (ϵ_r) and (b) loss tangent ($\tan\delta$) against temperature ($^{\circ}\text{C}$) for NBT-0.06BT-xLa, $0.0 \leq x \leq 1.0$ %, from room temperature up to 150°C at 1 kHz and T_d value of all samples.....	171
Figure 6-5: Pyroelectric coefficient (p) vs temperature ($^{\circ}\text{C}$) for the NBT-0.06BT-xLa ceramics, $0.0 \leq x \leq 1.0$ (%).....	173
Figure 7-1: (a) X-ray diffraction patterns of NBT-0.06BT-xTa, $0.0 \leq x \leq 1.0\%$. (b) enlargement of splitting [111] peak into [003] and [021] at 39.6° - 40.6° . (c) enlargement of splitting [200] peak into [200] and [002] at 46.0° – 47.5°	187
Figure 7-2: SEM surface morphology of the NBT-0.06BT-xTa, $0.0 \leq x \leq 1.0$ % ceramics.	189
Figure 7-3: The change of the relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) with temperature for Samples A to D at three different frequencies (1, 10, and 100) kHz.	193
Figure 7-4: The change of the relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) with temperature for Samples A-D at 1 kHz, and the identification of the depolarization temperature (T_d).....	194
Figure 7-5: The change of pyroelectric coefficient (p) as a function of Ta5+ content and temperature ($^{\circ}\text{C}$) for the NBT-0.06BT-xTa, $0.0 \leq x \leq 1.0$ %..	198
Figure 8-1: (a) XRD patterns of NBT-0.06BT and xLa-NBT-0.06BT-yTa; (b) enlargement of [111] peak split into [003] and [021] at 39.0° - 41.0° ; (c) enlargement of [200] peak split into [200] and [002] at 46.0° - 47.5°	212
Figure 8-2: SEM morphology of NBT-0.06BT and xLa-NBT-0.06BT-yTa ceramics.	213
Figure 8-3: Relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) vs temperature for (a) NBT-0.06BT, (b) 0.002La-NBT-0.06BT-0.002Ta, (c) 0.005La-NBT-0.06BT-	

0.002Ta and (d) 0.01La-NBT-0.06BT-0.002Ta at three different frequencies 1, 10, and 100 (kHz).....	217
Figure 8-4: The identification of the T_d values of all samples by dielectric method (loss tangent ($\tan\delta$) against temperature ($^{\circ}\text{C}$)) for all samples at 1 kHz.....	219
Figure 8-5: (a) Part of the (1-x)NBT-xBT phase diagram; (b) pyroelectric coefficient (p) vs temperature for all samples and the identification of the depolarization temperature (T_d). The two phase changes in Samples B and C that correspond to the change of FE ($Rh + Tr$) to FE (Tr) (phase change 1) and the change of FE (Tr) to AFE (phase change 2) were pointed out in the (1-x)NBT-xBT phase diagram (a).....	220
Figure 8-6: FOMs (F_V , F_D , and F_C) vs. frequency ranging from 33 to 2000 HZ. (a) F_V vs. f ; (b) F_D vs. f , and (c) F_C vs.	226
Figure 8-7: FOMs (F_V and F_D) vs. temperature ranging from 25 to 55 $^{\circ}\text{C}$. (a) F_V vs. T and (b) F_D vs. T	227
Figure 8-8: (a) XRD patterns of NBT-0.06BT and xLa-NBT-0.06BT-yTa; (b) enlargement of [111] peak split into [003] and [021] at 39.0 $^{\circ}$ to 41.0 $^{\circ}$; (c) enlargement of [200] peak split into [200] and [002] at 45.5 $^{\circ}$ to 47.5 $^{\circ}$	237
Figure 8-9: SEM morphology of NBT-0.06BT and xLa-NBT-0.06BT-yTa ceramics.	239
Figure 8-10: Relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) vs temperature for (a) NBT-0.06BT, (b) 0.005La-NBT-0.06BT-0.002Ta, (c) 0.005La-NBT-0.06BT-0.005Ta, and (d) 0.005La-NBT-0.06BT-0.01Ta at three frequencies 1, 10, and 100	242
Figure 8-11: The identification of the T_d values of all samples by dielectric method (loss tangent ($\tan\delta$) against temperature ($^{\circ}\text{C}$)) for all samples at 1 kHz.....	243
Figure 8-12: Pyroelectric coefficient (p) vs. temperature for all samples and identification of the depolarization temperature (T_d).	244
Figure 9-1: (a) XRD patterns of compositions M, A (0.002La-NBT0.06BT), and B (0.005La-NBT0.06BT); (b) enlargement of [111] peak split into [003] and [021] at 39.0 $^{\circ}$ to 41.0 $^{\circ}$; (c) enlargement of [200] peak split into [200] and [002] at 45.5 $^{\circ}$ to 47.5 $^{\circ}$	259
Figure 9-2: The SEM morphology of Compositions M (a), A (b), and B (c).....	261
Figure 9-3: (a-c) the temperature dependence of the dielectric permittivity (ϵ_r) and dielectric loss ($\tan\delta$) respectively of Compositions M to B, in wide temperature range and at 1 kHz and identify of the depolarization temperature (T_d).	263
Figure 9-4: (a) the pyroelectric coefficient (p) vs temperature ($^{\circ}\text{C}$) for Compositions M, A, and B, at temperature from 20 $^{\circ}\text{C}$ to 90 $^{\circ}\text{C}$, and identify of the T_d for Compositions A, and B. (b) enlargement of the pyroelectric	

coefficient curve of Composition M with identify of the T_d for the same Compositions.....	265
--	-----

LIST OF TABLES

Table 1-1: Thesis structure.	40
Table 2-1: The reagents were used in the study.....	66
Table 3-1: The preparation parameters of NBT-0.06BT samples synthesis.	82
Table 3-2: The lattice parameters, c/a ratio, average grain size, density and the density value compared with the theoretical density (6 gm.cm^{-3}) of Samples A to F in this study.	86
Table 3-3: The pyroelectric coefficients (p) and the figure of merit (F_D) for all the samples (A to E).	92
Table 4-1: Composition (sample name), lattice parameter, c/a ratio, average grain size and density of all samples in this study.	102
Table 4-2: The pyroelectric coefficient (p) and the FOMS, F_i , F_V , and F_D for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at room temperature and 1 kHz.	114
Table 4-3: The pyroelectric coefficient (p) and the FOMs, F_i , F_V , and F_D for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at 90 °C and 1 kHz.....	115
Table 4-4: The FOM, F_V for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at RT and 90 °C or T_d and at frequency 0.1, 10, 100k Hz and 1 MHz.....	116
Table 4-5: The FOM, F_V for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at 90 °C or T_d and at frequency 10, 100k Hz and 1 MHz.....	116
Table 4-6: The FOM, F_D for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at RT and at frequency 0.1, 10, 100k Hz and 1 MHz.	117
Table 4-7: The FOM, F_D for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at 90 °C or T_d at and at frequency 10, 100k Hz and 1 MHz.....	117
Table 4-8: The FOM, F_C for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at RT and frequency range from 100 Hz to 1 MHz.	118
Table 5-1: The NBT-0.06B _{1-x} T, composition (sample) depending on the extra concentrations of Ba ²⁺ from A, x=0.00 to D, x=0.03; samples density (gm.cm^{-3}), comparing with the theoretical density (%) which is ($p=6 \text{ gm.cm}^{-3}$), and the relative permittivity (ϵ_r), dielectric loss ($\tan\delta$) both at 1kHz and RT, the depolarization temperature (T_d) value $0.0 \leq x \leq 0.03$	131

Table 5-2 Comparing the pyroelectric coefficients and the figures of merits (F_i , F_v , and F_D) of the NBT-0.06B _{1+x} T (0.0≤x≤0.03) ceramics at frequency 1kHz, at two different temperature RT, T_d or 90 °C with the other lead-free compositions and PZT.....	137
Table 5-3: Lattice parameters (Å), cells volume (Å ³), tolerance factor, grain size (μm) and density (gm.cm ⁻³) of NBT-0.06 and N _x B _y T-0.06B _z T ceramics. ..	146
Table 5-4: Pyroelectric coefficient (p) and FOMs (F_i , F_v , and F_D) results at RT of NBT-0.06BT and N _x B _y T-0.06B _z T in the present study and literature.....	155
Table 5-5: Pyroelectric coefficient (p) and FOMs (F_i , F_v , and F_D) results at T_d of NBT-0.06BT and N _x B _y T-0.06B _z T in the present study and literature.....	156
Table 5-6: The figure of merit F_C , results at room temperature and at 100 and 1000(Hz) of NBT-0.06BT and N _x B _y T-0.06B _z T ceramics.	157
Table 6-1: The lattice parameters (Å), c/a ratio for NBT-0.06BT and NBT-0.06BT-xLa (%) compositions.	167
Table 6-2: The pyroelectric coefficient and FOM F_i , F_v , and F_D results at room temperature (RT) in this study and in literature.....	175
Table 6-3: The pyroelectric coefficient and FOM F_i , F_v , and F_D results at 90 °C or depolarization temperature (T_d) in this study and in literature.	176
Table 7-1: The positions of the morphotropic phase boundary (MPB), the lattice parameters (Å), c/a ratio, the average grain size (μm), samples density (gm.cm ⁻³), and comparison with the theoretical density (%) which is ($\rho = 6$ gm.cm ⁻³).....	188
Table 7-2: The depolarization temperature (T_d) obtained by two methods in this work and others.	195
Table 7-3: The pyroelectric coefficient and FOMs F_i , F_v , and F_D results of the NBT-0.06BT-xTa, 0.0 ≤ x ≤1.0 %, at RT in the present work and in literature.	200
Table 7-4: The pyroelectric coefficient and FOMs F_i , F_v , and F_D results of the NBT-0.06BT-xTa, 0.0 ≤ x ≤1.0 %, at 90 °C or T_d in the present work and in literature.....	201
Table 7-5: The figure of merit, F_C in different frequencies 33, 100, and 1 Hz at RT.	201
Table 8-1: Lattice parameters (Å), c/a ratio and average grain size values of all NBT-0.06BT and xLa-nbt-0.06BT-yTa ceramic compositions.	213
Table 8-2: Relative permittivity (ϵ_r) and loss tangent (tanδ) values at room and depolarization temperatures.....	218

Table 8-3: Pyroelectric coefficient (p) and FOMs (F_i , F_v , and F_D) results at RT of NBT-0.06BT and xLa-NBT-0.06BT-yTa in the present study and literature.	223
Table 8-4: Pyroelectric coefficient (p) and FOMs (F_i , F_v , and F_D) results at 90 °C or T_d of NBT-0.06BT and xLa-NBT-0.06BT-yTa in the present study and literature.	224
Table 8-5: The figure of merit FC results at room temperature and wide frequency range from 33 to 1000 (Hz) of NBT-0.06BT and xLa-NBT-0.06BT-yTa ceramics in present study and literature.	225
Table 8-6: Lattice parameters ($\text{\AA}$), c/a ratio, and the average grain size of NBT-0.06BT and xLa-NBT-0.06BT-yTa ceramics.	238
Table 8-7: Pyroelectric coefficient (p) and FOMs (F_i , F_v , and F_D) results at room temperature (RT) of NBT-0.06BT and xLa-NBT-0.06BT-yTa in the present study and literature.	248
Table 8-8: Pyroelectric coefficient (p) and FOMs (F_i , F_v , and F_D) results at 90 °C or T_d of NBT-0.06BT and xLa-NBT-0.06BT-yTa in the present study and literature.	249
Table 9-1: The lattice parameters ($\text{\AA}$), c/a ratio, cell volume ($\text{\AA}^3$), average grain size (μm), and density (gm. cm^{-3}) of Composition M, A, and B.	260
Table 9-2: The pyroelectric coefficient (p) and the figure of merit FD at room (RT) and depolarization temperature (T_d).....	267

LIST OF ABBREVIATIONS

NBT	Sodium bismuth titanate
BT	Barium titanate
NBT-xBT	Sodium bismuth titanate modified by barium titanate
PZT	Lead zirconate titanate
p	Pyroelectric coefficient
I_p	Pyroelectric current
ϵ_r	Dielectric permittivity
ϵ_0	Dielectric permittivity of the free space
$\tan\delta$	Dielectric loss tangent
MPB	Morphotropic phase boundary
Rh	Rhombohedral
Tr	Tetragonal
C	Cubic
FE	Ferroelectric
AFE	Antiferroelectric
PE	Paraelectric
T	Temperature
RT	Room temperature
T_d	Depolarization temperature
T_m	Maximum dielectric permittivity
T_C	Curie temperature
E_C	Coercive field
E	External electric field
E_d	Depolarization field
C_0	Capacitance (empty parallel plate)
A	Area of the electrode
d	Distance between plates
D	Dielectric displacement
P_s	Spontaneous polarization
P_{induced}	Induced polarization
P_{sat}	Saturation polarisation
P_T	Total polarization

X	Dielectric susceptibility (Chi, pronounced “ky”)
PNRs	Polar nanoregions
t	Goldschmidt tolerance factor
CPCMs	Composite pyroelectric ceramic materials
FOMs	Figure of merits
F _i	High current detectivity FOM
F _v	High voltage detectivity FOM
F _D	High detectivity FOM
F _C	The pyroelectric FOM
i	Current
C _v	Specific heat
XRD	X-ray diffraction
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
EDS	Energy dispersive analysis
CSSR or SSRR	Conventional solid-state route or solid-state reaction route
SPS	Spark plasma sintering
PVA	Poly vinyl alcohol
PCMs _s	Pyroelectric composite materials
WEEE	Waste electrical and electronic equipment
ROHS	Restriction of use of certain hazardous substances

1 Introduction and Literature Review

1.1 Background

Pyroelectric ceramics are widely referred to as smart materials because they are relatively sensitive to any alteration in temperature and responsive to it. Pyroelectric ceramic materials are used as an active element in various electronic devices [1,2], such as sensors, infrared detectors, thermal cameras, remote medical diagnostic devices, gas detectors, airplanes, spacecraft and in many other applications. The most widely utilized pyroelectric ceramics are lead-containing materials, such as lead zirconate titanate, $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT), and PZT-based multicomponent materials, due to their superior pyroelectric properties; they possess high pyroelectric coefficients (p), moderate relative permittivity (ϵ_r), low dielectric loss ($\tan\delta$), high stability at a wide temperature range, and it is straightforward to alter their properties through doping with other chemical elements. In addition, PZT shows a morphotropic phase boundary (MPB) in its phase diagram between PbZrO_3 – PbTiO_3 compositions, which enhances their piezoelectric, pyroelectric and ferroelectric properties [3–6].

The toxicity of lead has been recognised for many centuries. When lead enters the body through blood, bone, teeth, or soft tissues, it causes numerous health problems, with its effects on children being much more severe than on adults [7–9]. There was an in-depth discussion concerning the impact of lead coming from electronic equipment at the 1992 Rio Earth Summit. Since then, the scientific community along with the electronics industry have been striving to remove lead from electronic equipment and to find lead-free alternatives [9].

However, the pyroelectric ceramics industry is still dominated by lead-containing materials as there currently are no suitable lead-free alternatives [10,11]. Exploration into a lead-free pyroelectric material, which can substitute PZT-based materials, is still ongoing, but the structure-property correlation of new materials still needs further research.

A large number of lead-free systems have been studied, but they are still at the research stage. However, sodium bismuth titanate, modified by barium titanate

(1-x)Na_{0.5}Bi_{0.5}TiO₃-xBaTiO₃ (NBT-xBT), is currently attracting worldwide interest [12–19]: it shows high ferroelectric properties, particularly for compositions at the morphotropic phase boundary (MPB) area ($x = 0.06-0.07$) where the rhombohedral (*Rh*) and tetragonal (*Tr*) phases coexist [12,20,21]. Moreover, the NBT-xBT has a lower coercive field (E_C) than E_C of the undoped NBT material, this makes the poling of NBT-xBT much easier [19]. However, the phase diagram of NBT-xBT is complex: it shows the presence of many phases such as ferroelectric (*FE*), polar phase, antiferroelectric (*AEF*) or relaxor, weakly polar, phase and paraelectric (*PE*), nonpolar, and needs further research in order to fully understand the structure-property correlation [15,20,22–25]. These phase transitions occur at different temperatures: firstly, ferroelectric (*FE*) to antiferroelectric (*AFE*) or to relaxor at depolarization temperature (T_d) at 100 to ~165 °C [26–28]; and secondly, antiferroelectric (*AFE*) to paraelectric (*PE*) phases at around 225 to 292 °C, which is either at the Curie temperature (T_c) or at the temperature of maximum dielectric permittivity (T_m) [15,22–25,27]. The NBT-xBT phase transitions are also accompanied by structural transitions: from rhombohedral and tetragonal (*Rh + Tr*) to tetragonal (*Tr*) if the composition is at the MPB, or from rhombohedral(*Rh*) to tetragonal (*Tr*) if the composition is out of MPB and from tetragonal (*Tr*) to cubic (*C*) [24,26,27]. These structural phase changes are very important to pyroelectric study and to pyroelectric applications because the maximum pyroelectric effects can be induced at these transitions. However, these phase transition temperatures are far too high to be useful for pyroelectric applications at room temperature. Thus, doping rare-earth elements into the materials is a widely used approach to bring down the phase transition temperature [2,29–37].

According to the literature, both undoped and doped NBT-0.06BT exhibit one explicit sharp peak of pyroelectric coefficient (p) at depolarization (T_d), temperature [2,15,23,24,35–38]. Such a pyroelectric response of these materials normally occurs within a narrow temperature range. Therefore, extending the working temperature range of undoped and doped NBT-0.06BT will undoubtedly broaden the range of pyroelectric material applications.

To increase the pyroelectric response over a wide temperature range, composite pyroelectric ceramic material (CPCM) was thought to be one of the possible solutions [39,40], with many CPCM demonstrating an enhancement in their properties and performance [39,40]. The fabrication technologies for these materials usually involve multiple steps and require sophisticated facilities. The advanced sintering method typically employed to obtain CPCM is the spark plasma sintering (SPS) technique. CPCM contain two compositions, and these compositions must remain individual without diffusing into a single composition. Thus, a high sintering temperature and long dwelling time must be avoided.

SPS technology enables completion of the synthesis of the graded materials within a very short time, leaving no time for diffusion occur. Therefore, in this project, new composite pyroelectric ceramic material has been designed using SPS technology.

1.2 Ferroelectricity and Related Phenomena

1.2.1 Dielectric Materials

Dielectric materials were defined as a sort of insulator that do not possess free charge carriers [41]. One of the main uses of these materials is in capacitor applications. A particular characteristic of this class of material is the polarization resulting when an external electric field (E) is applied. This polarization can be induced by a variety of forms (Fig.1-1). The best way to describe dielectric materials is by two parameters: the dielectric permittivity (ϵ_r) or dielectric constant; and dielectric loss tangent ($\tan\delta$).

As a capacitor with empty parallel plate, the capacitance C_o can be expressed:

$$C_o = \epsilon_o \frac{A}{d} \quad (1-1)$$

where ϵ_o represents permittivity of the free space, A the surface area of the plates, and d the distance between the parallel plates.

If an external electric field is applied (E) on a polar material, the total dielectric displacement D will be:

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}_T \quad (1-2)$$

where P_T is the total polarization equal to spontaneous polarization (P_s) and polarization ($P_{induced}$) which is induced due to electrical displacement.

$$\mathbf{P}_T = \mathbf{P}_s + \mathbf{P}_{induced} \quad (1-3)$$

Another important parameter in dielectrics is χ , (Chi, pronounced “ky”), which refers to dielectric susceptibility; it represents the ratio of the polarization (P) of dielectric materials to the external electric field (E) which has been applied on this material

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \chi \epsilon_0 \mathbf{E} \quad (1-4)$$

In the case that two plates of a capacitor are filled with a dielectric material of susceptibility χ , the capacitance will increase by the factor $1+\chi$.

The permittivity (ϵ) defined as:

$$\epsilon = \epsilon_0 (1 + \chi) \quad (1-5)$$

where,

$$1 + \chi = \frac{\epsilon}{\epsilon_0} = \epsilon_r \quad (1-6)$$

where ϵ_r is the dielectric relative permittivity or dielectric constant.

Thus total capacity [42,43]:

$$C = \epsilon_r \frac{A}{d} \quad (1-7)$$

According to Eq. 1-2, there are different mechanisms to generate the polarization in dielectric materials. The total polarization occurring in these materials is mainly dependent on the frequency of the applied electric field. The following different types of polarization will contribute to the dielectric permittivity by changing the total polarization (Eq. 1-3) of the dielectric material (Fig 1-1) [42].

- Electronic or atomic polarization
- Ionic polarization
- Orientation or dipolar polarization
- Space charge or diffusion polarization

The contribution of each one of these types of polarization comes from the short-range movement of the charges, as a response to the E , but in a different time scale. Thus, every one of them has its own distinctive frequency, which represents reciprocal of the characteristic time (relaxation time) where the maximum $\tan\delta$ appears (Fig.1-2).

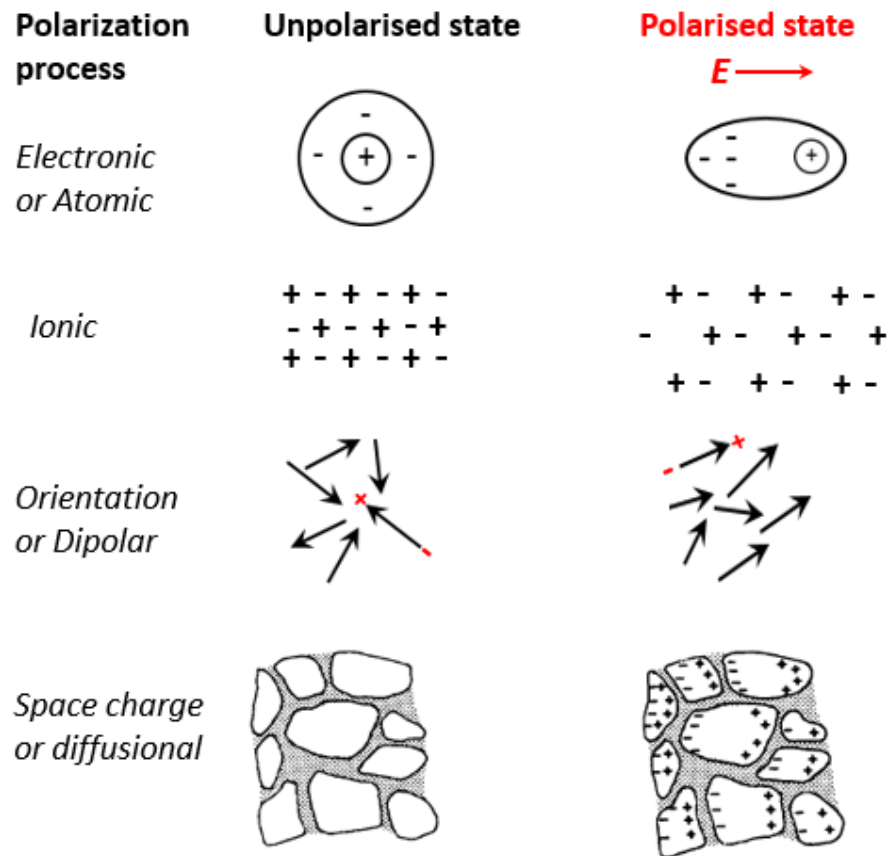


Figure 1-1: Different polarization processes [42].

1.2.2 Classification of materials based on Symmetry Principle

There are different types of crystals including single crystal and polycrystalline. The physical properties of those crystals are mainly affected by their symmetry. According to the symmetry principles of Neumann, the external properties of crystals reflect the symmetry of their internal structures [44].

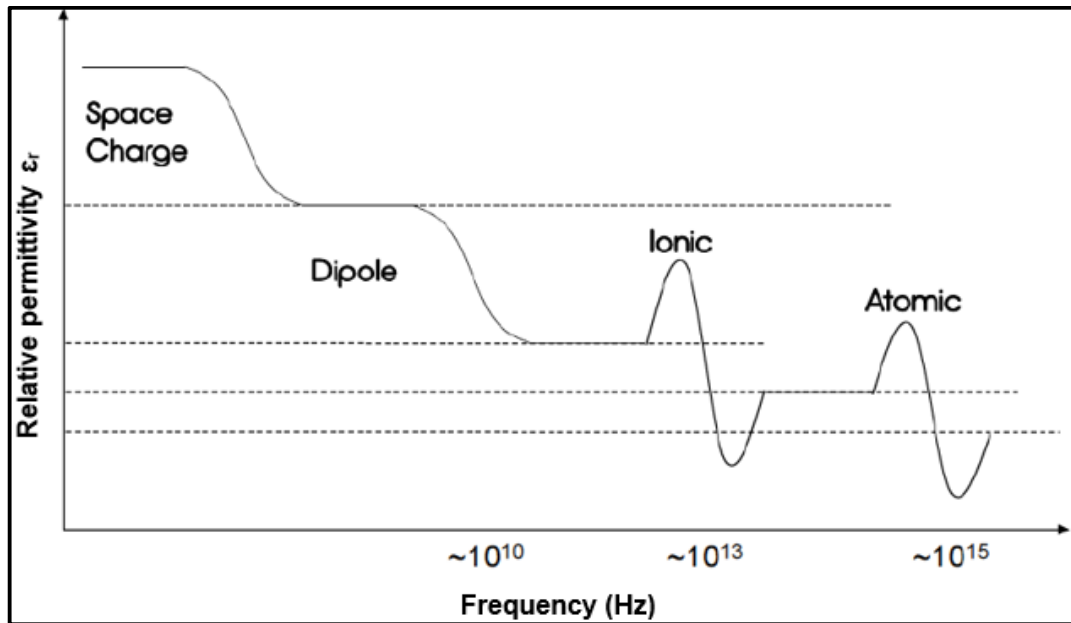


Figure 1-2: The dependant of relative permittivity (ϵ_r) on frequency of alternative electric field showing the contributions of the different types of polarization.

The crystal structure can be divided into 32 crystal classes or symmetry groups, dielectric materials can belong to any of those 32 symmetry groups. According to their symmetry elements, 21 of the 32 classes do not have a centre of symmetry and of these, 20 are piezoelectric crystals meaning they can be polarised under stress. Among the 20 piezoelectric crystal classes, 10 of them are polar materials; they have a unique polar axis and possess a spontaneous polarization in the absence of external electric field or mechanical stress. These dielectric materials are known as pyroelectrics. In a pyroelectric crystal, its spontaneous polarization will change by heating the material. Another category of those polar materials,

where the direction of spontaneous polarization can be switched by applying an external electric field, are commonly called ferroelectrics (Fig 1-3) [42,45,46].

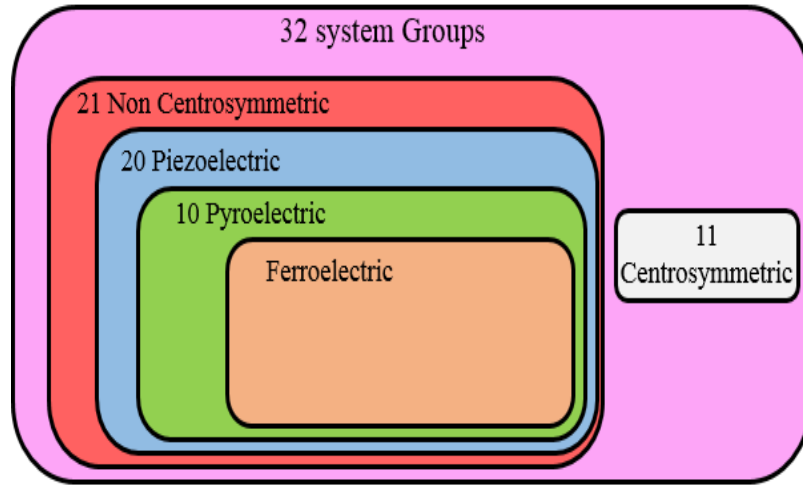


Figure 1-3: The relation between the 32 Symmetry Groups.

1.2.3 Piezoelectric Materials

The word piezoelectric is derived from the Ancient Greek word, piezoein, which means squeeze. Thus, piezoelectric materials can produce electricity from an applied mechanical stress or conversely, by applying an external electric field a mechanical stress can be generated. Therefore, these materials act as a coupling mechanism between electrical and mechanical energy [47,48].

In piezoelectric materials, unit cells are non-centrosymmetric. This special asymmetrical configuration in the unit cell of this sort of material can create dissimilar charge distribution; as a result, electric dipoles will form in the crystal. This macroscopic asymmetric charge displacement is proportional to the applied mechanical stress. It has also been discovered that by applying a voltage to the surface of piezoelectric material a small change in the dimensions of the material can be created [47].

The piezoelectric direct or converse effects are represented as:

$$D_i = d_{ijk}\sigma_{ijk} \quad (1-8)$$

$$S_{ij} = d_{kij}E_k \quad (1-9)$$

where equation 1-8 describes the direct effect and 1-9 describes the converse effect. D_i represents the polarization produced along the i-axis in response to the applied external stress σ_{jk} whereas, for the converse effect, S_{ij} refers to the strain produced in a special orientation of the crystal in response of the external electric field E_k along the k-axis. The parameters d_{ijk} and d_{kij} are the piezoelectric coefficients of both direct and converse effects respectively [44,47].

1.2.4 Pyroelectric Materials

Pyroelectric materials are a subclass of piezoelectric category, exhibition their own spontaneous polarization (P_s). In general, the P_s in these materials is not necessarily able to switch directions by the application of an external electric field. The net polarization in the unit cell of this type of material has been induced due to inherent dipole moment. This net polarization can be changed by manipulating the temperature. The pyroelectric coefficient (p) is defined as the ratio of change in P_s to the uniform changes in temperature (T) [49–52]:

$$p = \frac{dP_s}{dT} \quad (1-10)$$

where p is measured by $C.m^{-2}.^{\circ}C^{-1}$ or $C.m^{-2}.K^{-1}$, and will be calculated using the relationship:

$$p = \frac{I_p}{A \frac{dT}{dt}} \quad (1-11)$$

Where, I_p is the pyroelectric current, and can be measured during the heating cycle; A the area of material electrode, and dT/dt the rate of heating within time [51].

1.2.4.1 Pyroelectricity

Pyroelectricity (combining two “*pyro-*” the Greek word for *heat*, and electricity) means generating electricity from heat [48]. It is commonly understood as a number of electrical changes in a crystal that produced as a result of uniform heating [48], or production of an electric dipole moment in a dielectric material due to a homogeneous increase in temperature. The dielectric displacement already existent in crystalline materials will increase as a result of thermal expansion as temperature rise [50]. Pyroelectricity is one of the most effective means to detect change in temperature [53].

Pyroelectricity as a physical phenomenon was discovered at around 314 BC by the Greek philosopher Theophrastus [54] described the behaviour of a stone named Lyngourion or Lyncurium which has the ability to attract pieces of wood and straw. The behaviour of this material is because the electrostatic effects produced due to the temperature change [54]. The same type of behaviour was also noticed in another mineral, called tourmaline [54]. In 1707, Johann Georg Schmidt reintroduced the concept of pyroelectricity back to European countries, observing that tourmaline could not only attract ashes from warm coals, but also could repel them [54].

Ten years later, the chemist Louis Lemery detailed the scientific characteristics of pyroelectricity in a journal [54]. After that, the naturalist Linnaeus (Carl von Linne) linked the pyroelectric property of tourmaline to electricity and designated it as an electric stone. During the eighteenth century, the research of scientists such as Franz U. T. Aepinus, Johann K. Wilcke, Benjamin Wilson and others made the main contributions to the development of the electrostatics field [54], in 1824 the word “pyroelectricity” was first coined by David Brewster. John M. Gaugain is the first scientist to have accurately measured pyroelectric charges in 1859, making the following important conclusions:

- The total amount of electricity that is produced by the element tourmaline depends on the change in its temperature within exact limits.

- The quantity of electricity, which is generated through increasing the temperature, should be produced through decreasing the temperature of the material [54].

In 1878, W. Thomson (Lord Kelvin) formulated the pyroelectric phenomenon with a theory. Ten years later, Voigt developed this theory, and Born, in 1921 and 1928, made further developments to this theory based on the dynamics of the crystal lattice [48,55]. In 1933, French chemist Yeou Ta published a highly significant paper and concluded that the element tourmaline might be utilized as infrared sensor in spectroscopy [55]. However, pyroelectricity as a phenomenon has been technically considered in the industrial use at more 45 years later [42,45,46].

The pyroelectric effect has been mainly utilised in the detection of electromagnetic radiation especially infrared radiation (*IR*). The importance of the pyroelectric effect in infrared detection was becoming obvious from 1970 onwards and a widely acclaimed review of pyroelectric detectors was published in that year [49,51,56].

The materials that show the best pyroelectric effect are ferroelectrics, which can be in the form of single crystal, ceramic or polymer [45,51].

Most ferroelectric materials are pyroelectric materials (Fig 1-4), which means that by applying a suitable electric field (E) it is possible to reverse the direction of polarization them. In addition, this polarization will gradually reduce to zero at Curie Temperature (T_C).

The typical relationship between polarization and temperature illustrated in Fig. 1-4 [49,50], and the gradient (dP/dT) of the curve in Fig. 1-4 at certain temperature (T) represents the pyroelectric coefficient (p). Pyroelectric coefficient has several definitions and one of them is the change in the spontaneous polarization caused by fluctuations in temperature [52]. In addition, its value at a certain temperature is considered as one of the most important parameters regarding material selection for pyroelectric applications. Pyroelectric coefficient

shows the highest value at T_C , whereas P_s is zero at this temperature, (Fig. 1-4) [49,50].

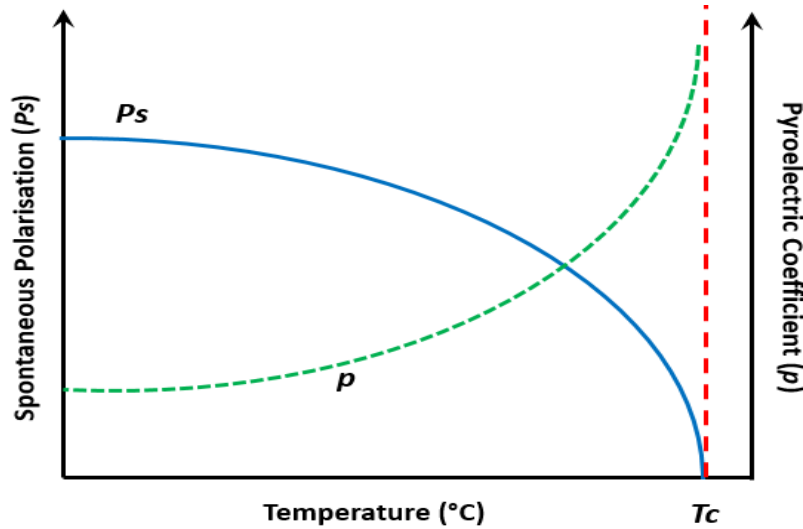


Figure 1-4: Schematic of the relationship between spontaneous polarisation (P_s) and temperature, where, T_C is Curie temperature.

1.2.4.2 Pyroelectric Effect

In solid materials, one of the least known properties is pyroelectricity [54]. At the microscopic scale, there are several types of electric dipole moment in dielectric materials. One of these is the dipole moment generated due to asymmetrical distribution to the dissimilarly charged species, which is electronic or atomic polarization (Fig 1-1) [50,51]. This asymmetric distribution, when temperature changes, shifts the negative charge centre to the positive charge centre and produces a spontaneous polarization (P_s), or electric dipole moments. Thus, the material that has this kind of permanent P_s in its unit cell is generally known as a pyroelectric material [54].

The pyroelectric effect can be demonstrated as a flow of current generated from a piece of pyroelectric material which has been connected to an external circuit due to fluctuations in temperature [51]. The characteristic example of a structure

that shows a P_s with changing temperatures is the perovskite structure [57], (Fig 1-12).

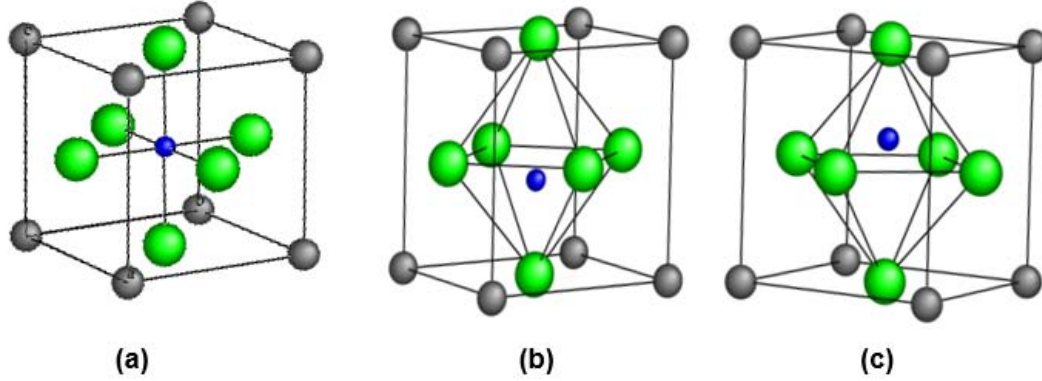


Figure 1-5: Schematic of perovskite structure (ABO_3); Grey spheres refer to A-site cations, smaller blue sphere are the B-site cations, and green spheres are oxygen. (a) centrosymmetric, (b and c) non-centrosymmetric [9].

The pyroelectric coefficient (p) which has been defined previously is the ratio of change in P_s to the uniform changes in temperature (T) [49–52].

$$\Delta P_s = p \Delta T \quad (1-12)$$

If a uniform piece of pyroelectric material has an electrode on both faces (Fig 1-13), the p as a vector, has a perpendicular component on the surface of the pyroelectric element (*electrode*). The pyroelectric charges will be detected as a pyroelectric current (I_p) by ammeter connect in the external circuit:

$$I_p = A p \frac{dT}{dt} \quad (1-13)$$

where I_p is the pyroelectric current; A is the electrode surface area; p the pyroelectric coefficient; T is absolute temperature; t the time; dT/dt is the rate of change of the temperature of the pyroelectric element over time [51]. Therefore, the pyroelectric element is linked to the changes of input energy such as infrared

radiation (IR) that can produce a change in the material temperature; it is this temperature change will generate a pyroelectric current.

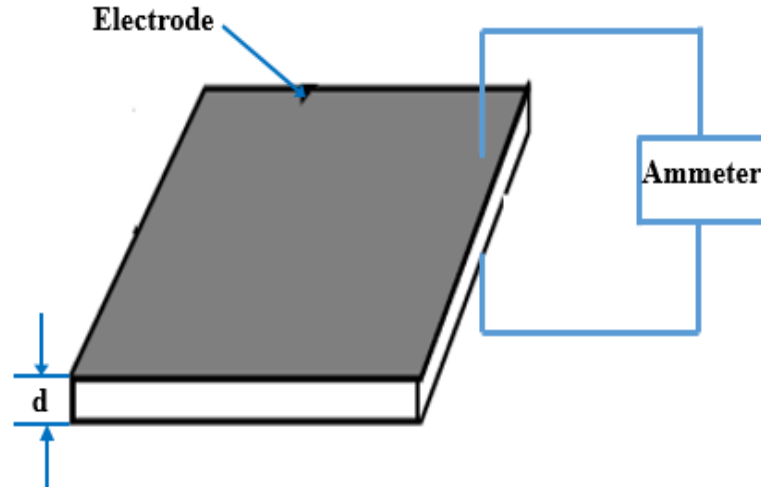


Figure 1-6: Schematic of a pyroelectric detector element.

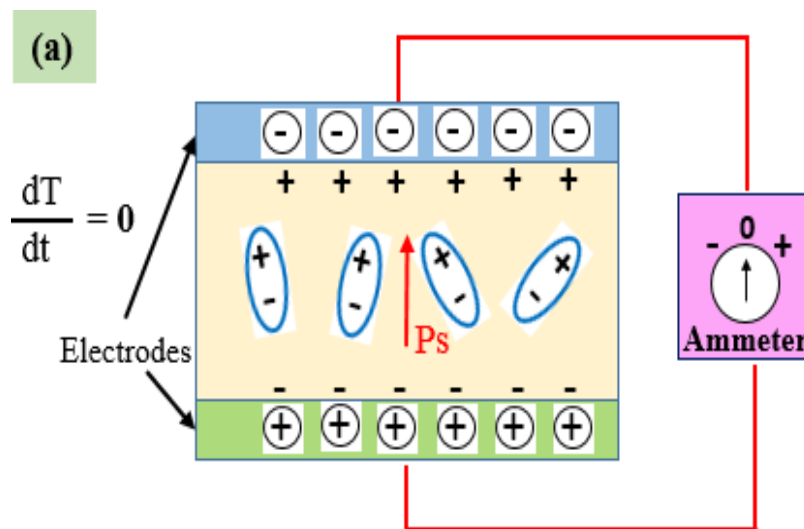
At room temperature, the ammeter shows no current flow through the circuit (Fig 1-14 (a)), because there is no change in the temperature [50]. However, with an increase in temperature of the pyroelectric element, the net spontaneous polarization will be changed, as a result, a I_p flows in the external circuit (Fig 1-14 (b)). The pyroelectric current represents the change in electric charge per unit time; therefore, current will be generated due to the manipulation in the temperature of pyroelectric material.

Although there are different types of pyroelectric materials, the highest pyroelectric effect can be obtained from polar dielectric materials which are ferroelectric materials [45,51,57].

In ferroelectric materials, the maximum value of P_s can be achieved at phase change from low symmetry, such as, orthorhombic or rhombohedral or tetragonal phases which are related to high pyroelectric state (FE), to high symmetry phase (*cubic*) at T_C [45,51]. In addition, this maximum P_s value, which is obtained from

irregular assembly of crystallite, can be linked to the number of potential polar axes in the symmetry phase at $T \leq T_C$. For instance, in barium titanate ($BaTiO_3$), it shows a ferroelectric tetragonal phase with six polar axes below Curie temperature ($T_C = 120^\circ\text{C}$). Thus, is a much greater possibility for domains in the crystals to align themselves in the direction parallel to the external electric field and achieve a high P_S value, which is $\sim 83\%$ in comparison with the P_S value of a single crystal; this may be increased to about 87% in rhombohedral phase and around 91% in orthorhombic phase [42,45,51]. Thus, using ferroelectric ceramic materials in variety of industrial applications has been considered beneficial as a result of the promising properties that these materials have shown.

Because of the wide range of pyroelectric materials, choosing a material for pyroelectric applications should be made according to specific parameters. One of these considerations is the pyroelectric coefficient; its value at certain temperatures is considered an important parameter for selecting a material for pyroelectric applications.



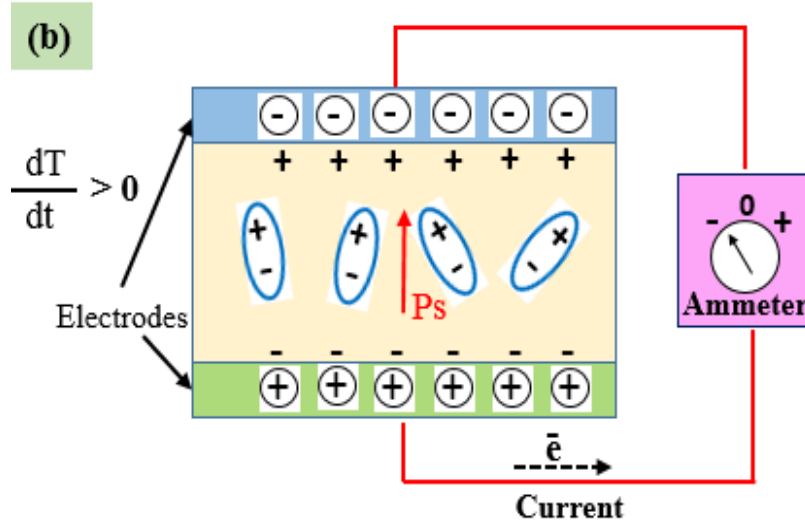


Figure 1-7: Schematic of pyroelectric a material detector element connects to the external circuit. (a) At room temperature (dT/dt) = 0. (b) Over increasing temperature (dT/dt) > 0.

However, the more efficient and accurate way for evaluating pyroelectric materials' performance can be achieved by calculating the figure of merits (FOMs) that represent the essential parameters for the pyroelectric applications [58].

The calculation of the FOMs is based on the values of the pyroelectric coefficient, relative dielectric permittivity, dielectric loss and the specific heat [53]. There are several types of FOMs depending on the specific type of pyroelectric application, such as infrared or thermal imaging [2,24,59–62].

The types of the FOMs depend on the input of thermal or electrical circuits, current or voltage. Therefore, for infrared applications that rely on the current responsivity, F_I is the relevant FOM. Similarly, to enlarge the pyroelectric voltage, the more suitable FOM is F_V that corresponds to high voltage (v) detectivity. Likewise, F_D is the FOM of the high and specific detectivity. F_C is a FOM of the infrared detector materials. These FOMs have been used to characterize and select the materials for thermal and infrared applications as sensors or transducers [23,58,63].

The measurement of the pyroelectric coefficient (p) can be carried out using Equation 1-14, while the measurement the FOMs can be done using the following equations [23,24,59,60]:

$$F_i = \frac{p}{C_v} \quad (1-14)$$

$$F_V = \frac{p}{C_v \epsilon_r \epsilon_o} \quad (1-15)$$

$$F_D = \frac{p}{C_v \sqrt{\epsilon_r \epsilon_o \tan \delta}} \quad (1-16)$$

$$F_C = \frac{p}{\sqrt{\epsilon_r}} \quad (1-17)$$

where p is the pyroelectric coefficient, F_i the high current (i) detectivity, F_V the high voltage (v) detectivity, F_D high detectivity, F_C the pyroelectric figure of merit. C_v the specific heat, which is defined as the amount of heat per unit of mass required to rise the temperature of a mass by one degree Celsius [64,65], the C_v value is quoted ($2.8 \text{ J.K}^{-1}.\text{cm}^{-3}$) from [63], ϵ_r the relative dielectric permittivity and ϵ_o the permittivity of free space.

Thus, the material that can show the highest FOMs F_i , F_V , F_D and F_C values or anyone of these FOMs (depending on the type of the pyroelectric application), at wide temperature range, represents the most suitable pyroelectric material for diverse pyroelectric applications.

1.2.5 Ferroelectric Materials:

The prefix “*ferro*” is derived from *ferum*, which means “iron” in Latin. This term is used in ferromagnetism and although analogous to ferroelectricity, there is in fact no iron in ferroelectric material [48,66].

Ferroelectrics are subclasses of pyroelectrics, and likewise, these materials possess P_S ; however, at applied E , its spontaneous polarization can be reversed. Thus, the hysteresis phenomenon can be generated by applied E , (Fig 1-5).

At RT and $E = 0$, the ferroelectric material does not show any ferroelectric response due to its polar domains being randomly orientated and these polar directions cancel each other out. Thus, the net polarization (P) in this material is zero (Fig 1-5 (1)).

By applying an electric field and increasing the field strength, the polarity of the ferroelectric material can change due to the dipoles switching inside domains in the direction of E and then the number of re-orientated domains increases. Therefore, the material shows net polarization (P) and at this stage, the material starts to be polarized, (Fig 1-5 (1 to 2)). With further increase in the E , the P will show a gradual increase up to certain value, while the material does not show further increase in net polarization, the P value at this stage represents the maximum (Fig. 1-5 (2)). So it can be assumed that at this stage, all the domains in the material will be aligned in one direction and the net polarization is widely known as the saturation polarisation (P_{sat}) (Fig. 1-5 (2)) [67,68]. By decreasing the E value to zero, (Fig. 1-5 (2 to 4)) the ferroelectric material still presents net polarization, which might be because parts of the domains are still aligned in the same direction following the previous direction of E . The value of the polarization in this case is commonly named remnant polarization (P_r) (Fig. 1-5 (3)). With further increasing the E but in opposite direction (Fig. 1-5 (4 to 5)), the material will show polarization reversed, which means that the material starts to polarize in the opposite direction, and with further increases in E , the P increases to another steady maximum that is also referred to as the P_{sat} (Fig. 1-5 (5)). The value of the external field, to eliminate the P_r and switch the domains direction to opposite direction, is called coercive field (E_c) [67–69] (Fig. 1-5). The value of E_c represents an important factor in ferroelectric applications for measuring the energy that is required to reinitiate the domains and switch the material polarization. The total area of hysteresis loop in ferroelectric materials refers to the total value of energy, which is required to switch or orientate the domains in the materials to the opposite side [67,68].

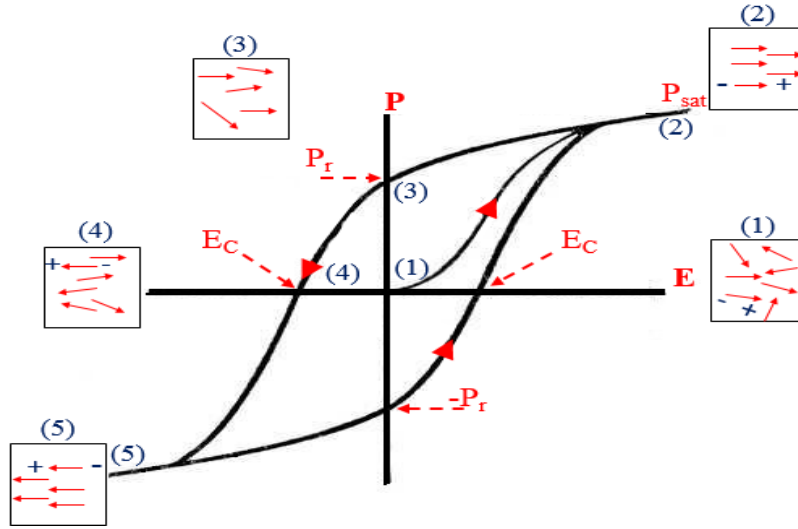


Figure 1-8: Hysteresis loop for a ferroelectric material. P = polarization; P_s = saturation polarization; P_r = remnant polarization; E = electric field; E_c = coercive field [69].

Ferroelectric material has the following specific characteristics [70]:

- Spontaneous polarization.
- Reversible spontaneous polarization.
- Hysteresis loop.
- Ferroelectric phase transition temperature.

1.2.5.1 Ferroelectricity and Ferroelectric domains

Ferroelectricity is a characteristic of specific materials and the ferroelectric crystal can be defined as one exhibiting spontaneous polarization (P_s) [66]. The P_s in this sort of crystal as a class of pyroelectric crystals, decreases with rising temperature, while it disappears at particular temperature named the Curie temperature (T_c) [48,66], (Fig 1-4). Curie point is identified by a peak in the permittivity in addition to the vanishing of the P_s . Therefore, T_c indicates the phase change from polar structure and a lower symmetry status at low temperatures to non-polar and a high symmetry structure at high temperatures. In general, the ferroelectric material shows paraelectric phase at $T \geq T_c$. [42,45,46].

At a temperature $T \leq T_c$ and without an applied external field, $E = 0$, the polarization in ferroelectric crystal can be developed in at least in two different directions. As a result, the depolarization field (E_d) will increase inside the crystal, (Fig 1-6). To decrease the energy that is related to E_d , ferroelectric crystals will split into several polar regions along with each of these directions to minimize this energy. These polar regions which are located inside the crystal are commonly called domains, and they can be defined as the uniform polarization regions per volume [71,72]. The interfaces or boundaries, which separate these domains, are widely known as domain walls. These walls can be switched by applied E , [73–75].

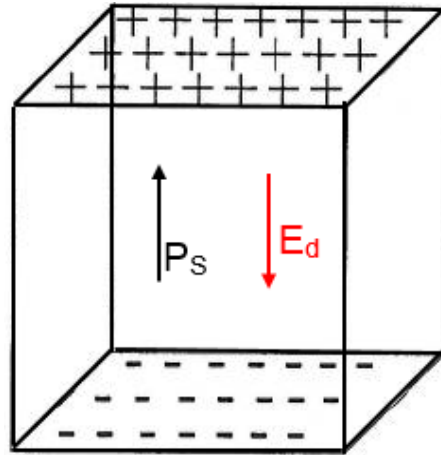


Figure 1-9: Schematic of surface charge, which is associated with spontaneous polarization, (P_s) and depolarization field (E_d).

One of the best examples of developing domains in a crystal is tetragonal phase with a perovskite structure (ABO_3). In this case, the polarization vector in the domains will be directed in one of the six $[001]$ directions of the unit cell, (Fig 1-7), or $[110]$ planes making 90° and 180° walls as the angles between the dipoles of adjacent domains they divide (Fig 1-8) [76].

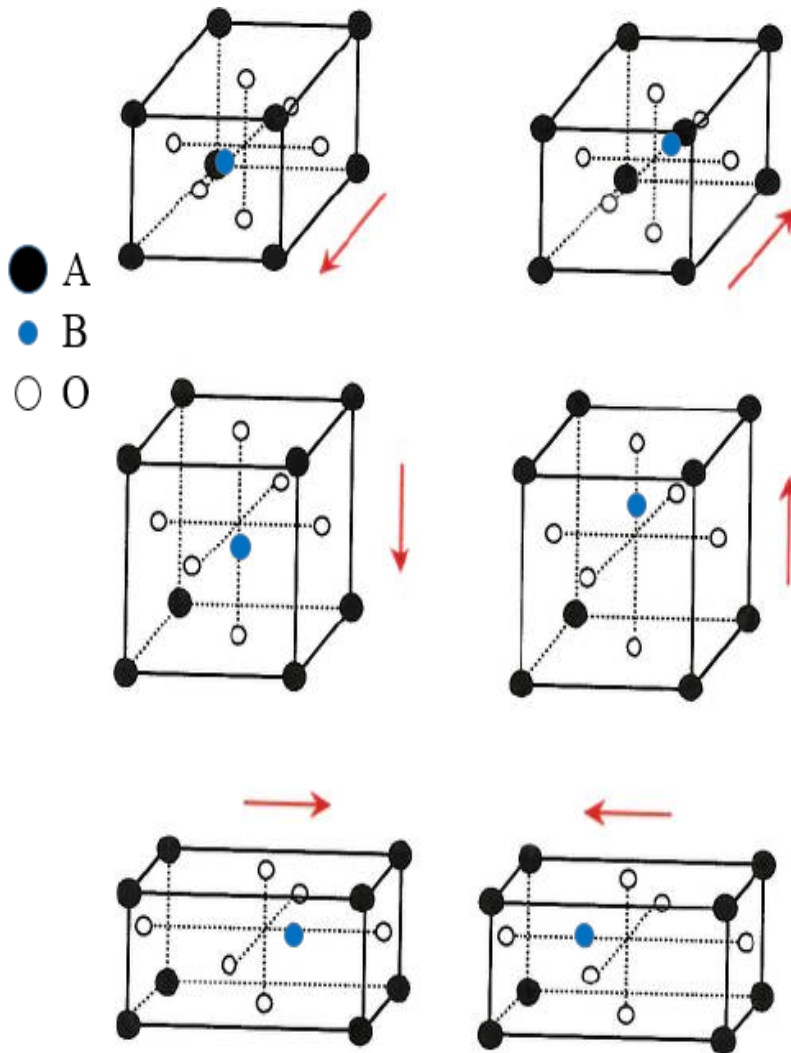


Figure 1-10: The schematic diagram of the six potential deformities of a tetragonal cell at temperature $T \leq T_c$ [9].

In seventeenth century, Rochelle discovered the potassium sodium tartrate tetrahydrate ($\text{KNaC}_4\text{H}_4\text{O}_6 \cdot 4\text{H}_2\text{O}$) and named as “*Rochelle salt*”. Rochelle salt is a single-crystal material. Two hundred years later, in 1921 ferroelectricity was discovered in Rochelle salt by Valasek [71,72] after that he successfully achieved another discovery which is finding the ferroelectric phenomenon polycrystalline ceramics (barium titanate (BaTiO_3)). This discovery has been represented the most beneficial finding [71,72].

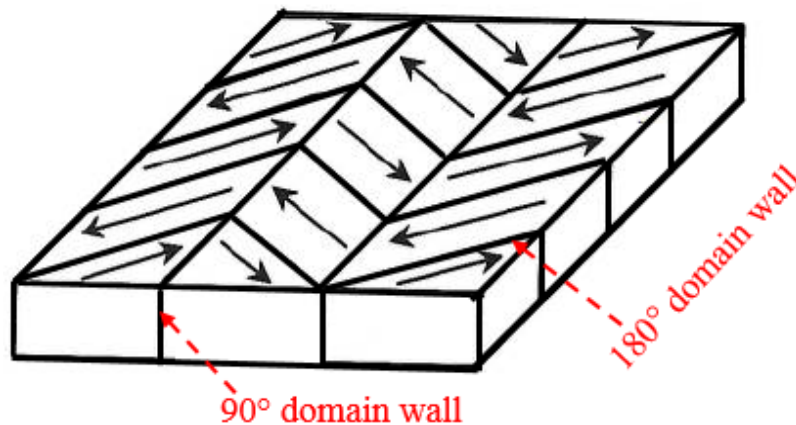


Figure 1-11: Schematic of domains in the tetragonal material [9].

The simple definition of “ceramic” is an agglomeration of tiny crystals, which are fitted together in unorganized way [42,77]. The domains within the ceramic materials can be permanently re-oriented and can be aligned in one direction by applying E , thus this process is named “poling” process. This opinion contravenes the prevailing opinion at that time (in 1945), which considered that ceramic materials could not be active ferroelectric materials due to the random orientation of their domains [72]. The discovery of electrical poling prompted considerable interest in utilizing ceramic materials in many industrial applications [72].

1.2.5.2 Relaxor Ferroelectrics

Relaxor ferroelectrics or relaxors are a specific type of ferroelectrics, which have received particular attention and generated considerable debate for a few years now, because of their exceptional dielectric properties, which are still not fully understood. [78–80]. These materials show wide and intriguing large dielectric maximums that make them ideal for many applications, such as multilayer capacitors (MLCs) [80], pyroelectric bolometers [81], electrostrictive actuators [82] and for electro-optics [83]. In addition, the existence of a MPB region in different solid solutions of relaxor compositions makes them one of the best candidates for piezoelectric transducers [83].

The general characteristics of relaxor materials are [84–86]:

- The dielectric permittivity vs. temperature graph illustrates wide peaks at the maximum dielectric permittivity (T_m).
- In dielectric relative permittivity and loss, the maximum corresponding temperature (T_m), which appears at dissimilar values of ϵ_r and $\tan\delta$ in addition presents a frequency dependent behaviour.
- The maximum dielectric permittivity value appears at T_m ; the relaxor materials will not follow Curie-Weiss law and cannot be associated with a phase transition from ferroelectric to paraelectric.
- These materials show polar nanoregions (PNRs) (Fig 1-9 (a)), in comparison with the normal ferroelectrics, (Fig 1-9 (b)).

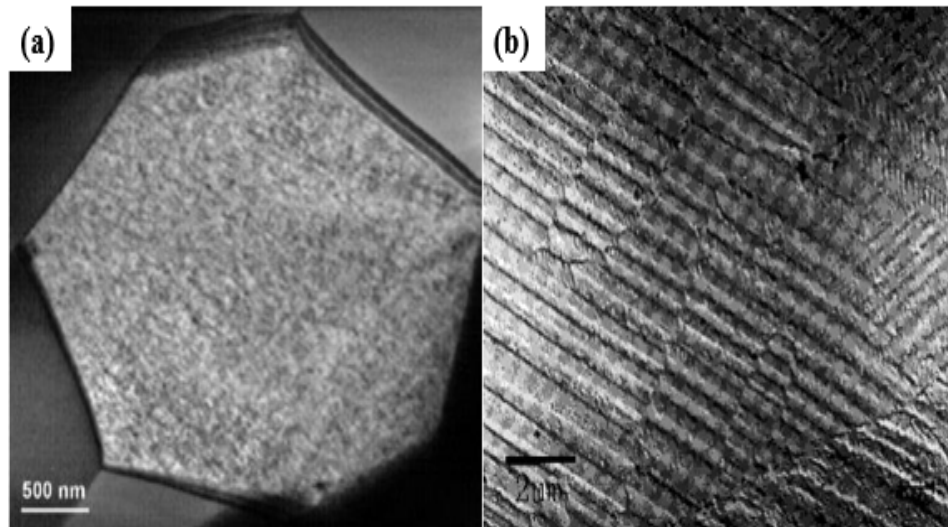


Figure 1-12: (a) TEM image of NBT-0.06BT illustrates the nanometre-sized domains in a virgin state [79]. (b) 180° domains for BaTiO₃ [78,88].

The PNRs can be considered as arranged or organized regions in an organized matrix [80], as demonstrated in the schematic Figure 1-10. These PNRs can dramatically affect the material behaviour [75–77].

The relaxor behaviour has been noticed in disordered perovskite (ABO₃) ferroelectrics, and in these materials, the functional response is mainly

dependent on the A and B sites' cations, like ionic radii, ionic charge and electronegativity [84–86]. The typical examples for relaxor materials are NBT, NBT-xBT, PLZT $((\text{Pb}_{1-x}\text{La}_{2/3x})(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3)$, PMN $((\text{PbMg}_{1/3}\text{Nb}_{2/3})\text{O}_3)$ PST $(\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3)$, etc., and these materials were discovered by Smolensk's group [87]. In relaxor materials, polarization does not disappear after T_m , but it still shows a value which then decreases gradually [89,90]. Furthermore, at T_m , these types of materials do not present symmetry change through the phase change; while at local length scales, the symmetry breaking into PNRs or nano domains exists well at temperatures higher than T_m substantially influencing the response of these materials.

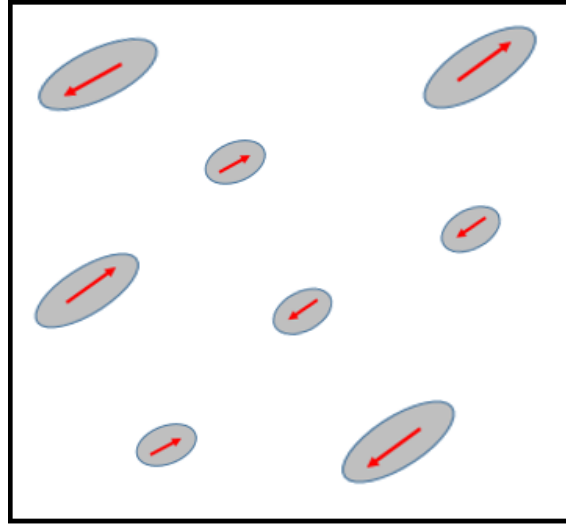


Figure 1-13: Schematic of polar nanodomains.

1.2.5.3 Types of ferroelectrics

Ferroelectric crystals can be classified into four different types [91]:

- a. Perovskite: PbZrTiO_3 , $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$, BaTiO_3 .
- b. Layer structure: $\text{SrBi}_2\text{Ta}_2\text{O}_9$.
- c. Tungsten bronze: PbNb_2O_6 .
- d. Pyrochlore: $\text{Cd}_2\text{Nb}_2\text{O}_7$.

In this study, we will focus on the perovskite ferroelectric materials.

Perovskite as a term is utilized to describe a large family of compound materials with a crystal structure similar to the mineral perovskite CaTiO_3 . The name perovskite was given in honour of Russian mineralogist Count Lev Alekseevich von Perovskite (1792-1856). In general, perovskites are considered the most important group of complex oxides [92,93]. In addition, they have received huge attention in the fields of physics, chemistry and materials science due to the large number of perovskite structures which have shown fascinating functional properties, and have therefore been widely utilized in various technological applications [94–98].

Perovskites have a general formula ABX_3 , where A and B refer to A and B-site cations. The A-site has cations such as: Na^+ , Bi^{3+} , Ba^{2+} , Pb^{2+} , La^{3+} , Ca^{2+} , Sr^{2+} , etc., occupying eight or twelve coordination number (CN) while B-site cations such as: Ti^{4+} , Ta^{5+} , Zr^{4+} , Sn^{4+} etc., has six CN. In addition, B-site cations have smaller sizes and are less electropositive in comparison with those located at A-sites. X is an anion and prefers to be an oxygen ion (O^{2-}) [93,99]. The basic or aristotype structure is cubic as shown in Fig 1-11 (a).

A-site cations are located among eight BX_6 octahedral units whereas B-site ions exist inside each of them and are surrounded by X anions, (Fig 1-11 (a)). Despite the fact that the basic structure of perovskite is not complex, there are however a wide variety of possible structures, which exhibit many differences. There is, because A and B cations that occupy the A and B sites are able to accommodate any element from the periodic table (Fig 1-11 (b)) [92,93,99,100].

The stability of a perovskite structure for any particular family of A, B, and O ions is related to the Goldschmidt tolerance factor (t) [93,99,101–103]:

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (1-18)$$

where, R_A , R_B and R_O are the radii of ions which occupy A, B, sites and the oxygen anion. The tolerance factor value of stable perovskite structure is in the range of 0.77-1.10 [93,103,104]. When $t = 1$, the structure is cubic, and when $t >$

1, it refers to the A-site being too small, and the B-site cation has less space to move. Moreover, if $t < 1$, it indicates that the A-site cation is too large to fit in its position while the B-site is a small cation; thus, the B-site cation has more space to move. In both cases, the structure will shift from the cubic structure to the tilting of the octahedral [93,99,103,104].

Although there are a wide variety of perovskite structures, two perovskite groups have been investigated thoroughly due to their pyroelectric properties. Firstly, rhombohedral (*Rh*) such as PbZrO_3 –based and NBT-based; and secondly, tetragonal (*Tr*) PbTiO_3 -based and BT-based [13,23,45,105,106]. In these structures, the change from aristotype or highest symmetry status to lower symmetry cases will increase the number of the possible polar axes in any ceramic crystals and also, can increase the theoretical percentage of the polarisation axis that may be achieved in the ceramic [45,51]. Thus, the domains in the ceramic crystals can have more possibilities to align in any of these directions. Moreover, the Rh and Tr systems can be doped with a wide range of elements resulting in multiphase ceramic structures which will significantly enhance the material properties.

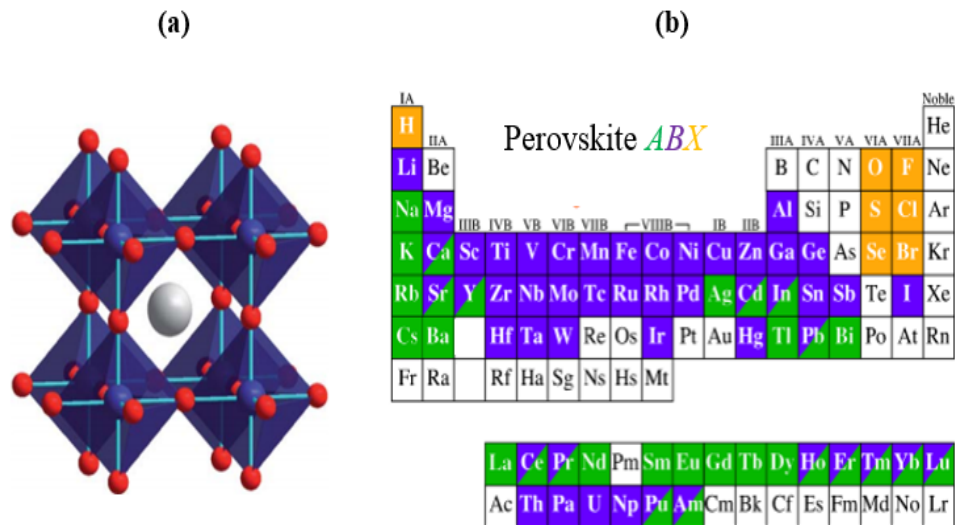


Figure 1-14: (a) the ideal perovskite structure (cubic) ABX_3 , Grey ball is the A-site ions, blue balls refer to the B-site ions, and oxygen is the green ball [92]. (b) the ions in the periodic table that can occupy A, B, and X sites of the perovskite structure [100].

As a result, the pyroelectric properties of these two ceramic groups have been comprehensively investigated and interested an enormous number of researchers [45,51].

1.2.5.4 Lead-contain ferroelectric material (Lead Zirconate Titanate (PZT))

Lead zirconate titanate ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$) or PZT-based materials refers to those most utilized in the majority of piezoelectric, pyroelectric, and ferroelectric industrial applications. The discovery of the solid solution of lead zirconate titanate ($\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$), as a new piezoelectric material in 1954 by B. Jaffe *et al.*, proved to be a major achievement. However, it should be remembered that this lead-based material contains around 60 % (wt.) of lead which is toxic [107,108].

PZT is originally formed from the solid-solution of lead titanate (PbTiO_3) as a ferroelectric material, and the antiferroelectric material lead zirconate (PbZrO_3) [3,109]. PZT-based materials have been considered as a multi-component system by modifying the zirconia to titanium ratio, different numbers of compounds can be obtained. The PZT phase diagram illustrates different phases (Fig 1-15). It shows rhombohedral (*Rh*) at $\text{Zr/Ti} > 54:46$ (*Zr-rich*), and tetragonal (*Tr*) at $\text{Zr/Ti} > 48:52$ (*Ti-rich*). However, both phases can exist at a Zr/Ti ratio of around 53:47, and this intermediate composition is commonly called morphotropic phase boundary (*MPB*) [3,9,109].

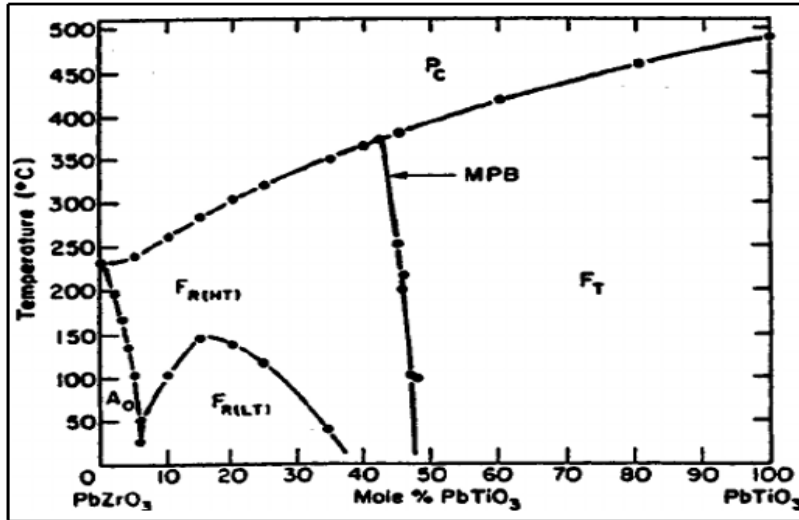


Figure 1-15: The phase diagram of the PbTiO₃-PbZrTiO₃ system PZT [3].

However, Neheda *et al.*, most recently reported PZT phase diagram from the year 2000 (Fig. 1-16), evidence was found for existence of another phase (*monoclinic*) between Rh and Tr phases [110]. The monoclinic phase (*Cm*) appears as a wedge shape (Fig. 1-16); this shape has been considered a bridge between Tr phase and Rh phase at the MPB [110].

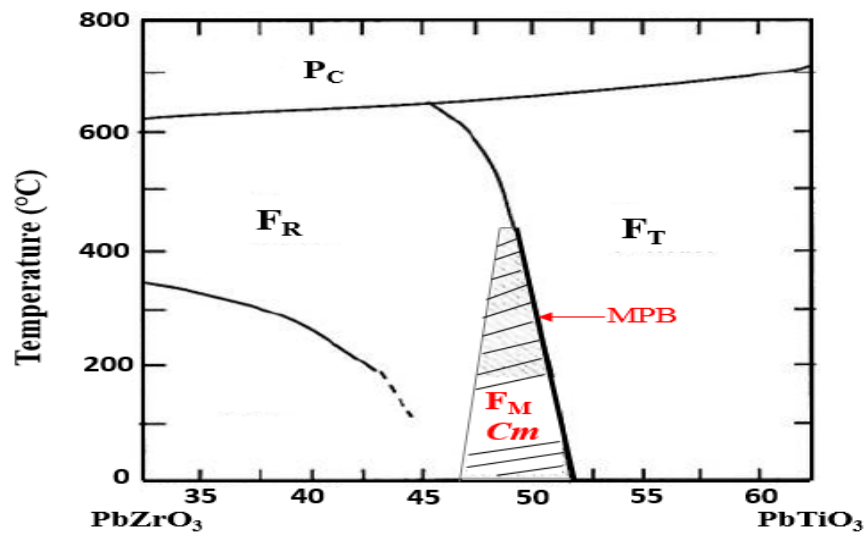


Figure 1-16: The latest PZT phase diagram [110].

MPB can be described as the boundary that separates areas of different symmetries [11,111]. MPB composition exhibits superior dielectric, piezoelectric, pyroelectric and ferroelectric properties. Although BaTiO_3 , (*BT*) was discovered earlier than PZT, PZT supplants BT in a wide range of applications due to its superior characteristics such as:

- High Curie temperature.
- High spontaneous polarization.
- High relative permittivity.
- Low dielectric loss.
- High electromechanical coupling coefficient.
- Easy to pole.
- Easy to modify its compositions with different with different dopants.

PZT-based materials provide quite high performance and for that reason they have prevalent in huge number of industrial applications [45,51,56,108,109].

1.2.5.5 Lead-free ferroelectric materials

1.2.5.6 Barium Titanate (BaTiO_3)

Barium titanate (BaTiO_3 or *BT*) is considered as the first oxide material to show ferroelectric properties and is deemed the first piezoceramic; it was utilized in commercial applications in 1947; and it demonstrates a perovskite structure [9,105,112]. BT, as a ferroelectric ceramic material was fundamental in proving that ferroelectric ceramics can show piezoelectric behaviour after a poling process [112].

BT was used initially for transducers and sensors as part of piezoelectric applications, since then it has been predominantly utilized for high dielectric constant capacitors applications [72]. BT illustrates different phase transitions at different temperatures (Fig. 1-17). These phase changes are accompanied with changes in mechanical and electrical properties; this can have as a consequence decrease in stability over a wide temperature range. In addition, BT presents low Curie temperature $\sim 120^\circ\text{C}$. Therefore, changes in its properties associated with

a fluctuation temperature along with the lower T_c have limited the usefulness of barium titanate in commercial applications [9,72,105,112].

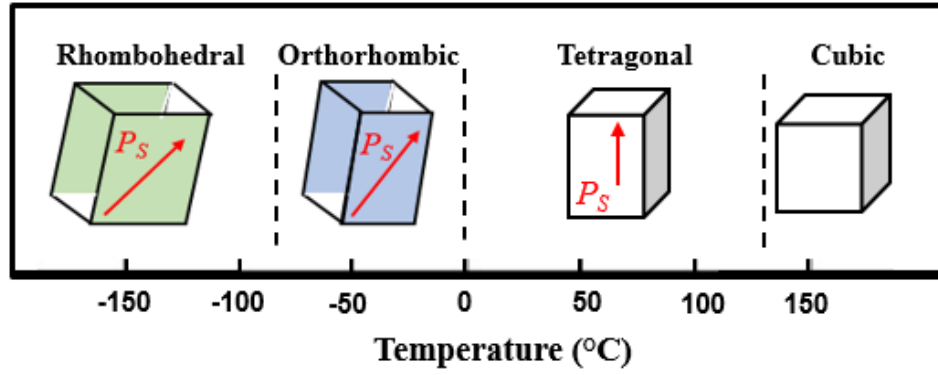


Figure 1-17: Schematic of the phase transitions of BaTiO_3 with temperature.

1.2.5.7 Sodium Bismuth Titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$)

The most important as well as promising system among bismuth containing lead-free ceramic systems is sodium bismuth titanate ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ or *NBT*). It was first discovered by Smolenskii *et al.*, in 1960 [72,112,113] and it presents very promising ferroelectric properties: these include high remnant polarization ($38 \mu\text{C}\cdot\text{cm}^{-1}$) and high Curie temperature ($\sim 320^\circ\text{C}$). However, it did not gain attention initially and it is only in the last twenty years, as a response to the pressure of the environmental changes to find lead-free alternatives to the lead-containing materials, that it has come to prominence [114].

In 1999, it was suggested that the main reason for the huge piezoelectric response of lead containing materials, especially in PZT, is results from the stereo-chemical activity of the pair ($6s^2$) in the Pb ion. This leads to the large structural distortion from the ideal perovskite phase structure (*cubic*), and this deformation can generate a sizable ferroelectric polarizations [115]. In 2005, Baetting *et al.*, suggested that bismuth-based materials can present a similar, or even larger, ion off centre cation in comparing with lead-based materials. The

stereo-chemical activity pair ($6s^2$) on the bismuth ion is also the driving force that leads to the production of substantial ferroelectric polarizations [116–118].

However, the main drawback of this system is the high conductivity, in addition to the high coercive field (E_C) ~ 73 kV. cm $^{-1}$, which makes the poling process in this material problematic. Furthermore, to achieve a dense ceramic body, NBT should be sintered at very high temperature at around 1200 °C and also for a long dwelling time [9,112]. The high conductivity issue is linked to the loss of Bi $^{3+}$ ions during sintering at a high temperature for a long time.

Uchida and Kikuchi in 1978 investigated the phase diagram of NBT material; they reported that NBT has a rhombohedral (*Rh*) lattice structure [119–121]. Wang *et al.* investigated the effects of doping bismuth in NBT material; they concluded that the leakage current was reduced when doped and the piezoelectric and dielectric properties were enhanced. Likewise, the NBT system with extra Bi $^{3+}$ content was reported by Hituma *et al.*; they found that this system showed an increase in its resistivity with more Bi $^{3+}$ content [122,123].

The NBT system presents a perovskite structure ABO $_3$ where, Na $^{+}$ and Bi $^{3+}$ occupy the A-site, while Ti $^{4+}$ occupies the B-site (Fig 1-18). Jones and Thomas reported that the NBT system presents Rh structure with space group *R3c* at room temperature; its structure may change with an increase of temperature to tetragonal (*Tr*) with space group (*P4bm*); and then to cubic (*C*) (*Pm3m*) with a further rise in temperature [124,125]. Another characteristic that was identified in the NBT system and has drawn considerable interest is its phase transition behaviour with dissimilar dielectric anomalies. The neutron diffraction results revealed that at temperature range 250-400 °C and 500-540 °C, the material structure shows coexistence of both Rh +Tr and Tr + C respectively [125,126]. However, another two transition temperatures were identified and those transitions represent the depolarization temperature (T_d) and the temperature of the maximum dielectric constant (T_M) [125,126]. Simultaneously, the phase change from Tr to C, which occurs at high temperature, has been proved by using different techniques [127–129]. However, the low temperature phase change at T_d that has been considered as the transition from Rh to Tr is somewhat

questionable [127–129]. Likewise, Vakhrushec *et al.*, investigated the coexistence of both Rh + Tr phases in NBT, and confirmed that this coexistence existed at a range temperature between T_d and T_M .

Furthermore, Dorcet *et al.* reported the electron transmission microscopy (*TEM*) data at the temperature of T_d up to T_M . It was concluded that there is an intermediate phase (orthorhombic phase) that can be formed between rhombohedral and tetragonal phases at this phase transition [121,130]. Although there a number of studies which have reported the phase transitions at a wide temperature range from T_d to T_M , in the literature, the exact interpretation to the behaviour of NBT system at this phase change is still under debate and needs further investigation.

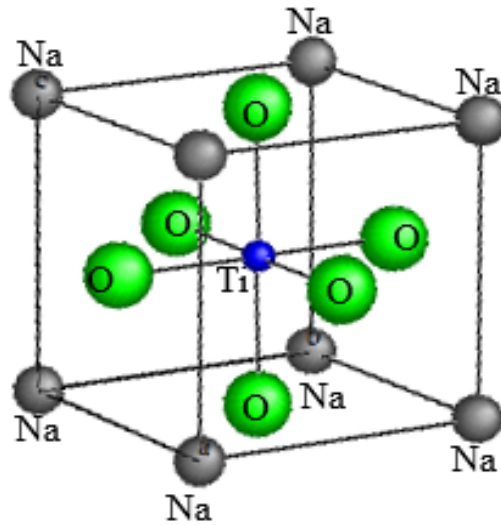


Figure 1-18: Cubic perovskite phase of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ system [9].

Despite the fact that the NBT system shows strong ferroelectric and other promising properties it still possesses some critical restrictions that can limit its utility in various applications. These limitations include:

- High conductivity.
- High coercive field.

- High leakage current.
- High dielectric loss.
- Difficult to achieve dense ceramic body.

Thus, to improve the NBT properties as well as its performance and to make it more suitable for variety applications, two techniques can be utilized:

- NBT can be combined with another perovskite ceramic compositions, such as BaTiO_3 , NaNbO_3 , $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$, and SrTiO_3 [23,25,131], forming a new composition. At RT, NBT shows Rh structure, while the BaTiO_3 , NaNbO_3 , $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$, and SrTiO_3 show Tr. Therefore, forming new solid solution from $(1-x)\text{NBT}-x\text{BT}$, or $(1-x)\text{NBT}-x\text{BKT}$, or $(1-x)\text{NBT}-x\text{SrTiO}_3$ in attempt to form new composition with morphotropic phase boundary (MPB) area where, Rh + Tr coexisted like PZT can highly enhance the dielectric, piezoelectric, pyroelectric, and ferroelectric properties of the new composition [132].
- Doping with other elements such as Mn, Eu, La, Zr, Al, Co, Nb, Zr, Ta and many other elements in both A and /or B-sites [19,133] can help enhance the performance of NBT and NBT-xBT.

1.2.5.7.1 ($\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$)-based Solid Solution with Morphotropic Phase Boundary (MPB)

Generally, the improvement in the piezoelectric response refers to the increase of the number of the polar axes in the composition. In any crystallographic symmetry, the number of polar axes that the dipoles can be aligned with in one direction is always fixed. Therefore, the Zr-rich side of the MPB area of PZT, (Fig. 1-15) has rhombohedral crystal symmetry with eight equivalent directions as polar axes. However, the PZT with Ti-rich side of MPB of the same material possesses tetragonal symmetry with six equivalent directions as polar axes. Because at MPB region two or more different phases coexist, the reorientation of the polar axes in PZT will be increased to 14 available directions under an external electric field. Therefore, the enhancement in dielectric and piezoelectric properties of the PZT composition at MPB has been attributed to this phenomenon [3,89].

In NBT-based system, the morphotropic phase boundary appears when it combines with 0.06 or 0.07 of BaTiO₃, to form (0.94 or 0.93)NBT-(0.06-0.07)BT system [20], which is reported by Takenaka *et al.*, in (1991). The phase structure of the MPB region at RT in this system encloses both Rh and Tr with applied $E_F \sim 3 \text{ kV.mm}^{-2}$ [134,135] (Fig. 1-19).

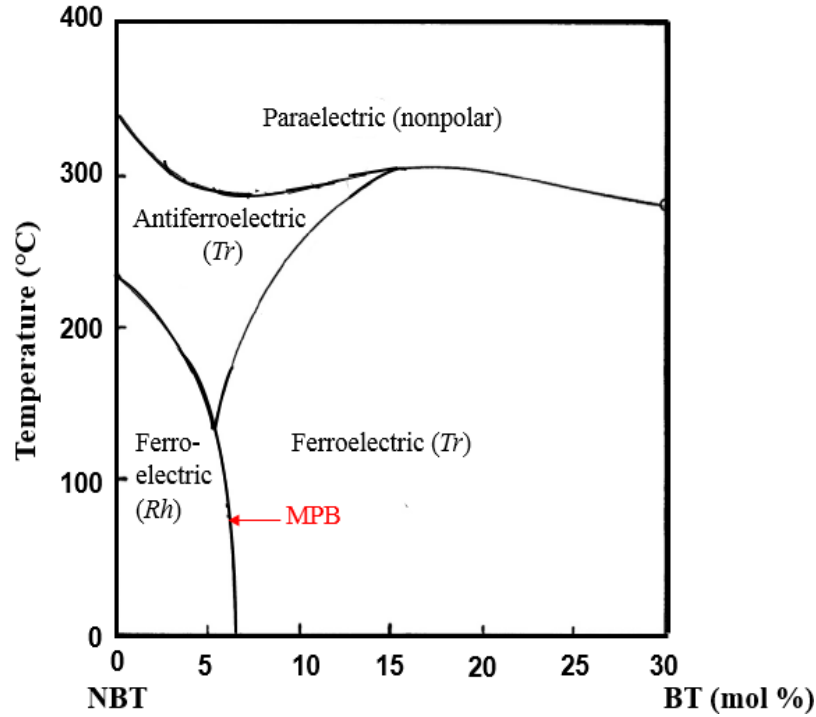


Figure 1-19: NBT-xBT phase diagram [20].

Although the position of the MPB in the NBT-xBT system is widely reported in the literature and the majority of researchers agree that it is located at $x=0.06$ of BaTiO₃ [12,13,15, 26, 29,101,104,134–138], it can be shifted to either the NBT-rich side or the BT-rich side by modifying the NBT-0.06BT composition or doping it with different elements. According to Hiruma *et al.* [139], the position of the MPB of perovskite structure can be determined by calculating the Goldschmidt tolerance factor (t) (Eqn. 1-12) BaTiO₃ and by calculating the (X_{MPB}) value for the new composition using the equation [34,104,139]:

$$X_{MPB} = \frac{t_{MPB} + t_{NBT}}{t_{BT} - t_{NBT}} \quad (1-19)$$

Therefore, the calculation from Eqn. 1-19 will reveal whether the position of MPB may shift to the NBT-rich or BT-rich side depending on the concentration of the elements doped in the system.

1.2.5.8 Sodium Bismuth Titanate modified with Barium titanate ((1-x)Na_{0.5}Bi_{0.5}TiO₃-xBaTiO₃)

This system was first discovered by Takenaka *et al.* in 1991 as a lead-free piezoelectric material. BT was added to NBT in order to form a composition that can have MPB, as in PZT [140]. In addition to high piezoelectric response, the solid solution of NBT-xBT is much easier to pole than undoped NBT. It is also much easier to obtain a high-density ceramic body compared with other lead-free piezoelectric ceramics, such as K_{0.5}Na_{0.5}NbO₃ (KNN). However, the utilization of NBT-xBT in industrial applications was limited and the progress in improving its properties was very slow due to a lack in the understanding of the general structure-properties correlation for NBT-xBT [19,136, 141-151].

The phase diagram of poled NBT-xBT shows a several phase transitions:

- From ferroelectric - antiferroelectric at depolarization temperature (T_d) ~100 to ~165 °C [26–28].
- From antiferroelectric - nonpolar phases to around 225 to 292 °C, at either the Curie temperature (T_c) or the temperature of maximum dielectric permittivity (T_m) [15,22–25,27].

The NBT-xBT phase transitions are also accompanied with structural transitions [24,26,27]:

- From MPB (*rhombohedral + tetragonal*) - tetragonal, if the composition is at the MPB area, or from rhombohedral - tetragonal, if the composition is out of MPB.
- From tetragonal to cubic.

The phase diagram of undoped NBT-xBT shows appreciably different features [152] (Fig. 1-20) compared with the poled phase diagram. There is an additional region which is relaxor antiferroelectric (*Re-anti-FE*) with a symmetry group (*P4bm*) existing between the ferroelectric (*R3c*) and ferroelectric (*P4mm*) phases at RT. Moreover, this diagram presents two MPB regions. Firstly, (*R3c* + *P4bm*) at $5\% \leq x \leq 6\%$ second, (*P4bm* + *P4mm*) at $10\% \leq x \leq 11\%$ [134,135,152–154].

Although the properties of undoped and doped NBT-xBT have been widely investigated and reported in the literature [151,152], such as dielectric, ferroelectric and piezoelectric; their pyroelectric properties have received less attention [15,59,63,150,151].

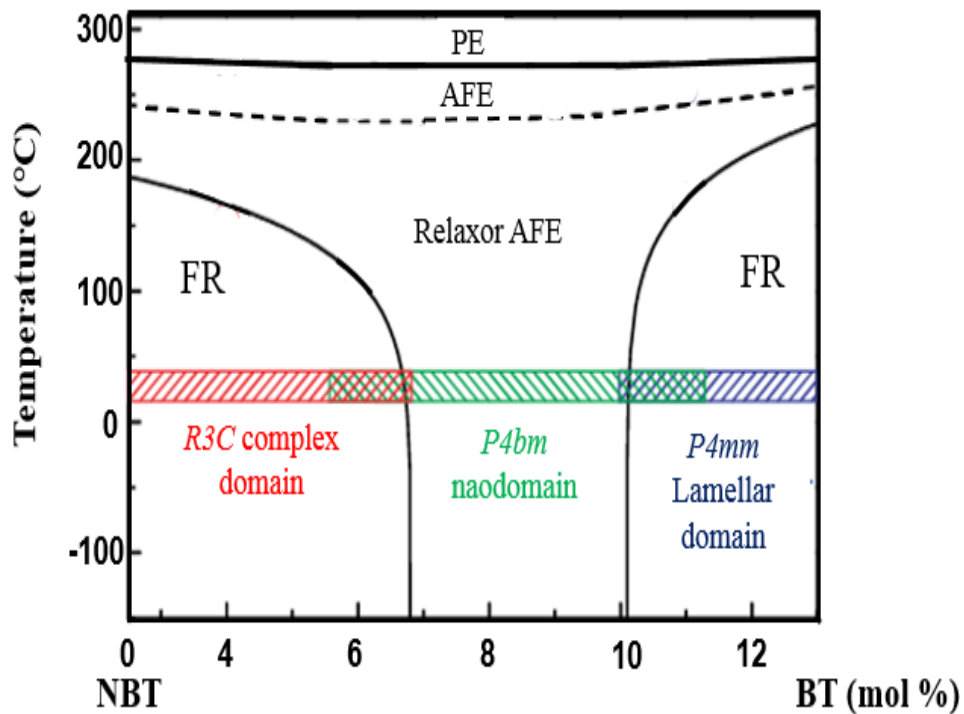


Figure 1-20: The phase diagram of unpoled NBT-xBT [152].

J. Abo *et al.* (2006) investigated the pyroelectric properties of xMn doped NBT-0.06BT, $0 \leq x \leq 0.8$ (wt%). The maximum pyroelectric coefficient (p) at RT was obtained in NBT-0.06BT-0.2Mn which is $\sim 3.5 \times 10^{-4} \text{ C. m}^{-2} \cdot ^\circ\text{C}^{-1}$ and this p is

higher than for undoped NBT-0.06BT $\sim 2.9 \times 10^{-4} \text{ C. m}^{-2} \cdot ^\circ\text{C}^{-1}$. In addition, the F_D value is around $4.5 \mu\text{Pa}^{-1/2}$, which is also higher than that for undoped NBT-0.06BT ($\sim 2.7 \mu\text{Pa}^{-1/2}$) [63].

Rodriguez Ruiz *et al.* studied the pyroelectric characteristics of the lead-free NBT-0.065BT ferroelectric ceramics for infrared detectors [59]. In this study the pyroelectric coefficient of this undoped material is around $1.7 \times 10^{-4} \text{ C. m}^{-2} \cdot ^\circ\text{C}^{-1}$ at room temperature. In addition, the FOM F_C for this undoped material was calculated and it was found to be $\sim 1.44 \times 10^{-9} \text{ C. cm}^{-2} \cdot ^\circ\text{C}^{-1}$, which was lower than the threshold F_C value $(3 \pm 1) \times 10^{-9} \text{ C. cm}^{-2} \cdot ^\circ\text{C}^{-1}$ for pyroelectric materials that are suitable for the use in pyroelectric sensors [59].

The pyroelectric properties of K and Li doped NBT-0.05BT (($\text{Na}_{0.94} \text{K}_{0.05} \text{Li}_{0.016}$) $_{0.5} \text{Bi}_{0.5} \text{TiO}_3$ -0.05BaTiO₃) were studied by Lau *et al.* The KLi-NBT-0.05BT shows quite good pyroelectric properties compared to $\text{K}_{0.5} \text{Na}_{0.5} \text{NbO}_3$ (KNN) and PZT ceramics. The pyroelectric coefficient of this system is around $3.6 \times 10^{-4} \text{ C. m}^{-2} \cdot ^\circ\text{C}^{-1}$, and FOMs, $F_i = 2.2 \times 10^{-10} \text{ m. V}^{-1}$, $F_V = 0.03 \text{ m}^2 \cdot \text{C}^{-1}$ and $F_D = 14.8 \times 10^{-6} \text{ Pa}^{-1/2}$ [23].

Guo and Gu investigated the pyroelectric response of undoped lead-free ($\text{Na}_y \text{Bi}_z$)TiO₃-xBaTiO₃ ($x=0.06$ -0.08, $z/y \geq 1$) ceramics. The results of this study revealed that the stability of the induced ferroelectric phase is mainly related to molar ratio of $\text{Bi}^{3+}/\text{Na}^+$. In addition, pyroelectric coefficient responses at the depolarization temperature were obtained [62].

Guo *et al.* explored the pyroelectric properties of NBT-xBa($\text{Zr}_{0.055} \text{Ti}_{0.0945}$)O₃ ($0 \leq x \leq 0.12$) lead free ceramics and deduced that the composition at $x=0.07$ improved pyroelectric properties from RT up to T_d (87 $^\circ\text{C}$), with $p = 5.7 \times 10^{-4} \text{ C. m}^{-2} \cdot ^\circ\text{C}^{-1}$ and FOMs $F_i = 2.3 \times 10^{-10} \text{ m. V}^{-1}$, $F_V = 0.022 \text{ m}^2 \cdot \text{C}^{-1}$ and $F_D = 10.5 \times 10^{-6} \text{ Pa}^{-1/2}$. In addition, the highest pyroelectric coefficient of $221 \times 10^{-4} \text{ C. m}^{-2} \cdot ^\circ\text{C}^{-1}$ was found around T_d [15].

Felix *et al.* reported the pyroelectric behaviour and the dielectric constant tunability at two microwave frequencies, 100 MHz and 3 GHz, of NBT-xBT ($x=0.04$ and 0.06). This research shows that the pyroelectric response and

dielectric constant tunability of the composition at MPB ($x=0.06$) are greater than the composition near the MPB ($x=0.04$) area. Also, pyroelectric figure of merit (F_C) of the composition NBT-0.06BT was found to be comparable to the commercial PZT pyroelectric material [24].

1.3 Aim and Objectives

The aim of the current research explore and enhance the pyroelectric performance of ceramic $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-x\text{BaTiO}_3$ (*NBT-xBT*), particularly at morphotropic phase boundary (*MPB*) where $x=0.6$. Efforts made to bring down the depolarization temperature to near room temperature through modifying or doping A and/or B sites. Furthermore, the operational temperature range of a pyroelectric material is extended by designing and producing a new pyroelectric composite material (*PCM*) in which two different but very close compositions are included.

To achieve the target, the subsequent objectives were set out:

- 1- Identify sodium bismuth titanate modified by barium titanate *NBT-xBT* at morphotropic phase boundary (*MPB*) as potential pyroelectric material.
- 2- Investigate the structure-property correlation at $0.05 \leq x \leq 0.08$.
- 3- Explore the effects of changing the A-site stoichiometry by modifying the sodium to bismuth (Bi/Na) ratio and also changing the barium content on the microstructure, depolarization, dielectric and pyroelectric properties of the *NBT-xBT* of the composition at MPB.
- 4- Investigate the effect of doping the A site of the *NBT-xBT* of the composition at MPB on the microstructure, depolarization, dielectric and pyroelectric properties.
- 5- Explore the effect of doping B site of the *NBT-xBT* of the composition at MPB on the microstructure, depolarization, dielectric and pyroelectric properties.
- 6- Study the effect of co-doping A and B sites of the *NBT-xBT* of the composition at MPB on the microstructure, depolarization, dielectric and pyroelectric properties.

- 7- Develop a new pyroelectric composite material (*PCM*) as inhomogeneous material using the spark plasma sintering (SPS) method as a novel method of merging two or more dissimilar but close compositions to broaden the operational temperature range of A or B site doped *NBT-xBT* of the composition at MPB.

1.4 Thesis Structure

This thesis is divided into eleven chapters. The outlines of these chapters are listed in Table 1-1, and the structure of the current thesis can be summarised as:

Chapter 1 includes introduction to the project background, various concepts about materials, a concise literature review followed by the aims and objectives of the current research.

Chapter 2 describes the sample preparation procedures and characterisation methods that have been used in this study.

Chapter 3 explores lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ as a potential pyroelectric material.

Chapter 4 describes the identification of the morphotropic phase boundary composition (*MPB*) in the $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}x\text{BaTiO}_3$ ceramics at $0.05 \leq x \leq 0.08$ and the effects of morphotropic phase boundary on the microstructure, depolarization, dielectric and pyroelectric properties.

Chapter 5 describes the effect of A-site nonstoichiometry compositions on the microstructure, depolarization, dielectric and pyroelectric properties of this material.

This chapter has been divided into two sections:

- A. Changing the barium content in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{Ba}_{1+x}\text{TiO}_3$.
- B. Changing the Na, Bi, and Ba contents of the $\text{N}_x\text{B}_y\text{T}\text{-}0.06\text{B}_z\text{T}$.

Chapter 6 explores the doping of the A-site of the $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ with $x\text{La}$, $0.0 \leq x \leq 1.0$ (mol%) on the microstructure, depolarization, dielectric and pyroelectric properties of this material.

Chapter 7 explores the effect of doping the B-site of the $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 with $x\text{Ta}$, $0.0 \leq x \leq 1.0$ (mol%) on the microstructure, depolarization, dielectric and pyroelectric properties of this material.

Chapter 8 explores the effect of co-doping the A and B-sites of the $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 with $x\text{La}$ and $y\text{Ta}$ on the microstructure, depolarization, dielectric and pyroelectric properties of this material.

This chapter has been divided into two sections:

- A. Giant pyroelectric properties in La and Ta co-doped lead-free 0.94NaBiTiO_3 - 0.06BaTiO_3 ceramics
- B. Improvement of pyroelectric properties of lead-free 0.94NaBiTiO_3 - 0.06BaTiO_3 ceramics at wide temperature range by co-doping La and Ta

Chapter 9 describes the investigation of a new composite pyroelectric material (*CPM*) that was prepared by sintering two dissimilar but very close compositions in SPS.

Chapter 10 bridges the previous chapters and presents the general and final discussion.

Chapter 11 this chapter presents the conclusion and future works.

Table 1-1: Thesis structure.

Chapter	Title	Objective addressed
1	Introduction & Literature Review	-
2	Experiential procedure and Material Characterisations	-
3	Investigate the NBT-0.06BT as a potential pyroelectric material	1
4	Identify the Morphotropic Phase Boundary Composition of $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - $x\text{BaTiO}_3$	2
5	Modify A-site Elements Content	3
6	Doping A-site	4
7	Doping B-site	5
8	Doping A&B sites	6
9	Pyroelectric Composite Material (<i>PCM</i>)	7
10	Thesis overall discussion	-
11	Conclusions and Recommendations for Future work	-

1.5 References

1. García JE. Elastic, dielectric and electromechanical properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{--BaTiO}_3$ piezoceramics at the morphotropic phase boundary region. *Journal of Alloys and Compounds*. Elsevier Ltd; 2016; Available at: DOI:10.1016/j.jallcom.2016.08.116
2. Balakt AM., Shaw CP., Zhang Q. The effects of Ba^{2+} content on depolarization temperature and pyroelectric properties of lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - 0.06\text{Ba}_{1+x}\text{TiO}_3$ ceramics. *Journal of Materials Science: Materials in Electronics*. 2016; 27: 12947–12954. Available at: DOI:10.1007/s10854-016-5433-1
3. Neppiras EA. Piezoelectric ceramics 1971. *Journal of Sound and Vibration*. 1972; 20(4): 562–563. Available at: DOI:10.1016/0022-460X(72)90684-0
4. Noheda B. Structure and high-piezoelectricity in lead oxide solid solutions. *Current Opinion in Solid State and Materials Science*. 2002; 6(1): 27–34. Available at: DOI:10.1016/S1359-0286(02)00015-3
5. Zhang G., Jiang S., Zhang Y., Xie T. Pyroelectric properties in three phases coexistence $\text{Pb}[(\text{Mn}_{0.33}\text{Nb}_{0.67})_{0.5}(\text{Mn}_{0.33}\text{Sb}_{0.67})_{0.5}]_{0.08}(\text{Zr}_x\text{Ti}_{1-x})_{0.92}\text{O}_3$ lead ceramics. *Current Applied Physics*. Elsevier B.V.; 2009; 9(6): 1434–1437. Available at: DOI:10.1016/j.cap.2009.03.019
6. Haun MJ., Furman E., Jang SJ., Cross LE. Thermodynamic theory of the lead zirconate-titanate solid solution system, part V: Theoretical calculations. *Ferroelectrics*. 1989; 99(1): 63–86. Available at: DOI:10.1080/00150198908221440
7. Tong S., Schirnding YE Von., Prapamontol T. Environmental lead exposure : a public health problem of global dimensions. 2000; 78(9): 5–10. Available at: DOI:10.1590/S0042-96862000000900003
8. J. Patocka KC. Inorganic lead toxicology . *Acta medica*. 2003; 46(2): 65–72.

9. Sanson A. Modified Bismuth Titanate Piezoelectric Ceramics. Thesis. Cranfield University; 2003.
10. Cross E. Lead-free at last. *Nuclear Medicine Communications*. 2011; 32(7): 666–668. Available at: DOI:10.1097/MNM.0b013e328348bcfb
11. Beveren W Van. Lead-free piezoceramics. *Physica Status Solidi B*. 2004; 432(November): 1–4. Available at: DOI:10.1038/nature03008.1.
12. Ranjan R., Dwiwedi A. Structure and dielectric properties of $(\text{Na}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$: $0 \leq x \leq 0.10$. *Solid State Communications*. 2005; 135: 394–399. Available at: DOI:10.1016/j.ssc.2005.03.053
13. Rawat M., Yadav KL., Kumar A., Patel PK., Adhlakha N., Rani J. Structural, dielectric and conductivity properties of Ba^{2+} doped $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramic. *Advanced Materials Letters*. 2012; 3(4): 286–292. Available at: DOI:10.5185/amlett.2012.2322
14. Craciun F., Galassi C., Birjega R. Electric-field-induced and spontaneous relaxor-ferroelectric phase transitions in $(\text{Na}_{1/2}\text{Bi}_{1/2})_{1-x}\text{Ba}_x\text{TiO}_3$. *Journal of Applied Physics*. 2012; 112(2012). Available at: DOI:10.1063/1.4770326
15. Guo F., Yang B., Zhang S., Wu F., Liu D., Hu P., et al. Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition. *Applied Physics Letters*. 2013; 103(18): 182906. Available at: DOI:10.1063/1.4828675
16. Xu C., Lin D., Kwok KW. Structure, electrical properties and depolarization temperature of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{--BaTiO}_3$ lead-free piezoelectric ceramics. *Solid State Sciences*. 2008; 10(7): 934–940. Available at: DOI:10.1016/j.solidstatesciences.2007.11.003
17. Xu Q., Huang DP., Chen M., Chen W., Liu HX., Kim BH. Effect of bismuth excess on ferroelectric and piezoelectric properties of a $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{--BaTiO}_3$ composition near the morphotropic phase boundary. *Journal of*

- Alloys and Compounds. 2009; 471(1–2): 310–316. Available at: DOI:10.1016/j.jallcom.2008.03.078
18. Wang X., Tang X., Chan H. Electromechanical and ferroelectric properties of (Bi 1/2 Na 1/2) TiO 3–(Bi 1/2 K 1/2) TiO 3–BaTiO 3 lead-free piezoelectric ceramics. Applied physics letters. 2004; 85(1): 91. Available at: DOI:10.1063/1.1767592
 19. McQuade RR., Dolgos MR. A review of the structure-property relationships in lead-free piezoelectric (1-x)Na0.5Bi0.5TiO3-(x)BaTiO3. Journal of Solid State Chemistry. Elsevier; 2015; 3: 1–8. Available at: DOI:10.1016/j.jssc.2016.01.008
 20. Search H., Journals C., Contact A., Iopscience M. (Bi1 / 2Na1 / 2) TiO3-BaTiO3 System for Lead-Free Piezoelectric Ceramics. Jpn. J. Appl. Phys. 1991; 2236(20/07/1991): 2236–2239.
 21. Ma C., Tan X. Phase diagram of unpoled lead-free – ceramics. Solid State Communications. 2010; 150(33–34): 1497–1500. Available at: DOI:10.1016/j.ssc.2010.06.006
 22. Cheng SY., Shieh J., Lu HY., Shen CY., Tang YC., Ho NJ. Structure analysis of bismuth sodium titanate-based A-site relaxor ferroelectrics by electron diffraction. Journal of the European Ceramic Society. Elsevier Ltd; 2013; 33(11): 2141–2153. Available at: DOI:10.1016/j.jeurceramsoc.2013.03.020
 23. Lau ST., Cheng CH., Choy SH., Lin DM., Kwok KW., Chan HLW. Lead-free ceramics for pyroelectric applications. Journal of Applied Physics. 2008; 103(10): 10–13. Available at: DOI:10.1063/1.2927252
 24. Martínez FL., Hinojosa J., Doménech G., Fernández-luque FJ., Zapata J., Ruiz R., et al. Dielectric Constant Tunability at Microwave Frequencies and Pyroelectric Behavior. IEEE transactions on ultrasonics, ferroelectrics, and frequency control. 2013; 60(8): 1595–1602. Available at: DOI:10.1109/TUFFC.2013.2740.

25. Razak KA., Yip CJ., Sreekantan S. Synthesis of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) and Pr doped BNT using the soft combustion technique and its properties. *Journal of Alloys and Compounds*. Elsevier B.V.; 2011; 509(6): 2936–2941. Available at: DOI:10.1016/j.jallcom.2010.11.163
26. Chen M., Xu Q., Kim BH., Ahn BK., Ko JH., Kang WJ., et al. Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ piezoelectric ceramics. *Journal of the European Ceramic Society*. 2008; 28: 843–849. Available at: DOI:10.1016/j.jeurceramsoc.2007.08.007
27. Kanuru SR., Baskar K., Dhanasekaran R. Synthesis, structural, morphological and electrical properties of NBT–BT ceramics for piezoelectric applications. *Ceramics International*. Elsevier; 2016; 42(5): 6054–6064. Available at: DOI:10.1016/j.ceramint.2015.12.162
28. Jo W., Daniels J., Damjanovic D., Kleemann W., Rodel J. Two-stage processes of electrically induced-ferroelectric to relaxor transition in $0.94(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - 0.06BaTiO_3 . *Applied Physics Letters*. 2013; 102(19): 0–4. Available at: DOI:10.1063/1.4805360
29. Li Q., Wang J., Ma L., Fan H., Li Z. Large electrocaloric effect in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ferroelectric ceramics by La_2O_3 addition. *Materials Research Bulletin*. Elsevier Ltd; 2016; 74: 57–61. Available at: DOI:10.1016/j.materresbull.2015.10.010
30. Li Q., Wang H., Fan H., Long C., Liu X. Ferroelectric, electromechanical, and dielectric properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ co-doped MnO_2 and La_2O_3 lead-free ceramics. *Journal of Materials Science*. 2013; 49(1): 211–217. Available at: DOI:10.1007/s10853-013-7694-x
31. ABE J., KOBUNE M., NISHIMURA T., YAZAW T., NAKAI Y. Effects of manganese addition on pyroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)_{0.94}(\text{BaTiO}_3)_{0.06}$ ceramics. *Integrated Ferroelectrics*. 2006; 80(1): 87–95. Available at: DOI:10.1080/10584580600656502
32. Lee SG., Kim C Il., Kim BC. Dielectric properties of screen-printed

- (Ba,Sr,Ca)TiO₃ thick films modified with Al₂O₃ for microwave device applications. *Journal of the European Ceramic Society*. 2004; 24(1): 157–162. Available at: DOI:10.1016/S0955-2219(03)00252-8
33. Peng Fu, Zhijun Xu, Ruiqing Chu, Wei Li, Qian Xie, Yanjie Zhang QC. Effect of Dy₂O₃ on the structure and electrical properties of (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ lead-free piezoelectric ceramics. *Journal of Alloys and Compounds*. Elsevier B.V.; 2010; 508: 546–553. Available at: DOI:10.1016/j.jallcom.2010.08.117
 34. Le Goupil F., Bennett J., Axelsson AK., Valant M., Berenov A., Bell AJ., et al. Electrocaloric enhancement near the morphotropic phase boundary in lead-free NBT-KBT ceramics. *Applied Physics Letters*. 2015; 107(17): 103–107. Available at: DOI:10.1063/1.4934759
 35. Balakt AM., Shaw CP., Zhang Q. Enhancement of pyroelectric properties of lead-free 0.94Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃ ceramics by La doping. *Journal of the European Ceramic Society*. 2017; 37(4): 1459–1466. Available at: DOI:10.1016/j.jeurceramsoc.2016.12.021
 36. Balakt AM., Shaw CP., Zhang Q. The decrease of depolarization temperature and the improvement of pyroelectric properties by doping Ta in lead-free 0.94Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃ ceramics. *Ceramics International*. December 2017; 43: 3726–3733. Available at: DOI:10.1016/j.ceramint.2016.12.004
 37. Balakt AM., Shaw CP., Zhang Q. Giant pyroelectric properties in La and Ta co-doped lead-free 0.94Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃ ceramics. *Journal of Alloys and Compounds*. 2017; 709: 82–91. Available at: DOI:10.1016/j.jallcom.2017.03.143
 38. Balakt AM., Shaw CP., Zhang Q. Large pyroelectric properties at reduced depolarization temperature in A-site nonstoichiometry composition of lead-free 0.94Na_xBi_yTiO₃–0.06Ba_zTiO₃ ceramics. *Journal of Materials Science*. 2017; 52(12): 7382–7393. Available at: DOI:10.1007/s10853-017-0973-1

39. Naebe M., Shirvanimoghaddam K. Functionally graded materials: A review of fabrication and properties. *Applied Materials Today*. 2016; 5(December): 223–245. Available at: DOI:10.1016/j.apmt.2016.10.001
40. Hong CQ., Zhang XH., Li WJ., Han JC., Meng SH. A novel functionally graded material in the ZrB₂-SiC and ZrO₂ system by spark plasma sintering. *Materials Science and Engineering A*. 2008; 498(1–2): 437–441. Available at: DOI:10.1016/j.msea.2008.08.032
41. Swain S. Synthesis and Characterizations of SrBi₂Ta₂O₉ Modified NBT-BT and NBT-KNN Ferroelectric Ceramics near Morphotropic Phase Boundary. National Institute of Technology Rourkela; 2015.
42. Moulson a. J., Herbert JM. *Electroceramics: Materials, Properties, Applications*. 2003. 576 p. Available at: DOI:10.1002/0470867965
43. Kittel C. *Introduction to Solid State Physics*. John Wiley & Sons, New York; 2005.
44. Nye JF. *Physical Properties of Crystals , Their Representation by Tensors and Matrices*. Virginia; 1985. 343 p.
45. Whatmore RW. Pyroelectric devices and materials. *Reports on Progress in Physics*. 1986; 49(12): 1335–1386. Available at: DOI:10.1088/0034-4885/49/12/002
46. Whatmore RW. Pyroelectric devices and materials. *Reports on Progress in Physics*. 1999; 49(12): 1335–1386. Available at: DOI:10.1088/0034-4885/49/12/002
47. Jordan TL., Langley N. Piezoelectric Ceramics Characterization. Contract. 2001; : 23. Available at: DOI:NASA/CR-2001-211225 ICASE Report No. 2001-28
48. Kao KC., Kao KC. Ferroelectrics, Piezoelectrics, and Pyroelectrics. *Dielectric Phenomena in Solids*. 2004; : 213–282. Available at: DOI:10.1016/B978-012396561-5/50014-1

49. Porter SG. A brief guide to pyroelectric detectors. *Ferroelectrics*. 1981. pp. 193–206. Available at: DOI:10.1080/00150198108008086
50. Rashid MH. Pyroelectric Detectors and Their Applications. *IEEE Transactions on Industry Applications*. 1991; 27(5): 824–829. Available at: DOI:10.1109/28.90335
51. Whatmore RW., Watton R. Chapter 5 PYROELECTRIC MATERIALS AND DEVICES. 2001. 99-148 p.
52. Yoon MS., Khansur NH., Ur SC. The effect of pre-milling/pre-synthesis process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized $0.94[(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3]-0.06[\text{Ba}(1+x)\text{TiO}_3]$. *Ceramics International*. Elsevier Ltd and Techna Group S.r.l.; 2010; 36(4): 1265–1275. Available at: DOI:10.1016/j.ceramint.2010.01.011
53. Muralt P. Micromachined infrared detectors based on pyroelectric thin films. *Reports on Progress in Physics*. 2001; 64(10): 1339–1388. Available at: DOI:10.1088/0034-4885/64/10/203
54. Lang SB. Pyroelectricity : From Ancient Changes in the net dipole moment of certain materials form. *Physics Today*. 2005; 58(August): 31–36. Available at: DOI:10.1063/1.2062916
55. Born M., Kuang H. *Dynamical Theory of Crystal Lattices*. Oxford University Press. 1962. p. 431. Available at: DOI:10.1119/1.1934059
56. Keller HJ. 30 Years of Passive Infrared Motion Detectors - a Technology Review. 2000;
57. Glass MEL and AM. *Principle and Applications of Ferroelectric and Related Materials*. Book. 2001; Available at: DOI:10.1093/acprof:oso/9780198507789.001.0001
58. Tayi AS., Kaeser A., Matsumoto M., Aida T., Stupp SI. Supramolecular ferroelectrics. *Nature chemistry*. Nature Publishing Group; 2015; 7(4): 281–294. Available at: DOI:10.1038/nchem.2206

59. Xu YH. Ferroelectric materials and their applications. 1991;
60. Yukio Ito and Uchino K. Wiley Encyclopedia of Electrical and Electronics Engineering. 2005. Available at: DOI:10.1002/0471654507.eme319
61. Damjanovic D. Ferroelectric , dielectric and piezoelectric properties of ferroelectric thin films and ceramics. Rep. Prog. Phys. 1998; 61(1998): 1267–1324. Available at: DOI:10.1088/0034-4885/61/9/002
62. Valasek J. Piezo-electric and allied phenomena in Rochelle salt. Physical Review. 1921; 17(4): 475–481. Available at: DOI:10.1103/PhysRev.17.475
63. Haertling GH. Ferroelectric Ceramics: History and Technology. Journal of the American Ceramic Society. 1999; 82(4): 797–818. Available at: DOI:10.1111/j.1151-2916.1999.tb01840.x
64. Arlt G. Twinning in ferroelectric and ferroelastic ceramics: stress relief. Journal of Materials Science. 1990; 25(6): 2655–2666. Available at: DOI:10.1007/BF00584864
65. Ghosh D., Sakata A., Carter J., Thomas PA., Han H., Nino JC., et al. Domain wall displacement is the origin of superior permittivity and piezoelectricity in BaTiO₃ at intermediate grain sizes. Advanced Functional Materials. 2014; 24(7): 885–896. Available at: DOI:10.1002/adfm.201301913
66. García JE., Guerra JDS., Araújo EB., Pérez R. Domain wall contribution to dielectric and piezoelectric responses in 0.65Pb(Mg ^{1/3} Nb ^{2/3})–0.35PbTiO₃ ferroelectric ceramics. Journal of Physics D: Applied Physics. 2009; 42(11): 115421. Available at: DOI:10.1088/0022-3727/42/11/115421
67. Guyonnet J. Ferroelectric Domain Walls. Springer Thesis. 2014; : Chap. 2. Available at: DOI:10.1007/978-3-319-05750-7
68. Maeder MD., Damjanovic D., Setter N. Lead free piezoelectric materials. Journal of Electroceramics. 2004; 13(1–3): 385–392. Available at: DOI:10.1007/s10832-004-5130-y

69. Bokov AA., Ye ZG. Recent progress in relaxor ferroelectrics with perovskite structure. *Journal of Materials Science*. 2006; 41(1): 31–52. Available at: DOI:10.1007/s10853-005-5915-7
70. Samara G a. The relaxational properties of compositionally disordered ABO_3 perovskites. *Journal of Physics: Condensed Matter*. 2003; 15(9): R367–R411. Available at: DOI:10.1088/0953-8984/15/9/202
71. Shrout TR., Halliyal A. Preparation of Lead-Based Ferroelectric Relaxors For Capacitors. *American Ceramics Society. Bulletin*. 1987; 66(4): 704–711. Available at: DOI:10.1080/00150198708201313
72. Whatmore RW., Osbond PC., Shorrocks NM. Ferroelectric materials for thermal IR detectors. *Ferroelectrics*. 1987; 76(July 2012): 351–367. Available at: DOI:10.1080/00150198708016956
73. Uchino K. Electrostrictive Actuators: Materials and Applications. *American Ceramic Society Bulletin*. 1986; 65(4): 647–652.
74. McHenry DA., Giniewicz J., Jang SJ., Bhalla A., Shrout TR. Optical properties of hot pressed relaxor ferroelectrics. *Ferroelectrics*. 1989; 93(1): 351–359. Available at: DOI:10.1080/00150198908017367
75. Peláiz-Barranco A., González-Carmenate I., Calderón-Piñar F. Relaxor behaviour in PZN-PT-BT ferroelectric ceramics. *Solid State Communications*. 2005; 134(8): 519–522. Available at: DOI:10.1016/j.ssc.2005.03.001
76. Cowley RA., Gvasaliya SN., Lushnikov SG., Roessli B., Rotaru GM. Relaxing with relaxors: a review of relaxor ferroelectrics. *Advances in Physics*. 2011; 60(2): 229–327. Available at: DOI:10.1080/00018732.2011.555385
77. Shrout TR., Fielding J. Relaxor ferroelectric materials. *IEEE Symposium on Ultrasonics*. 1990; : 711–720. Available at: DOI:10.1109/ULTSYM.1990.171456

78. Agranovskaya GAS and Al. Soiet Physics Solid State. Soiet Physics Solid State. 1959; 1(5): 1429. Available at: DOI:10.1063/1.1723278
79. Ma C., Guo H., Beckman SP., Tan X. Creation and destruction of morphotropic phase boundaries through electrical poling: A case study of lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ piezoelectrics. Physical Review Letters. 2012; 109(10): 107602. Available at: DOI:10.1103/PhysRevLett.109.107602
80. Uchino K. Ferroelectric Devices 2nd Edition. 2, illustr edn. CRC Press, 2009; 2009. 339 p.
81. Samara GA. Ferroelectricity revisited-Advances in materials and physics. Solid State Physics - Advances in Research and Applications. 2001; 56(C): 239–458. Available at: DOI:10.1016/S0081-1947(01)80020-5
82. Haertling G. Ferroelectric ceramics: history and technology. J. Am. Ceram. Soc. 1999; 82(4): 718–818. Available at: DOI:10.1111/j.1151-2916.1999.tb01840.x
83. King G., Woodward PM. Cation ordering in perovskites. 2010; : 5785–5796. Available at: DOI:10.1039/b926757c
84. Moure, Carlos OP. Recent advances in perovskites: Processing and properties. Solid State Chemistry. 2015; 43: 123–148. Available at: DOI:10.1016/j.progsolidstchem.2015.09.001
85. Cheong S-W., Mostovoy M. Multiferroics: a magnetic twist for ferroelectricity. Nature Materials. 2007; 6(1): 13–20. Available at: DOI:10.1038/nmat1804
86. Moritomo Y., Asamitsu a., Kuwahara H., Tokura Y. Giant magnetoresistance of manganese oxides with a layered perovskite structure. Nature. 1996; 380(6570): 141–144. Available at: DOI:10.1038/380141a0
87. Rodríguez-Martínez LM., Ehrenberg H., Attfield JPP., Rodríguez-Martínez

- L. M., Ehrenberg H., Attfield JPP. Cation Size Variance Effects in High-Tolerance Factor $\text{Ln}_{0.7}\text{M}_{0.3}\text{MnO}_3$ Perovskites. *Journal of Solid State Chemistry*. 1999; 148(1): 20–25. Available at: DOI:<http://dx.doi.org/10.1006/jssc.1999.8291>
88. Feng LM., Jiang LQ., Zhu M., Liu HB., Zhou X., Li CH. Formability of ABO_3 cubic perovskites. *Journal of Physics and Chemistry of Solids*. 2008; 69(4): 967–974. Available at: DOI:10.1016/j.jpcs.2007.11.007
 89. Li C., Soh KCK., Wu P. Formability of ABO_3 perovskites. *Journal of Alloys and Compounds*. 2004; 372(1–2): 40–48. Available at: DOI:10.1016/j.jallcom.2003.10.017
 90. Chellappan V., Ramakrishna S. Perovskites: Solar cells & engineering applications – materials and device developments. *Solar Energy*. 2015; 122: 678–699. Available at: DOI:10.1016/j.solener.2015.09.041
 91. Schlom DG., Chen L., Pan X., Schmehl A., Zurbuchen MA. A Thin Film Approach to Engineering Functionality into Oxides. 2008; 2454: 2429–2454. Available at: DOI:10.1111/j.1551-2916.2008.02556.x
 92. Dinh TH., Lee H-Y., Yoon C-H., Malik RA., Kong Y-M., Lee J-S., et al. Effect of lanthanum doping on the structural, ferroelectric, and strain properties of $\text{Bi}_{1/2}(\text{Na}_{0.82}\text{K}_{0.18})_{1/2}\text{TiO}_3$ lead-free ceramics. *Journal of the Korean Physical Society*. 2013; 62(7): 1004–1008. Available at: DOI:10.3938/jkps.62.1004
 93. Islam MR., Galib RH., Sharif A., Hasan M., Zubair MA., Islam MF. Correlation of charge defects and morphology with magnetic and electrical properties of Sr and Ta codoped BiFeO_3 . *Journal of Alloys and Compounds*. Elsevier Ltd; 2016; 688: 1186–1194. Available at: DOI:10.1016/j.jallcom.2016.07.134
 94. Li Z., Yang M., Park JS., Wei SH., Berry JJ., Zhu K. Stabilizing Perovskite Structures by Tuning Tolerance Factor: Formation of Formamidinium and Cesium Lead Iodide Solid-State Alloys. *Chemistry of Materials*. 2016;

- 28(1): 284–292. Available at: DOI:10.1021/acs.chemmater.5b04107
95. Cho J-H., Jeong Y-H., Nam J-H., Yun J-S., Park Y-J. Phase transition and piezoelectric properties of lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--BaTiO}_3$ ceramics. *Ceramics International*. 2014; 40: 8419–8425. Available at: DOI:10.1016/j.ceramint.2014.01.051
 96. Panda PK. Review: Environmental friendly lead-free piezoelectric materials. *Journal of Materials Science*. 2009; 44(19): 5049–5062. Available at: DOI:10.1007/s10853-009-3643-0
 97. Petnoi N., Bomlai P., Jiansirisomboon S., Watcharapasorn A. Effects of Nb-doping on the micro-structure and dielectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramics. *Ceramics International*. Elsevier; 2013; 39(SUPPL.1): S113–S117. Available at: DOI:10.1016/j.ceramint.2012.10.045
 98. Aksel E., Jones JL. Advances in lead-free piezoelectric materials for sensors and actuators. *Sensors*. 2010; 10(3): 1935–1954. Available at: DOI:10.3390/s100301935
 99. Anton EM., Jo W., Damjanovic D., Rdel J. Determination of depolarization temperature of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based lead-free piezoceramics. *Journal of Applied Physics*. 2011; 110(9): 1–14. Available at: DOI:10.1063/1.3660253
 100. Rodríguez-Ruiz R., González-Ballesteros R., Flores-Cuautle a., Suaste-Gómez E. Determination of the Pyroelectric Coefficient for $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.935}\text{Ba}_{0.065}\text{TiO}_3$ Piezoelectric Ceramics. *Ferroelectrics*. 2008; 368(1): 216–223. Available at: DOI:10.1080/00150190802368537
 101. Byer RL., Roundy CB. Pyroelectric coefficient direct measurement technique and application to a nsec response time detector. *IEEE Transactions on Sonics and Ultrasonics*. 1972; 19(2): 333–338. Available at: DOI:10.1109/T-SU.1972.29679
 102. Patel S., Chauhan A., Kundu S., Madhar NA., Llahi B., Vaish R., et al. Tuning of dielectric, pyroelectric and ferroelectric properties of

- 0.715Bi0.5Na0.5TiO3-0.065BaTiO3-0.22SrTiO3 ceramic by internal clamping. *AIP Advances*. 2015; 5(8): 87145. Available at: DOI:10.1063/1.4929328
103. Guo Y., Gu M., Luo H. Antiferroelectric phase and pyroelectric response in (NayBi z)Ti1-xO3(1-x)-xBaTi3 ceramics. *Journal of the American Ceramic Society*. 2011; 94(5): 1350–1353. Available at: DOI:10.1111/j.1551-2916.2011.04509.x
 104. Abo, Jiro Kobune M., Nishimura T., Yazaw T., Nakai Y. Effects of manganese addition on pyroelectric properties of (Bi 0.5 Na 0.5 TiO 3) 0.94 (BaTiO 3) 0.06 ceramics. *Integrated Ferroelectrics*. 2006; 80(1): 87–95. Available at: DOI:10.1080/10584580600656502
 105. He Y. Heat capacity, thermal conductivity, and thermal expansion of barium titanate-based ceramics. *Thermochimica Acta*. 2004; 419(1–2): 135–141. Available at: DOI:10.1016/j.tca.2004.02.008
 106. Setter N., Waser R. Electroceramic materials. *Acta Materialia*. 2000; 48(1): 151–178. Available at: DOI:10.1016/S1359-6454(99)00293-1
 107. Ringgaard E., Wurlitzer T. Lead-free piezoceramics based on alkali niobates. *Journal of the European Ceramic Society*. 2005; 25(12 SPEC. ISS.): 2701–2706. Available at: DOI:10.1016/j.jeurceramsoc.2005.03.126
 108. Jaffe B., Roth RS., Marzullo S. Properties of piezoelectric ceramics in the solid-solution series lead titanate-lead zirconate-lead oxide: Tin oxide and lead titanate-lead hafnate. *Journal of Research of the National Bureau of Standards*. 1955; 55(5): 239–254. Available at: DOI:10.6028/jres.055.028
 109. Panda PK., Sahoo B. PZT to Lead Free Piezo Ceramics A Review.pdf. *Ferroelectrics*. 2015; 474(1): 128–143. Available at: DOI:10.1080/00150193.2015.997146
 110. Noheda B., Gonzalo J., Cross L., Guo R. Tetragonal-to-monoclinic phase transition in a ferroelectric perovskite: The structure of PbZr_{0.52}Ti_{0.48}O₃. *Physical Review B*. 2000; 61(13): 8687–8695. Available at:

DOI:10.1103/PhysRevB.61.8687

111. Ahart M., Somayazulu M., Cohen RE., Ganesh P., Dera P., Mao H., et al. Origin of morphotropic phase boundaries in ferroelectrics. *Nature*. 2008; 451(7178): 545–548. Available at: DOI:10.1038/nature06459
112. López-juárez R., González F. Lead-Free Ferroelectric Ceramics with Perovskite Structure. *Ferroelectrics - Material Aspects*. Mexico; 2011. pp. 305–330. Available at: DOI:10.5772/20107
113. G. A. Smolenski, V. A. Isupov, A. I. Agranovskaya NNK. New ferroelectrics of complex composition. *Soviet Physics Solid State*. 1961; 2: 2651.
114. Rödel J., Jo W., Seifert KTP., Anton EM., Granzow T., Damjanovic D. Perspective on the development of lead-free piezoceramics. *Journal of the American Ceramic Society*. 2009; 92(6): 1153–1177. Available at: DOI:10.1111/j.1551-2916.2009.03061.x
115. Hill N a., Rabe KM. First-principles investigation of ferromagnetism and ferroelectricity in bismuth manganite. *Physical Review B*. 1999; 59(13): 8759. Available at: DOI:10.1103/PhysRevB.59.8759
116. Baettig P., Schelle CF., LeSar R., Waghmare U V., Spaldin NA. Theoretical prediction of new high-performance lead-free piezoelectrics. *Chemistry of Materials*. 2005; 17(6): 1376–1380. Available at: DOI:10.1021/cm0480418
117. Takenaka T., Sakata K. Dielectric, piezoelectric and pyroelectric properties of (BiNa) 1/2 TiO 3- based ceramics. *Ferroelectrics*. 1989; 95(1): 153–156. Available at: DOI:10.1080/00150198908245194
118. Tekenaka HN and T. (Bi1/2Na1/2)TiO3-based Non-lead piezoelectric ceramics. *Japanese Journal of Applied Physics*. 1997; 36(9B): 6055–6057.
119. Uchida K., Kikuchi T. Subsolidus Phase Equilibria in the System Na2O-Bi2O3-TiO2 at 1000 ° C. *Journal of The American Ceramic Society*. 1978. pp. 5–8. Available at: DOI:10.1111/j.1151-2916.1978.tb09217.x
120. Zvirgzds JA., Kapostin PP., Zvirgzde J V., Kruzina T V. X-ray study of

- phase transitions in ferroelectric $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Ferroelectrics*. 1982; 40(1): 75–77. Available at: DOI:10.1080/00150198208210600
121. Vakhrushev SB., Isupov V a., Kvyatkovsky BE., Okuneva NM., Pronin IP., Smolensky GA., et al. Phase transitions and soft modes in sodium bismuth titanate. *Ferroelectrics*. 1985; 63(1): 153–160. Available at: DOI:10.1080/00150198508221396
 122. Wang XX., Kwok KW., Tang XG., Chan HLW., Choy CL. ‘Electromechanical properties and dielectric behavior of $(\text{Bi}_{1/2}\text{Na}_{1/2})(1-1.5x)\text{Bi}_x\text{TiO}_3$ lead-free piezoelectric ceramics’. *Solid State Communications*. 2004; 129(5): 319–323. Available at: DOI:10.1016/j.ssc.2003.10.017
 123. Hiruma Y., Nagata H., Takenaka T. Thermal depoling process and piezoelectric properties of bismuth sodium titanate ceramics. *Journal of Applied Physics*. 2009; 105(8). Available at: DOI:10.1063/1.3115409
 124. Suchanicz J., Kwapulinski J. X-ray diffraction study of the phase transitions in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Ferroelectrics*. 1995; 165(1): 249–253. Available at: DOI:10.1080/00150199508228304
 125. Jones GO., Thomas PA. Investigation of the structure and phase transitions in the novel A-site substituted distorted perovskite compound $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Acta Crystallographica Section B: Structural Science*. International Union of Crystallography; 2002; 58(2): 168–178. Available at: DOI:10.1107/S0108768101020845
 126. Yang Z., Hou Y., Liu B., Wei L. Structure and electrical properties of Nd_2O_3 -doped $0.82\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - $0.18\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ ceramics. *Ceramics International*. 2009; 35(4): 1423–1427. Available at: DOI:10.1016/j.ceramint.2008.07.014
 127. Hiruma Y., Yoshii K., Nagata H., Takenaka T. Phase transition temperature and electrical properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $(\text{Bi}_{1/2}\text{A}_{1/2})\text{TiO}_3$ (A=Li and K) lead-free ferroelectric ceramics. *Journal of Applied Physics*. 2008; 103(8):

84121. Available at: DOI:10.1063/1.2903498

128. Wang X., Tang X., Chan H. Electromechanical and ferroelectric properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ – BaTiO_3 lead-free piezoelectric ceramics. *Applied physics letters*. 2004; 85(1): 91. Available at: DOI:10.1063/1.1767592
129. Pronin IP., Syrnikov PP., Isupov VA., Egorov VM., Zaitseva N V. Peculiarities of phase transitions in sodium-bismuth titanate. *Ferroelectrics*. 1980; 25(1): 395–397. Available at: DOI:10.1080/00150198008207029
130. Dorcet V., Trolliard G., Boullay P. Reinvestigation of Phase Transitions in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ by TEM . Part I : First Order Rhombohedral to Orthorhombic Phase Transition Reinvestigation of Phase Transitions in $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ by TEM . Part I : First Order Rhombohedral to Orthorhombic Phase . 2008; 77(6): 5061–5073. Available at: DOI:10.1021/cm8004634
131. Liu LY., Zhu MK., Hou YD., Yan H., Liu RP. Abnormal piezoelectric and dielectric behavior of $0.92\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – 0.08BaTiO_3 induced by La doping. *Journal of Materials Research*. 2007; 22(5): 1188–1192. Available at: DOI:10.1557/Jmr.2007.0173
132. Elkechai O., Manier M., Mercurio JP. $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ – $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT-KBT) system: A structural and electrical study. *Physica Status Solidi A*. 1996; 157(2): 499–506. Available at: DOI:10.1002/pssa.2211570234
133. Herabut A., Safari A. Processing and Electromechanical Properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})(1-1.5x)\text{La}_x\text{TiO}_3$ ceramics. *Journal of American ceramic society*. 1997; 80: 2954–2958. Available at: DOI:10.1111/j.1151-2916.1997.tb03219.x
134. Ma C., Guo H., Beckman SP., Tan X. Creation and destruction of morphotropic phase boundaries through electrical poling: A case study of lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – BaTiO_3 piezoelectrics. *Physical Review*

- Letters. 2012; 109(10). Available at:
DOI:10.1103/PhysRevLett.109.107602
135. Mahajan A., Zhang H., Wu J., Ramana EV., Reece MJ., Yan H. Effect of Phase Transitions on Thermal Depoling in Lead-Free $0.94(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3) - 0.06(\text{BaTiO}_3)$ Based Piezoelectrics. The Journal of Physical Chemistry C. 2017; 121(10): 5709–5718. Available at: DOI:10.1021/acs.jpcc.6b12501
 136. Jo W., Schaab S., Sapper E., Schmitt L a., Kleebe HJ., Bell AJ., et al. On the phase identity and its thermal evolution of lead free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -6 mol BaTiO_3 . Journal of Applied Physics. 2011; 110(2011). Available at: DOI:10.1063/1.3645054
 137. McQuade R., Dolgos MR. A review of the structure-property relationships in lead-free piezoelectric $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -(x) BaTiO_3 . Journal of Solid State Chemistry. 2016; : 0–19. Available at: DOI:10.1016/j.jssc.2016.01.008
 138. Xu Q., Chen S., Chen W., Wu S., Lee J., Zhou J., et al. Structure, piezoelectric properties and ferroelectric properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ system. Journal of Alloys and Compounds. 2004; 381: 221–225. Available at: DOI:10.1016/j.jallcom.2004.02.057
 139. Hiruma Y., Nagata H., Takenaka T. Formation of Morphotropic Phase Boundary and Electrical Properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - \text{Ba}(\text{Al}_{1/2}\text{Nb}_{1/2})\text{O}_3$ Solid Solution Ceramics. Japanese Journal of Applied Physics. 2009; 48(9): 09KC08. Available at: DOI:10.1143/JJAP.48.09KC08
 140. Takenaka T., Maruyama K., Sakata K. $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 System for Lead-Free Piezoelectric Ceramics. Japanese Journal of Applied Physics. 1991; 30(Part 1, No. 9B): 2236–2239. Available at: DOI:10.1143/JJAP.30.2236
 141. Woodward DL., Knudsen J., Reaney IM. Review of crystal and domain structures in the $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$ solid solution. Physical Review B - Condensed Matter and Materials Physics. 2005; 72(10): 104110. Available

at: DOI:10.1103/PhysRevB.72.104110

142. Zhang N., Yokota H., Glazer M., Ren Z., Keen D., Keeble DS., et al. The missing boundary in the phase diagram of $\text{PbZr}_{1-x}\text{Ti}_x\text{O}_3$. *Nature communications*. 2014; 5(May): 5231. Available at: DOI:10.1038/ncomms6231
143. Glazer AM., Thomas PA., Baba-Kishi KZ., Pang GKH., Tai CW. Influence of short-range and long-range order on the evolution of the morphotropic phase boundary in $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$. *Physical Review B - Condensed Matter and Materials Physics*. 2004; 70(18): 1–9. Available at: DOI:10.1103/PhysRevB.70.184123
144. Frantti J., Ivanov S., Eriksson S., Rundlöf H., Lantto V., Lappalainen J., et al. Phase transitions of $\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ceramics. *Physical Review B - Condensed Matter and Materials Physics*. 2002; 66(6): 641081–6410815. Available at: DOI:10.1103/PhysRevB.66.064108
145. Frantti J., Fujioka Y., Puretzky A., Xie Y., Ye ZG., Glazer AM. A statistical model approximation for perovskite solid-solutions: A Raman study of lead-zirconate-titanate single crystal. *Journal of Applied Physics*. 2013; 113(17). Available at: DOI:10.1063/1.4798391
146. Corker DL., Glazer a M., Whatmore RW., Stallard a., Fauth F. A neutron diffraction investigation into the rhombohedral phases of the perovskite series. *Journal of Physics: Condensed Matter*. 1999; 10(28): 6251–6269. Available at: DOI:10.1088/0953-8984/10/28/007
147. Buixaderas E., Gregora I., Savinov M., Hlinka J., Jin L., Damjanovic D., et al. Compositional behavior of raman-active phonons in $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ ceramics. *Physical Review B - Condensed Matter and Materials Physics*. 2015; 91(1): 14104. Available at: DOI:10.1103/PhysRevB.91.014104
148. Baba-Kishi KZ., Welberry TR., Withers RL. An electron diffraction and Monte Carlo simulation study of diffuse scattering in $\text{Pb}(\text{Zr,Ti})\text{O}_3$. *Journal of Applied Crystallography*. 2008; 41(5): 930–938. Available at:

DOI:10.1107/S0021889808026253

149. Notes GG. Sustainable development and Environment EC Directive on WEEE and ROHS in electrical and electronic equipment. 2005; (November).
150. Zheng Q., Xu C., Lin D., Gao D., Kwok KW. Piezoelectric and ferroelectric properties of $(\text{Bi}_{0.94-x}\text{La}_x\text{Na}_{0.94})_{0.5}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ceramics. *Journal of Physics D: Applied Physics*. 2008; 41(12): 125411. Available at: DOI:10.1088/0022-3727/41/12/125411
151. Li H., Feng C., Yao W. Some effects of different additives on dielectric and piezoelectric properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – BaTiO_3 morphotropic-phase-boundary composition. *Materials Letters*. 2004; 58(7–8): 1194–1198. Available at: DOI:10.1016/j.matlet.2003.08.034
152. Ma C., Tan X. Phase diagram of unpoled lead-free $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $x\text{BaTiO}_3$ ceramics. *Solid State Communications*. 2010; 150(33): 1497–1500. Available at: DOI:10.1016/j.ssc.2010.06.006
153. Ma C., Tan X., Dul'Kin E., Roth M. Domain structure-dielectric property relationship in lead-free $(1-x)(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $x\text{BaTiO}_3$ ceramics. *Journal of Applied Physics*. 2010; 108(10). Available at: DOI:10.1063/1.3514093
154. Viola G., McKinnon R. Lithium-Induced Phase Transitions in Lead-Free $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ Based Ceramics. *The Journal of ...* 2014; Available at: <http://pubs.acs.org/doi/abs/10.1021/jp500609h>

2 Experimental Procedure and Material Characterisation

2.1 Introduction

This chapter describes the synthesis procedure and the characterisation of the unmodified, modified, undoped, and doped lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 ceramic materials, in addition to the composite pyroelectric ceramic materials (*CCPCM*).

The synthesis procedure that was implemented in the study is the conventional solid-state route (*CSSR*) or the solid-state reaction route (*SSRR*). However, in Chapter 9, *CCPCM* was sintered by using spark plasma sintering (*SPS*).

2.2 Synthesis Procedure

The performance of ceramic materials is closely linked to the means by which they are synthesised [1]. Thus, the processing technique plays an essential role in achieving the required microstructure, dielectric and pyroelectric properties of synthesised materials. Nowadays, the increasing demand for advanced functional “green” ceramic materials which possess specific properties has encouraged advanced modification and optimisation of the existing synthesis techniques, in addition to invention of new synthesis techniques [2,3].

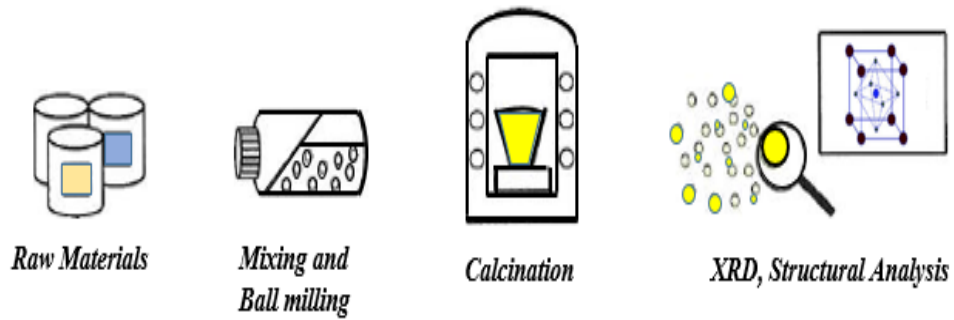
One of the most interesting techniques that has been utilised to synthesize and also to prepare lead-free ceramic materials is the *CSSR* [4]. This synthesis technique does have some shortcomings in that it consumes large amount of energy at both calcination and sintering stages; there is a reasonable chance of contamination; and it does not guarantee full homogeneity in the materials produced. However, the *CSSR* does offer specific advantages, in that it is a low-cost technique in comparison with other synthesis techniques; it offers high reliability; it is easy to reproduce the ceramic materials; it is the mostly widely used route for a large-scale production of ceramic materials; and it is suitable for laboratory scale production of ceramics [4].

2.2.1 CSSR

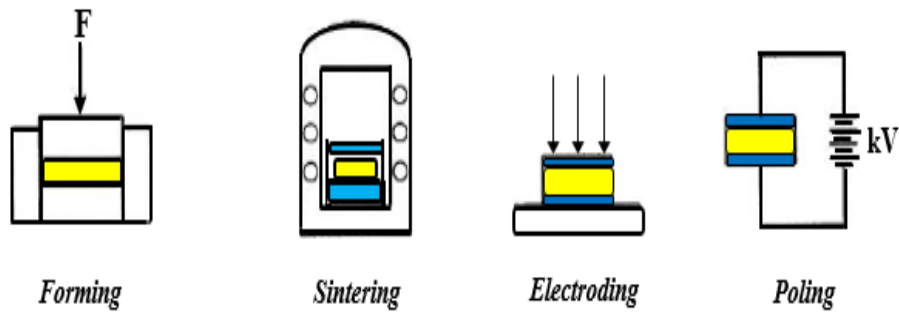
The CSSR route is the most widely utilised processing procedure for the synthesis of polycrystalline bulk ceramics. This method involves a selection of starting materials, such as oxides, carbonates and other materials. As solids do not react at RT, it is essential to heat the solid reactants to high temperatures for desired reactions to take place at a specific rate. Therefore, these solid materials can chemically react without the existence of any type of solvent at the reaction temperature. The main advantage of this process is that it produces the end compound a solid form with the desired structure and properties [5,6].

The general steps of the CSSR are illustrated in Fig. 2-1. In the current study, the synthesis technical route, was followed to make the unmodified, modified, undoped and doped $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 ceramic compositions, and is presented in Fig. 2-2. And the fabrication procedure of the synthesis of the CPCM in this study is illustrated in Fig. 2-3.

1. Powder Processing



2. Form powder to ceramics



3. Dielectric and Pyroelectric Characterisations

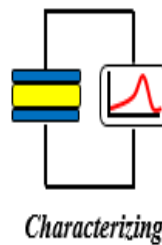


Figure 2-1: Schematic of the synthesis steps in the solid-state reaction route [7].

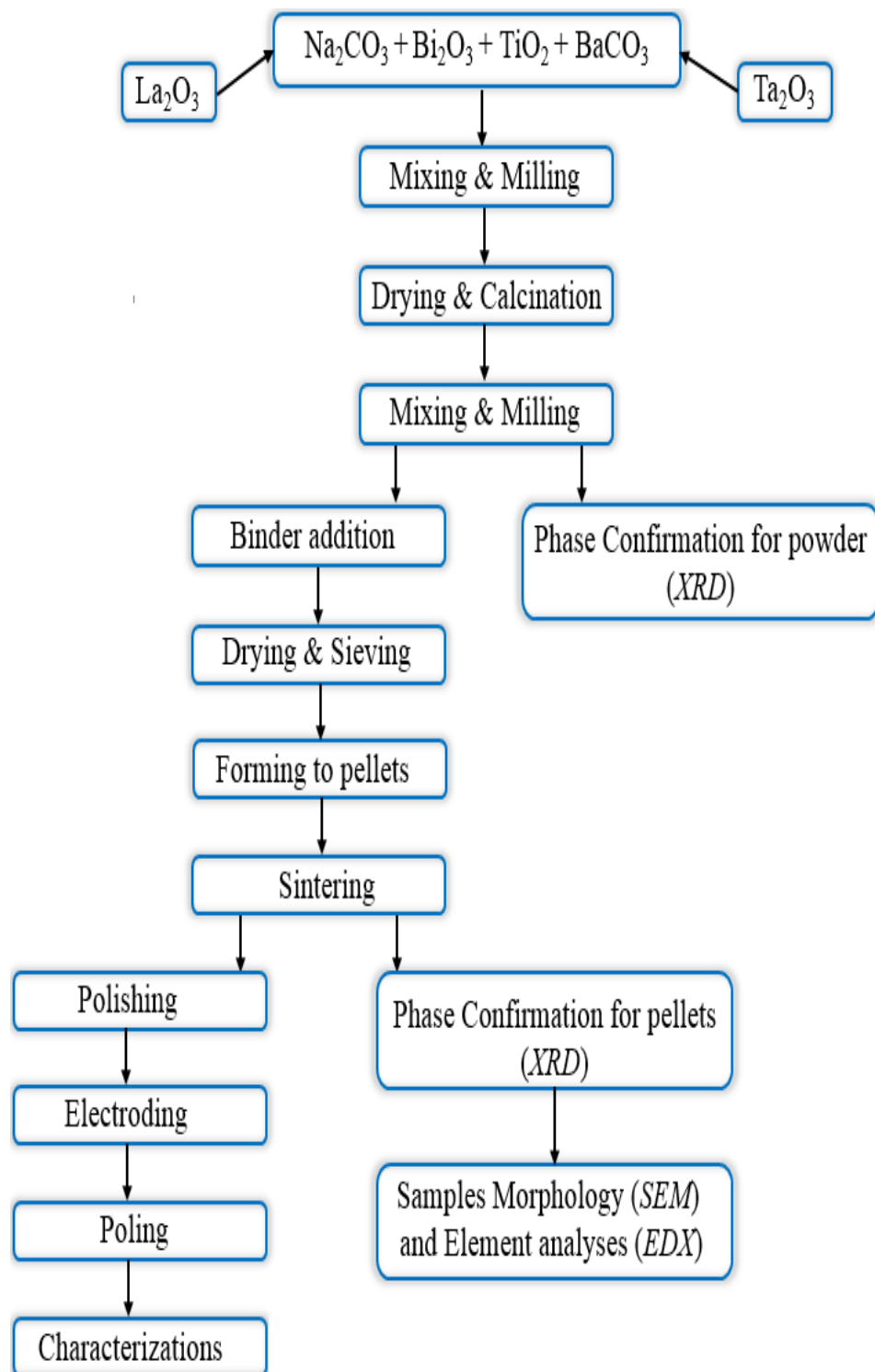


Figure 2-2: The synthesis steps of the conventional solid-state reaction route, which was followed in this study.

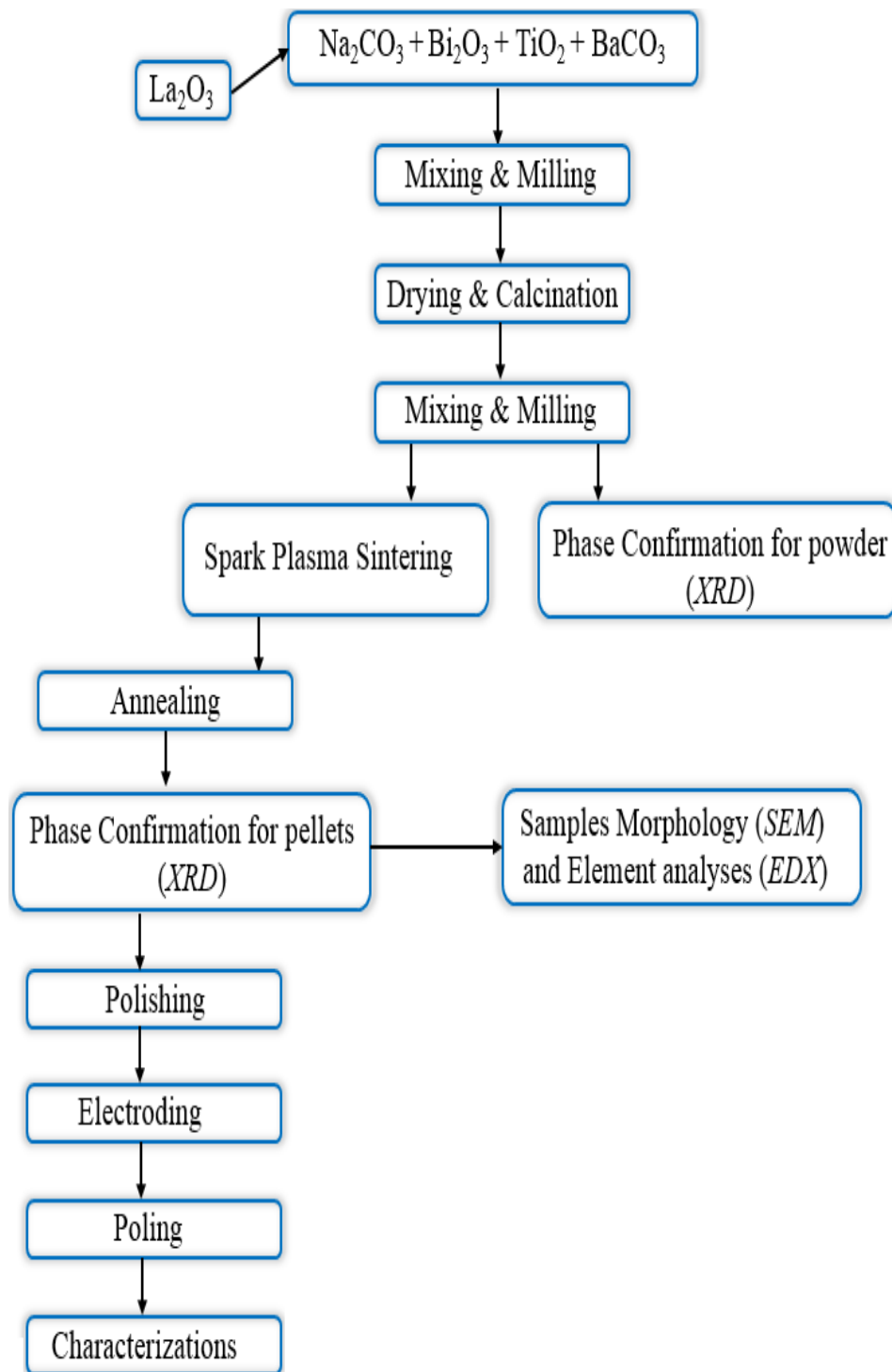


Figure 2-3: The flow chart for the synthesis of the composite pyroelectric ceramic material (CPCM).

2.2.2 Preparation of sodium bismuth titanate modified by barium titanate materials and dopants targeting A and B sites

2.2.2.1 Raw materials

The starting raw materials are commonly termed reagents [7]. The nature and the quality of these materials have a significant effect on the final ceramic compositions. The quality of reagents depends on the purity (%), which represents the weight percentage of impurities, such as the minerals, from the total weight. Most reagents contain different percentages of impurities. These impurities may affect the properties of the final ceramic compositions [5,6].

The reagents that were used in the study are listed in Table 2-1:

Table 2-1: The reagents were used in the study.

Name	Formula	Purity %	Form	Supplier
Sodium carbonate	Na ₂ CO ₃	99.50	Powder	Sigma- Aldrich
Bismuth oxide	Bi ₂ O ₃	99.99	Powder	Sigma- Aldrich
Barium carbonate	BaCO ₃	99.98	Powder	Sigma- Aldrich
Titanium oxide	TiO ₂	99.99	Powder	Sigma- Aldrich
Lanthanum oxide	La ₂ O ₃	99.50	Powder	Sigma- Aldrich
Tantalum oxide	Ta ₂ O ₃	99.00	Powder	Sigma- Aldrich

2.2.2.2 Weighing, mixing and ball milling of raw materials

The reagents were dried in an oven for 6 hrs, to remove moisture, before weighing; the amounts of powders were then calculated according to the chemical formula of the final product.

In a situation where there are several kinds of reagent powders, in order to achieve a fine and well mixed powder, ball milling is used to grind and simultaneously mix reagents together. In the milling process, the particles of the powders are subjected to mechanical compression and shear stresses at their contact points with the milling media. The size of the particles can play an essential role in the formation of the final composition and also on its properties [8].

In this work, the raw materials were ball-milled (zirconia milling media) in acetone in polyethylene pots for 24 hrs, to mix and mill the powders.

2.2.2.3 Drying, Grinding, Sieving and Calcination

The resultant slurries from the previous step were dried overnight at 50 °C in an oven. The dried powder cakes were ground in a mortar for 10 -15 min. and sieved through a 250 µm mesh in order to aid the calcination step.

The calcination process is an endothermic process with a decomposition reaction for the raw materials, which results in a single phase with liberation of gases. In this process, the phase formation of the composition will take place by solid phase reaction that includes the chemical reaction through atomic diffusion at high temperature, but the temperature must be below the melting temperature of the reagents [8,9].

In this study, the powders were calcined at 850 °C for 180 min., in a closed alumina crucible with a heating ramp rate of 1 °C per minute, and cooling rate of 5 °C per minute in a furnace (Pyro Therm, ITEMP 14/6).

2.2.2.4 Mixing and Ball milling (Second time), Drying (Second time), Adding binder (PVA) and Sieving.

The calcined powders, which were obtained from the calcination stage, were re-milled in acetone for 24 hrs., and then 2 %(wt.) of poly vinyl alcohol (*PVA*) was added as an organic binder to the dried powders to enhance the mechanical strength of the pellets during pressing. After that, the powders were fully dried in oven at 80 °C. The dried powders were ground for 10 -15 min. and sieved (250 µm mesh).

Note: This step is not part of the synthesis route of CGPCMs, (Fig. 2-3).

2.2.2.5 Forming and Sintering

Following on from the previous step, the dried powders were pressed into green pellets with a diameter (*D*) of ~10 mm and thickness (*t*) around 1.65 mm under a uniaxial compaction with a load of ~78 MPa for 5 min at RT (Fig 2-4). After that, the green pellets were sintered in a furnace (Pyro Therm, ITEMP 14/6) at temperatures of up to 1150 °C for 120 min in closed crucibles, to minimize the loss of volatile Na⁺ and Bi³⁺ (Fig. 2-5). After sintering the dimensions *D* and *t* of the samples were around 1.5 mm and 1.00 mm respectively.

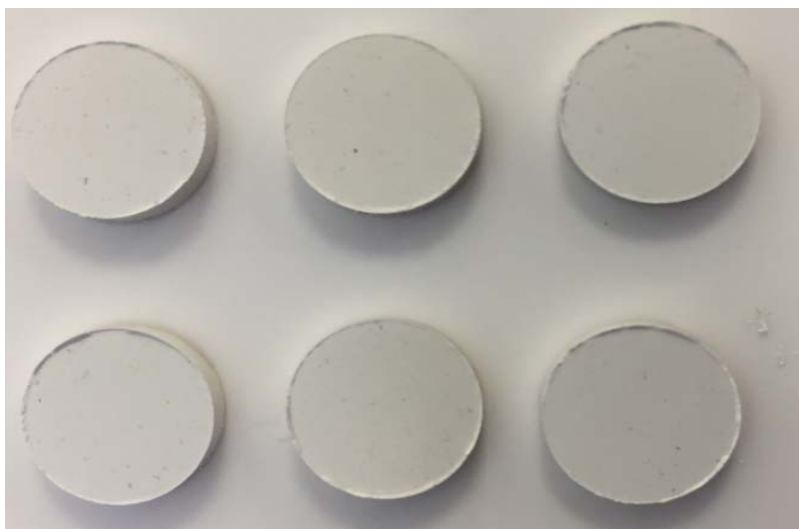


Figure 2-4: Picture of the samples before sintering.

The green pellets are densified through the sintering stage. At the sintering stage, several mechanisms can take place in the polycrystalline ceramic materials through bonding and growth of necks between the particles. These mechanisms are [10]:

- a. Surface diffusion.
- b. Lattice diffusion from the surface.
- c. Vapour transport.
- d. Lattice diffusion from the grain boundary.
- e. Grain boundary diffusion.



Figure 2-5: Picture of the samples after sintering.

However, the lattice diffusion and grain boundary diffusion are the most important mechanisms in the densification process in the ceramic materials.

In the sintering process, the green pellets were heated to a high temperature of between 50 and 80 (%) of the reagents melting temperature [11]. Although, the

pellets did not melt in this process, the particles were joined together, and the porosity were reduced in the final composition (Fig. 2-6) [10].

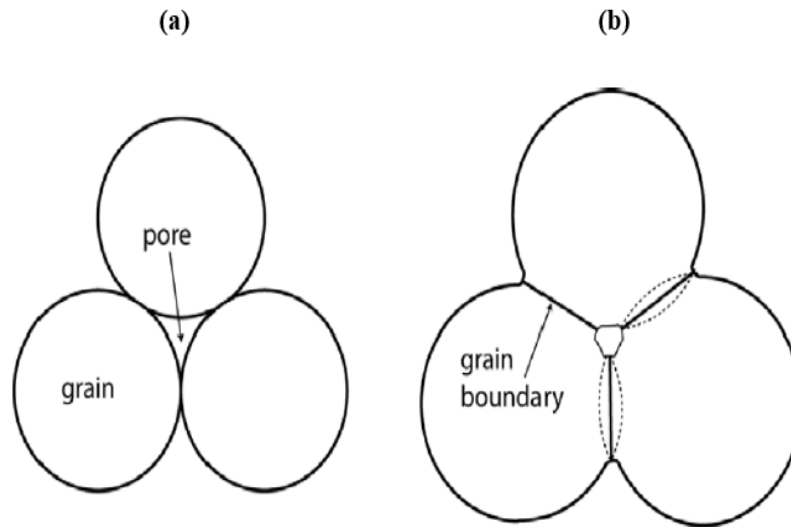


Figure 2-6: Schematic of sintering process: (a) three grains before sintering, (b) after sintering [12].

Note: This step is not part of the synthesis route of PCM (Fig. 2-3).

2.2.2.5.1 Spark plasma sintering (SPS)

SPS is a pressure-sintering route and is the newest, as well as one of the more advanced sintering methods (Fig. 2-6) [1,13,14]. This method is based on high temperature spark-plasma, which is produced for a short time in the gaps between powder particles using electrical discharge at the start of a DC pulse (Fig. 2-7) [13]. The large DC electric current pulse stimulation method will produce:

- a. Spark plasma.
- b. Spark impact pressure.
- c. Joule heating
- d. An electrical field diffusion effect.

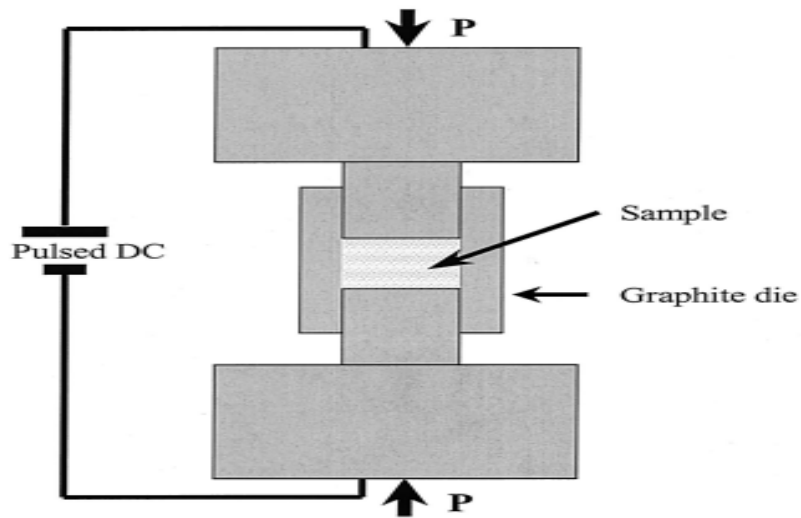


Figure 2-7: Schematic of the features of a SPS apparatus [15].

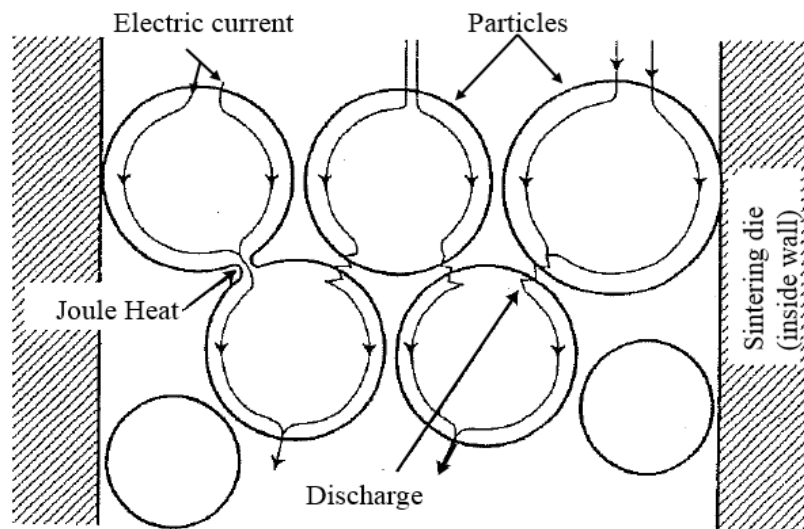


Figure 2-8: Schematic of pulsed current flow through powder particles in the SPS method [13].

This method enables sintering the powdered materials in a very short period of time, and also generates high quality materials.

The SPS method provides a number of advantages over conventional sintering methods; these include accurate control of the final product, very high sintering

speed, high reproducibility, and reliability. Nowadays, it is increasingly utilised in the fabrication of various materials such as: functionally graded materials (FGMs), intermetallic compounds, fibre reinforced ceramics and many other advanced materials [13,16,17].

In this study, the powders were prepared by spark-plasma sintering (SPS) in a HPD 25/1 FCT (Germany).

After the SPS stage, the samples' colour changed from a white-coloured powder to dark grey (Fig. 2-9 (a)) due to oxygen deficiency and it being fully contaminated with carbon (C), which was caused by the reduced atmosphere of the SPS. The annealing treatment in air changed the samples colour back to cream white (Fig. 2-9 (b)) possibly because the oxygen was supplied during annealing process. This annealing as a heat treatment is considered an important procedure to eliminate residual stress, which occurs as a result of either the SPS sintering process or from the polishing process. In addition, it removes the surface C contamination described previously [17].

In this study, the samples were annealed in the furnace in air at temperature 850°C for 20 hrs.

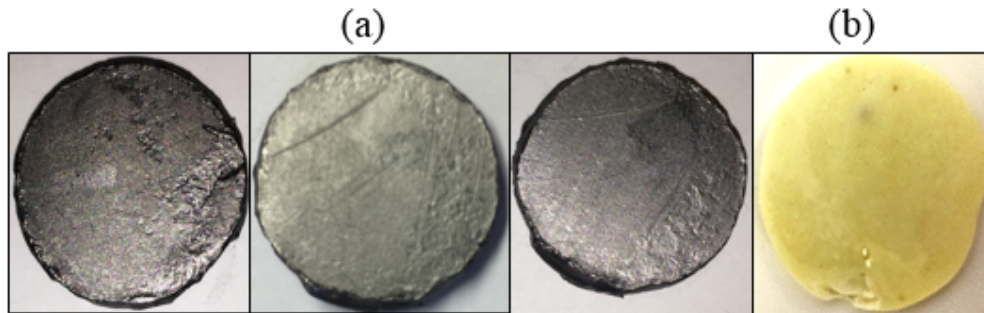


Figure 2-9: Composite pyroelectric ceramic material (CPCM) pellets; (a) before removal of carbon; (b) after removal of carbon.

Note: The SPS step is not part of the synthesis route of unmodified, undoped, modified and doped NBT-0.06BT (Fig. 2-2).

2.2.2.6 Polishing, Electroding and Poling

The pellets were manually polished on both sides using different grades of silicon carbide papers and then mechanically polished using cloths. Silver conductive paint (*RS limited*) was used to electrode the pellets. In addition, the pellets were electrically poled at 6.5 kV/mm for 10 min at RT in mineral oil, carried out using a Keithley (*6517 Electrometer/high resistance*) Dc power supply. Afterwards, the poled samples were washed thoroughly by using isopropanol in order to remove the mineral oil and then left in air for 3 hrs, to dry. The poled samples were placed at RT for 60 min with their electrodes short-circuited to eliminate any unwanted trapped charges.

On completion of all these stages, the pellets were ready to receive the required characteristics.



Figure 2-10: Picture of polished samples.

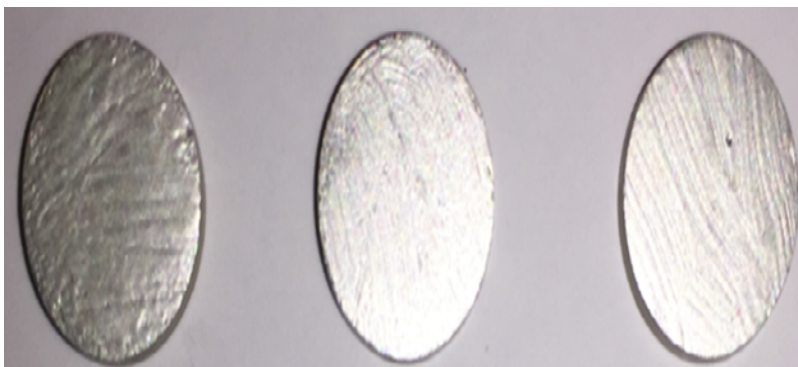


Figure 2-11: Samples electroded with silver conductive paint.

2.3 Characterisation Techniques

Pyroelectric ceramics as electronic ceramics exhibit special properties, and can be characterised by various experimental techniques. Part of the characterisations relates to the synthesis method whereas, the other hand, the second part was linked to the characterisations of the final ceramic materials in the aim of analysing their use in the pyroelectric applications.

In this study, the following techniques have been utilised to achieve this goal:

- A. X-ray diffraction (*XRD*).
- B. Scanning electron microscopy (*SEM*).
- C. Energy dispersive analysis (*SEM-EDS*) or *Energy dispersive X-ray spectroscopy (SEM-EDX)*
- D. Dielectric characteristics.
- E. Pyroelectric properties.

2.3.1 X-Ray Diffraction (*XRD*)

In the current study, X-ray analysis was used to investigate crystallisation and phase of the test samples using a Siemens Ltd Model: D500 X-ray diffractometer, with a Cu K α source. The test samples were calcined powders and / or sintered pellets. In the case of powders, before the measurement, they are put into a rectangle shaped metal mould attached to a glass slide. In the case of the pellet, it was placed directly on the XRD device stage. The X-ray measurements were

carried out in an angular range $2\theta = 20^\circ - 90^\circ$ with a scan range of 0.05° per second. The data collected was evaluated with a DIFFRAC.SUITE EVA XRD evaluation software (Bruker AXS), and then transferred into Excel to be normalised, with the aim of enhancing its clarity.

2.3.2 Scanning Electron Microscopy (SEM)

In this study, SEM (FEG-SEM, model XL30 SFEG, Philips) was used to look at the grain morphology of the sintered samples. In order to obtain high resolution images, the samples were coated with a thin layer of conductive film of mineral (gold or silver or platinum) to make the samples conductive.

2.3.3 Energy Dispersive analysis (SEM-EDS) or Energy Dispersive X-ray spectroscopy (SEM-EDX)

In this study, EDS (EDS, Oxford Instruments-AZTEC) was utilised to analyse elements of the samples. For the testing, the samples were coated with a thin layer of conductive mineral (gold, silver or platinum) to make the samples conductive.

2.3.4 Dielectric Characterisations

Ferroelectric materials show noteworthy dielectric properties, such as high relative permittivity (ϵ_r) and low dielectric loss tangent ($\tan\delta$); these are important characteristics for a wide range of applications [7,18]. Therefore, studying the dielectric properties at both room and high temperatures can provide valuable information relating to the usefulness of these materials for various industrial applications.

In the current study, two techniques to make dielectric measurements were used: Firstly: at room temperature, the ϵ_r and $\tan\delta$ were measured at a broad range of frequencies from 30 Hz to 10 kHz using WK, WAYNE KERR Precision Component Analyser 6425. Dielectric properties were measured on both unpoled and poled samples.



Figure 2-12: Photo to the device that used to measure the dielectric properties at room temperature and at different frequencies.

Secondly, at high temperature, the dielectric measurements for the poled samples with changing temperature were performed on an impedance analyser (*Wayne Kerr Electronics Ltd. Model 3245 and Hewlett Packard HP4092A*), over a temperature range from 20 to 150 °C using a custom-built temperature-controlled hotplate in the frequency range of 0.1 - 10 kHz.

With both techniques, the relative permittivity of the ceramic samples was calculated using:

$$\epsilon_r = \frac{C \times d}{\epsilon_0 \times A} \quad (2-1)$$

where ϵ_r is relative permittivity or dielectric constant of the samples; C is sample capacitance; d is the thickness of the samples; A is the electrode surface area for each sample.

2.3.5 Pyroelectric Characterisations

Pyroelectric measurements were made using the Byer-Roundy method [19] on a custom-built computer-controlled rig which uses thermoelectric heaters at a constant rate of 1°C/min to ramp the temperature between 20 °C and 90 °C whilst

under vacuum conditions. The temperature was controlled using a computer (a Viglen Contender Executive 40X40 running WorkBench 3.00, working with a Eurotherm R20 temperature controller) and the pyroelectric current produced was measured using a Keithley model 6517, (Fig. 2-12).

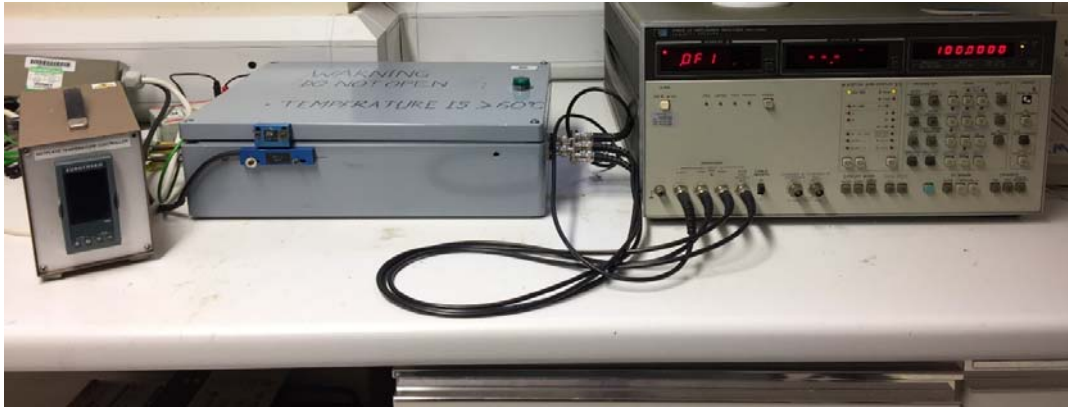


Figure 2-13: Photo to the device that used to measure the dielectric properties with increase temperature from room upto 150 °C and at different frequencies.

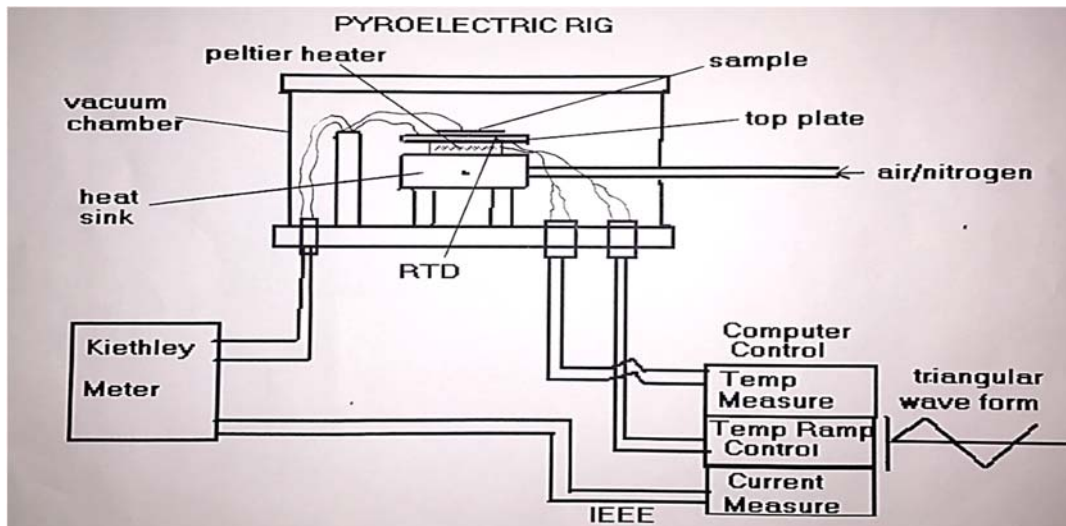


Figure 2-14: Schematic of Byer-Roundy pyroelectric rig.

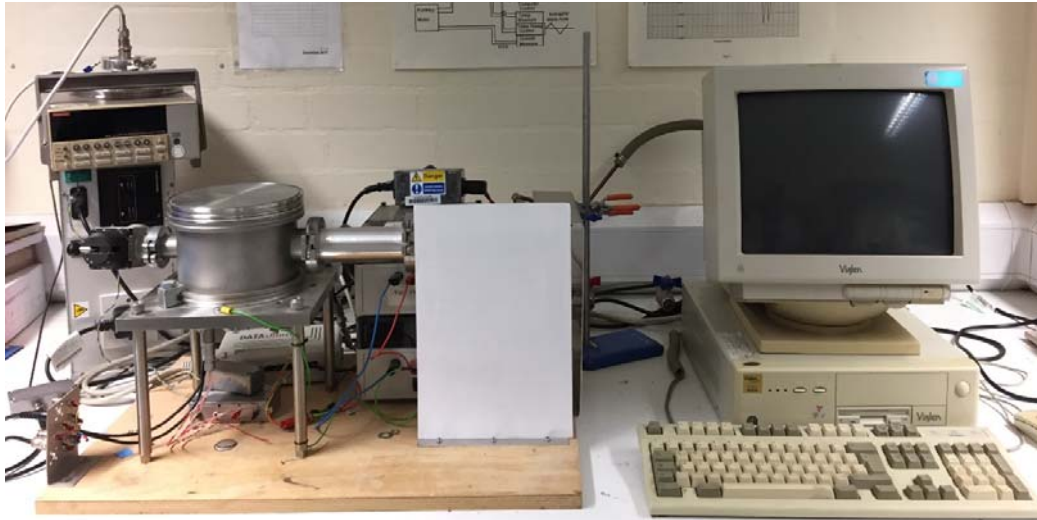


Figure 2-15: Photo to the Byer-Roundy pyroelectric rig which used in this study.

The calculation of the pyroelectric coefficient was carried out using Equation 1-14:

2.4 References

1. Hungria T., Galy J., Castro A. Spark plasma sintering as a useful technique to the nanostructuration of piezo-ferroelectric materials. *Advanced Engineering Materials*. 2009. pp. 615–631. Available at: DOI:10.1002/adem.200900052
2. Keizer K., Janssen EHJ., de Vries KJ., Burggraaf AJ. Influence of particle size and structure of ZrO₂ on microstructure development and dielectric constant of PbZr_{0.5}Ti_{0.5}O₃. *Materials Research Bulletin*. 1973; 8(5): 533–544. Available at: DOI:10.1016/0025-5408(73)90129-3
3. Arlt G. The influence of microstructure on the properties of ferroelectric ceramics. *Ferroelectrics*. 1990; 104(1): 217–227. Available at: DOI:10.1080/00150199008223825
4. Moulson a. J., Herbert JM. *Electroceramics: Materials, Properties, Applications*. 2003. 576 p. Available at: DOI:10.1002/0470867965
5. Ecija A., Vidal K., Larrañaga A., Ortega San Martin L., Arriortua MI. *Synthetic Methods for Perovskite Materials: Structure and Morphology. Advanced in Crystallization Processes*. 2012; : 485–506. Available at: DOI:10.5772/36540
6. Hauffe K. Solid State Chemistry. *Zeitschrift für Physikalische Chemie*. 2014; 58: 331–332. Available at: DOI:10.1524/zpch.1968.58.5_6.331a
7. Sanson A. *Modified Bismuth Titanate Piezoelectric Ceramics*. Thesis. Cranfield University; 2003.
8. Hsyung, N.B., Beddow, J.K., Vetter AF. *Particle Texture Analysis. PARTICLE TEXTURE ANALYSIS*. 1984. 501-509 p.
9. Gilchrist JD. *Extraction Metallurgy (Materials Science & Technology Monographs)*. Oxford ; Pergamon Press, 1979; 1979. 460 p.
10. Eggersdorfer ML., Kadau D., Herrmann HJ., Pratsinis SE. Multiparticle sintering dynamics: From fractal-like aggregates to compact structures. *Langmuir*. 2011; 27(10): 6358–6367. Available at: DOI:10.1021/la200546g

11. Rahaman M. Sintering of Ceramics. 2007. 388 p. Available at: DOI:10.1201/b15869
12. Gronotte a. Development of new chemical processes to lead-free piezoelectric and ferroelectric materials. 2006.
13. Tokita M., Bldg E., Sc K., Ksp P. Mechanism of Spark Plasma Sintering. Ceramics. 2011; 44903(Mmc): 605–608. Available at: DOI:10.1063/1.3622584
14. Anselmi-Tamburini U., Garay JE., Munir ZA. Fundamental investigations on the spark plasma sintering/synthesis process. Materials Science and Engineering A. 2005; 407(1–2): 24–30. Available at: DOI:10.1016/j.msea.2005.06.066
15. Shen Z., Johnsson M., Zhao Z., Nygren M. Spark Plasma Sintering of Alumina. Journal of the American Ceramic Society. 2002; 85(8): 1921–1927. Available at: DOI:10.1111/j.1151-2916.2002.tb00381.x
16. Mudinepalli VR., Leng F., Lin WC., Murty BS. Conventional and Spark Plasma Sintered Ba_{0.8}Pb_{0.2}TiO₃ Nano Ceramics: Structural, Dielectric, and Ferroelectric Properties. Metallurgical and Materials Transactions A. Springer US; 2016; 47(6): 2579–2586. Available at: DOI:10.1007/s11661-016-3441-7
17. Dudina D V., Mukherjee AK. Reactive spark plasma sintering: Successes and challenges of nanomaterial synthesis. Journal of Nanomaterials. 2013; 2013. Available at: DOI:10.1155/2013/625218
18. Swain S. Synthesis and Characterizations of SrBi₂Ta₂O₉ Modified NBT-BT and NBT-KNN Ferroelectric Ceramics near Morphotropic Phase Boundary. National Institute of Technology Rourkela; 2015.
19. Byer RL., Roundy CB. Pyroelectric coefficient direct measurement technique and application to a nsec response time detector. IEEE Transactions on Sonics and Ultrasonics. 1972; 19(2): 333–338. Available at: DOI:10.1109/T-SU.1972.29679

3 Investigation of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 as a potential pyroelectric material.

Abstract

This chapter presents the synthesis and characterisations of lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 (NBT-0.06BT) as a possible pyroelectric material.

3.1 Experimental

The $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 (NBT-0.06BT) ceramic was synthesised using the conventional solid-state route by the procedure described in Chapter 2 (Fig. 2-2).

The reagent materials used in this study were sodium carbonate (Na_2CO_3), bismuth oxide (Bi_2O_3), barium carbonate (BaCO_3), and Titanium dioxide (TiO_2). The samples preparation details are listed in Table 3-1:

3.2 Results and discussion

3.2.1 Microstructure

Fig. 3-1 (a) shows the XRD patterns of the NBT-0.06BT ceramic powders milled at two different milling times (Table 3-1) and calcined at a wide range of temperatures from 600 to 850 °C for 2 or 3 hrs., (Table 3-1).

Samples C, D, E, and F displayed a single crystalline perovskite phase without any detectable secondary phase. However, Sample A and B showed one extra peak at 65.0° - 70.0° , which might be considered as an indication of a second phase.

The X-ray spectrum of Sample F shows an obvious peak shift towards a lower angle compared to other samples. Likewise, Samples B and E also present a slight shift to lower 2θ , and this shift can be linked to these samples preparation conditions. Increasing the time of ball milling from 1 or 2 to 3 hours can have a considerable influence on structure, grain growth and physical properties. While, further increasing of milling time to more than 6 hours [1,2] has been shown to have a small effect on the lattice size [1,2].

Table 3-1: The preparation parameters of NBT-0.06BT samples synthesis.

Sample name	Milling time (h)	Calcination temp./time (°C/h)	Sintering temp./time (°C/h)
A	12	600/2	1150/2
B	12	700/2	1100/2
C	12	750/2	1100/2
D	24	800/2	1100/2
E	12	850/2	1100/2
F	24	850/3	1150/2

Thus, the effect of changing the milling time from 12 to 24 hours on the XRD peak shift can be negated. However, this peak shift towards a lower angle is most likely related to an increase in the lattice size from raising the calcination temperature in these samples.

Fig. 3-1 (b) shows a splitting of the peak [111] into [003] and [021] at 39.0° to 41.0° for all the samples indicating the existence of a rhombohedral (*Rh*) phase. This splitting agrees with the XRD of the undoped NBT patterns that was previously reported in the literature [3–6].

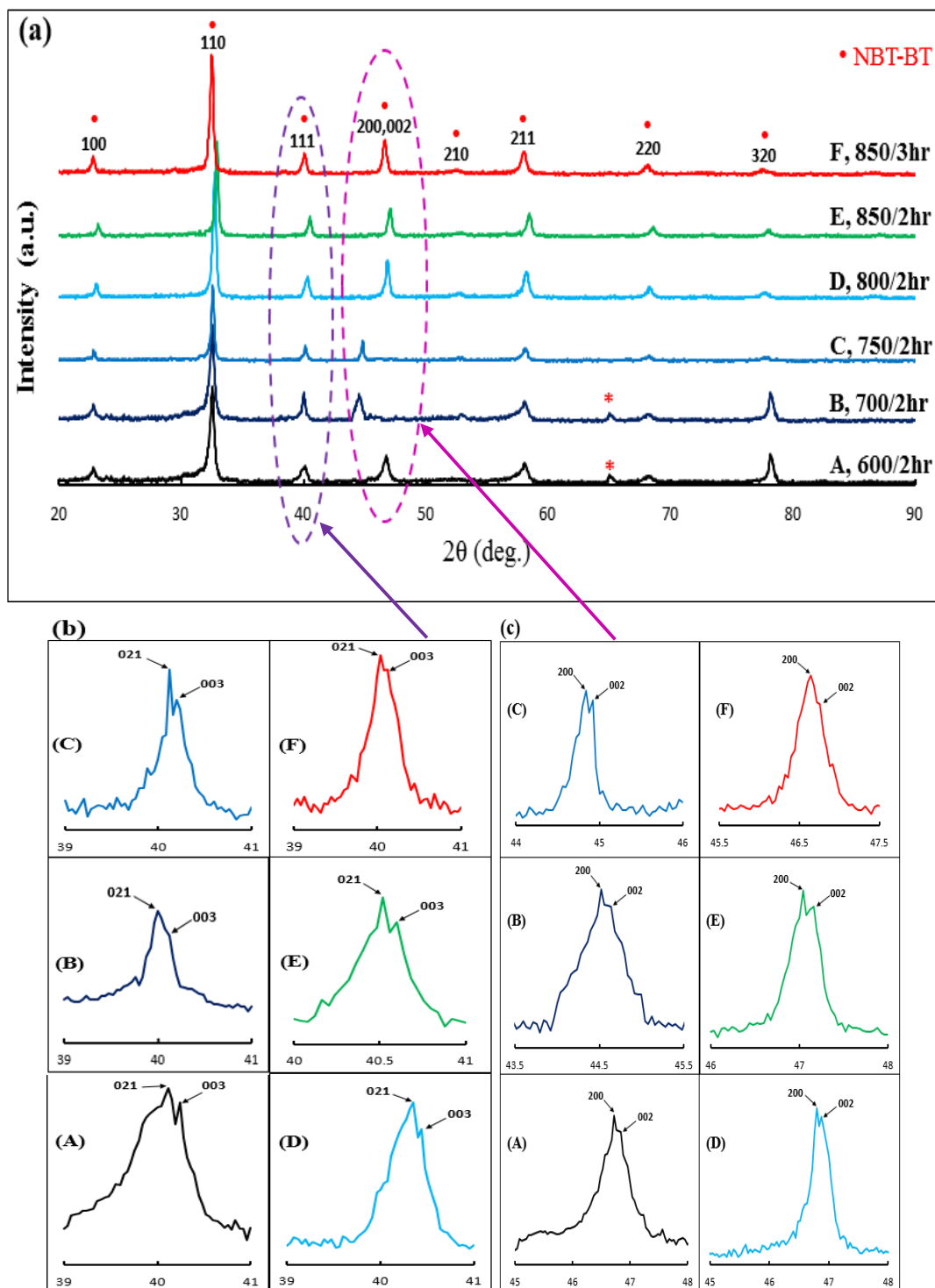


Figure 3-1: (a) XRD patterns of NBT-0.06BT calcined at different temperature (b) enlargement of [111] peak split into [003] and [021] at 39.0° to 41.0°; (c) enlargement of [200] peak split into [200] and [002] at 43.0° to 48.0°. (*) unknown peak.

Another splitting in all samples was spotted in the [200] peak into [200] and [002] at 43.0°- 48.0°; this indicates the existence of a tetragonal (*Tr*) phase in the NBT lattice (Fig. 3-1(c)). The co-existence of both *Rh* and *Tr* phases in NBT-0.06BT verifies that samples A to F are at a MPB area. In the undoped NBT-xBT the co-existence of *Rh* and *Tr* at $x = 0.06$ was widely reported in the literature [14–18]. Therefore, the phase structures of all samples are consistent with those reported in literature [7–11].

Fig. 3-2 (A to F) exhibits the morphology of all samples by SEM. Samples A to F show dense structures with some pores, particularly obvious in Samples A and B. Generally, samples (A to F) show distinguishable granular shaped grains with different grain sizes (Table 3-2). Sample A shows the biggest average grains sizes, which is around 2.2 μm , while Sample F presents the lowest size of grains (1.82 μm) (Table 3-2). The increase of the samples' grain sizes can be interpreted as a consequence of both calcination and sintering temperature/time. It is commonly known that increasing the calcination and sintering duration time and temperature can considerably enhance the average grains size in the ceramics, whilst simultaneously they may decrease the samples densities because the volatility of either Na^+ or Bi^{3+} , or both of them, at high temperatures [1,15–17]. Therefore, samples that have been calcined and/or sintered for a long time, as well as at high temperature, may have their composition changed to become Ba-rich due to the elements volatilization. As a result, the average grain sizes can be decreased due to the effect of barium. Generally, Ba^{2+} behaves as an inhibitor of grain growth in NBT systems, and a similar effect was also observed when lead was substituted with barium in lead-based ceramics, such as PZT and PLZT (La-containing PZT), [10,13,18]. In addition, the volatilization of Bi^{3+} and/or Na^+ will create A-site vacancies and these vacancies may be located at the grain boundaries, which can prevent grain growth [19,20].

All the samples show close to an average density value, which is around $5.81 \pm 0.167 \text{ gm.cm}^{-3}$ (Table 3-2). Sample B demonstrates the highest density, whereas Sample E shows the lowest density value (Table 3-2).

Table 3-2 illustrates the lattice parameters (a , b , and c) and the c/a ratios of Samples A to F. The measurement of the (a , b) and c reveals that the changes in the synthesis conditions (temperature and time) have been slightly affected the (a , b) and c parameters where they were changed from ($a = b$) = 5.489 Å and c = 13.385 Å in Sample A to ($a = b$) = 5.511 Å and c = 13.468 Å in Sample F, respectively (Table 3-2). Sample F presents the biggest lattice parameters (($a = b$) = 5.511 Å, c = 13.474 Å)), whereas Sample C has the smallest lattice parameters (($a = b$) = 5.485 Å, c = 13.381 Å)) among all other samples (Table 3-2). Sample F, lattice parameters result is supported by the XRD spectra which showed shifting toward low 2θ .

The c/a ratio shows that Sample F also has the biggest c/a ratio, while Sample D presents the lower c/a ratio among all other samples in this study. The biggest c/a ratio (2.445 Å) of Sample F can be linked to the structure of this sample, which means that this sample displays more tetragonality in its structure than all other samples (Table 3-2).

Fig. 3-3 (A to F) illustrates the *SEM-EDS* element analysis of all samples. All samples contain the four elements (*Na*, *Bi*, *Ba* and *Ti*) apart from oxygen.

3.2.2 Dielectric properties

Figs. 3-4 (a, b) and 3-5 (a, b) illustrate the dielectric properties of the unpoled and poled lead-free NBT-0.06BT ceramics at a wide frequency ranging from 80 Hz up to 10 kHz at room temperature (RT). The relative permittivity (ϵ_r) and the dielectric loss tangent ($\tan\delta$) show a strong frequency dependence on the samples preparation conditions.

The change of the dielectric relative permittivity (ϵ_r) before and after poling decreases with increasing frequencies represents a characteristic of dielectric and ferroelectric materials. This behavior is because the dipoles in these materials follow the field at low frequency, which contributes to the permittivity value. This contribution decreases as frequency increases and the dipoles start to struggle to follow the changing field [13,18,21,22].

Table 3-2: The lattice parameters, c/a ratio, average grain size, density and the density value compared with the theoretical density (6 gm.cm⁻³) of Samples A to F in this study.

Sample name	Lattice parameters (Å)		c/a ratio	Average grain size (µm)	Density (ρ) gm.cm⁻³	Compare with theoretical density %
	a=b	c				
A	5.489	13.385	2.4385	2.20	5.843	97.38
B	5.485	13.382	2.4398	2.11	5.891	98.18
C	5.485	13.381	2.4396	2.12	5.824	97.06
D	5.511	13.468	2.4384	1.85	5.815	96.91
E	5.52	13.469	2.4400	1.89	5.722	95.36
F	5.511	13.474	2.4449	1.82	5.757	95.95

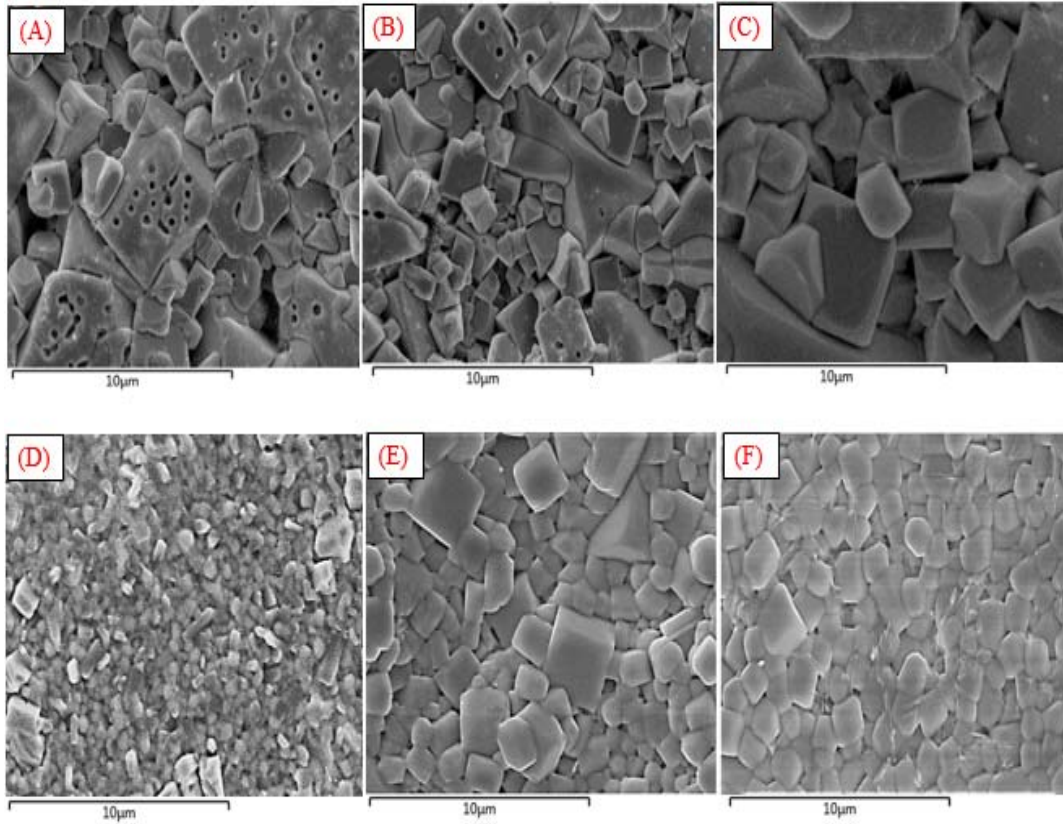


Figure 3-2: SEM morphology of Samples A to F respectively in this study.

In poled NBT-0.06BT samples, the reduction in both ϵ_r and $\tan\delta$ at RT is indicative of the poling field having induced long-range ferroelectric order [18,23], and this is similar to the conventional relaxers PLZT and PMN [18,24].

In Fig. 3-4 (a), Sample C shows the highest $\epsilon_r \sim 477$ among all samples before poling whereas, Sample D presents the maximum ϵ_r , which is around 225 after the poling process at RT (Fig. 3-4 (b)). Likewise, Sample F shows the lowest ϵ_r at both before (~ 648) and after (~ 427) poling, respectively, among all samples (Fig. 3-4 (a, b)).

The lower relative permittivity (ϵ_r) of Sample F can be understood according to samples preparation conditions. It has been reported that the ϵ_r decreases with increased in the milling time [1,17].

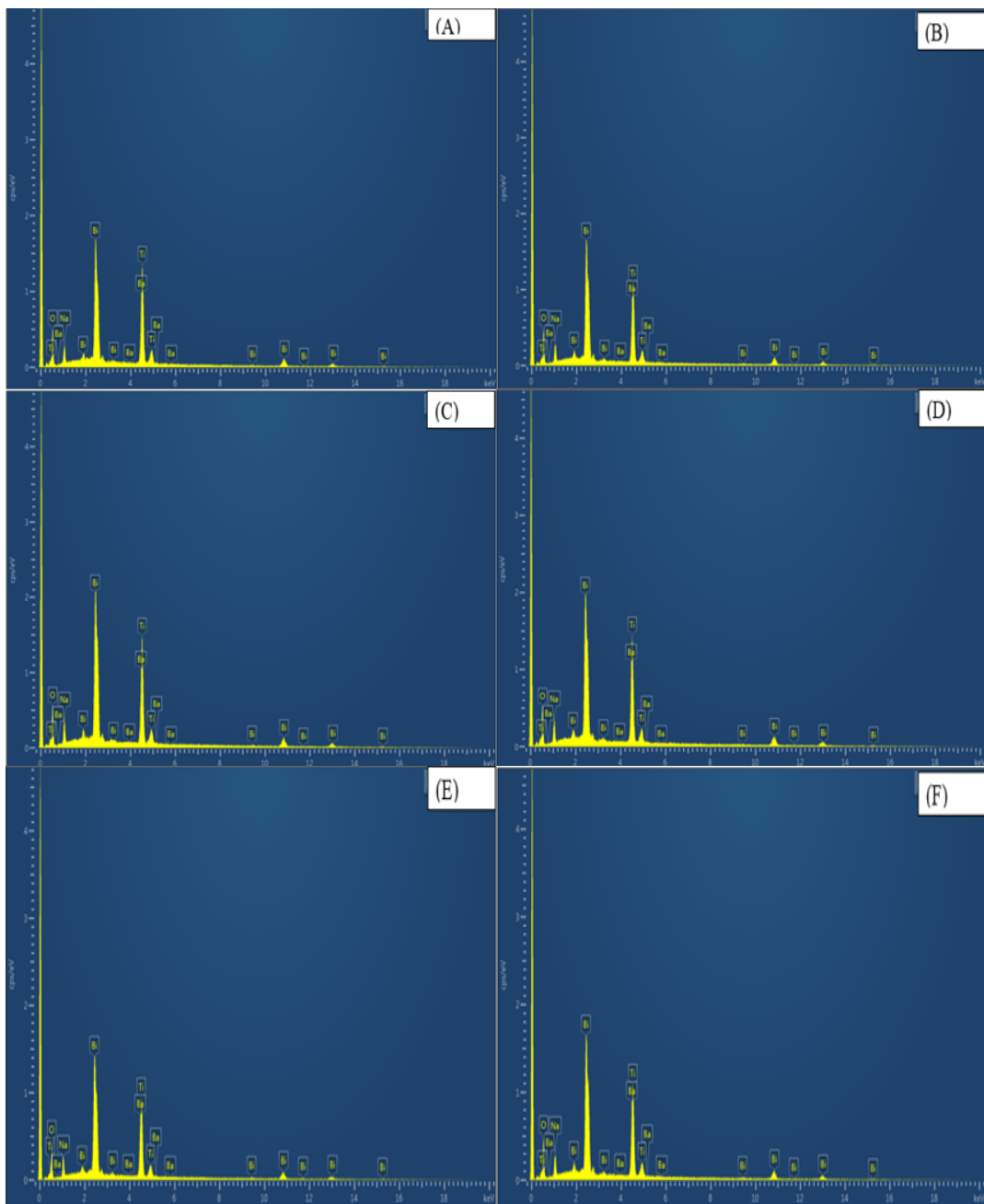


Figure 3-3: The energy dispersive analysis (*SEM-EDS*) of the all samples A to F.

Increasing milling time will initially reduce the grain size, as has been mentioned before, but with quite long milling time, the average grains size of the samples

may be slightly affected, hence the effect of increasing milling time from 12 to 24 hours cannot be considered as a significant factor in this case.

It is well known that a sample that has small average grains size can present lower ϵ_r than a sample with bigger average grains size [25,26]. Therefore, Sample F shows the lowest relative permittivity among all other samples. Sample A displays bigger average grains size whilst, Sample C shows a highest ϵ_r value than all other samples. This result can be linked to those samples structures. The XRD pattern of Sample A reveals that there is an extra peak in XRD spectra of Sample A (Fig. 3-1(a)); this extra peak can be considered as an indication of the existence of a non-ferroelectric secondary phase. This second phase has a considerable effect on the dielectric permittivity and it may lead to a decrease in the ϵ_r of this sample [25].

The dielectric loss shows similar downward trend as in the ϵ_r , with the increase of frequency before and after poling (Fig. 3-5 (a, b)). Fig. 3-5 (b) shows that the $\tan\delta$ of Samples A, B, C, D, and F were significantly decreased after poling (Fig. 3-5 (a, b)). Before poling, Sample C presented the highest $\tan\delta \sim 0.85$, while Sample E showed the lowest $\tan\delta$ value among all other samples (Fig. 3-5 (a)). After poling Sample D (~ 0.084) showed the highest dielectric loss value whereas, Samples C (~ 0.034) displayed the lowest $\tan\delta$ value (Fig. 3-5 (b)).

In addition, Samples C and E exhibited an unexpected $\tan\delta$ trend, slightly increasing with an increase the frequency from ~ 0.034 and ~ 0.037 at low frequency to around 0.040 and 0.036 at high frequency after poling. These slight increases in $\tan\delta$ of both samples might be because of some defects or distortions in the structure of these samples [23,27].

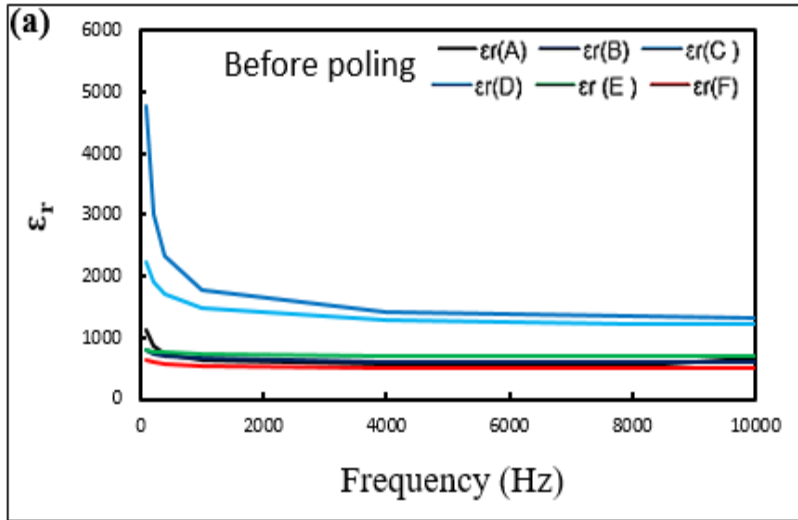
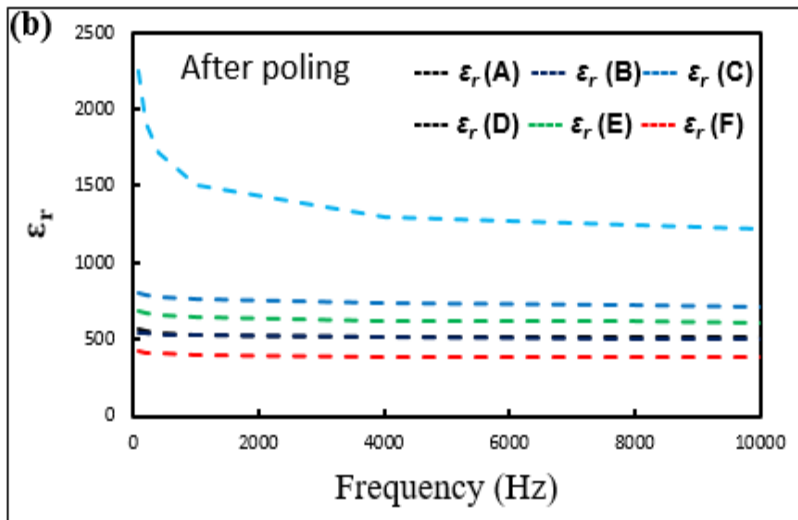


Figure 3-4: the relative permittivity of all samples (a) before and (b) after poling process.

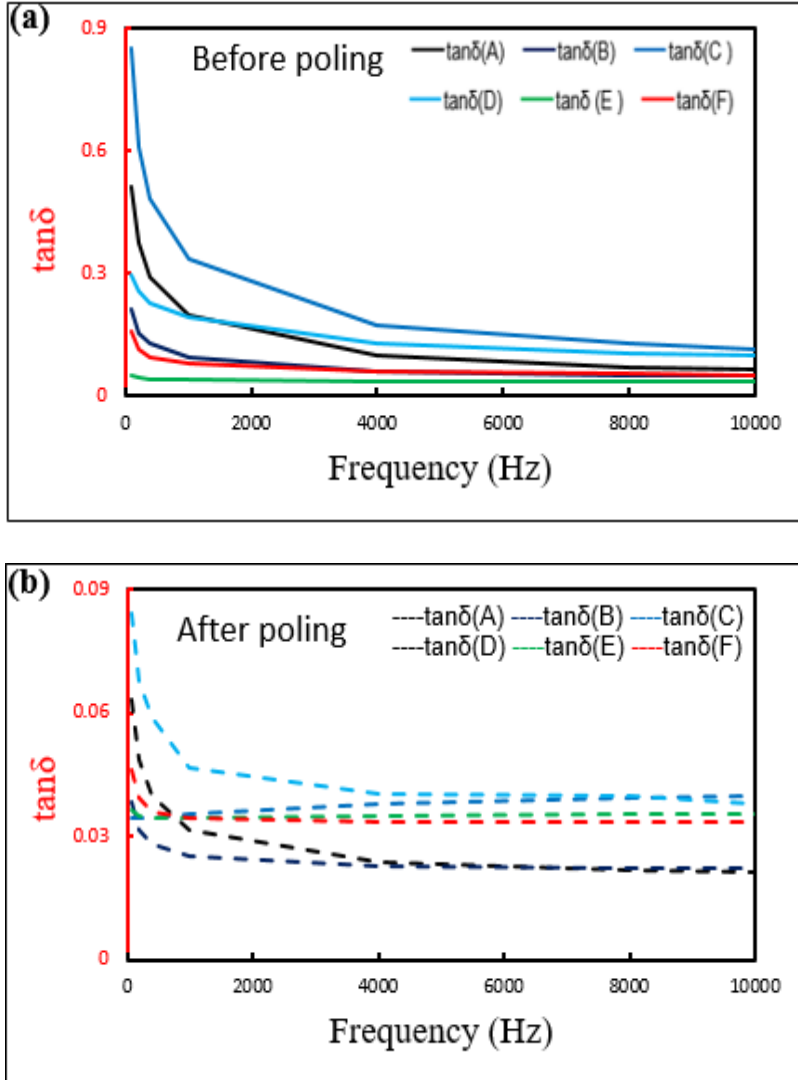


Figure 3-5: The dielectric loss of all samples where (a) before and (b) after poling process.

3.2.3 Pyroelectric properties

In order to evaluate the pyroelectric performance of the NBT-0.06BT judge if it can consider to be a pyroelectric material, its pyroelectric coefficient (p) and figure of merit (FOM) F_D of all samples were calculated at RT in this study. Both p and FOM values are essential parameters for selecting any material for a pyroelectric application.

The calculations of the pyroelectric coefficient (p) and FOM (F_D) were carried out using Equations 1-11 and 1-17 in Chapter 1 [19,28–31].

Table 3-3 illustrates the pyroelectric coefficients (p) and the FOM (F_D) for all the samples in this study.

Table 3-3: The pyroelectric coefficients (p) and the figure of merit (F_D) for all the samples (A to E).

Samples name	$p \times 10^{-4}$ (C.m⁻².°C⁻¹) at RT	$F_D \times 10^{-6}$ (Pa^{-1/2}) at 1kHz at RT
A	0.63	1.85
B	1.08	3.58
C	1.34	3.10
D	1.53	1.57
E	1.34	1.96
F	3.14	9.08

The p and the F_D values show a strong correlation with the samples structures in this study. In addition, the pyroelectric coefficient and the figure of merit (F_D) followed the same trend as in the c/a ratio, which increased from A to F. Sample F presents the highest $p \sim 3.14 \times 10^{-4}$ C.m⁻².°C⁻¹, whereas Sample A (0.63×10^{-4} C.m⁻².°C⁻¹) demonstrates the lowest value among all samples.

The low p values of Samples A and B may be related to the structures of these samples. The extra peaks, which were noticed in the XRD spectra of Samples A and B (Fig. 3-1(a)), refers to the existence of a non-ferroelectric secondary phase. This second phase can lead to decrease the pyroelectric coefficients value due to reduce the ferroelectricity in Samples A and B [25]. However, the high p value

of Sample F can be comprehended due to the c/a ratio. Sample F has the highest c/a ratio compared with all other samples in the study; this means that this sample possesses more tetragonality in its structure than all other samples.

Sample D presents the lowest F_D , which is around $1.57 \times 10^{-6} \text{ Pa}^{-1/2}$, while Sample F shows the highest $F_D \sim 9.08 \times 10^{-6} \text{ Pa}^{-1/2}$ compared with all other samples. The F_D result of Sample D can be directly linked to its higher ϵ_r and $\tan\delta$ values compared with all other samples (after poling).

Although, Sample F shows a lower p value in comparison with PZT ($4.14 \times 10^{-4} \text{ C.m}^{-2}.\text{°C}^{-1}$) [28,34], it presents slightly higher F_D value (Table 3-3) ($9.01 \times 10^{-6} \text{ Pa}^{-1/2}$) [19,23]. Thus, Sample F illustrates good pyroelectric properties demonstrating that the NBT-0.06BT can be considered as a pyroelectric material at room temperature.

The microstructure study confirmed that all the sample compositions are in MPB area; Sample F showing the highest pyroelectric properties. This might be linked to the synthesis parameters that were followed in this sample's preparation, which were slightly different from other samples in the study.

3.3 Conclusion

The correlation between the preparation method and the properties of NBT-0.06BT ceramics which were synthesised using a conventional solid-state route was investigated. The preparation conditions of the samples which were slightly changed included milling time, calcination, and sintering temperatures, in addition to, the duration time. It has been revealed by the study that the microstructure, dielectric, and pyroelectric properties of NBT-0.06BT at RT were mostly affected by the calcination and sintering temperature/time whilst, increasing the milling time from 12 to 24 hours has less effect on these materials properties. The pyroelectric study demonstrated that the composition, which was prepared by milling and mixing for 24 hours, calcined at $850^\circ\text{C}/3\text{hrs.}$, and sintered at $1150^\circ\text{C}/2\text{hrs.}$, presented the highest pyroelectric properties ($p \sim 3.14 \times 10^{-4} \text{ C.m}^{-2}.\text{°C}^{-1}$ and figure of merit F_D around $9.08 \mu\text{Pa}^{-1/2}$ at RT) than all other compositions. It has

therefore been proven by this study that NBT-0.06BT can be considered as a pyroelectric ceramic material with the pyroelectric properties comparable to PZT.

3.4 References

1. Wang H., Zuo R., Ji X., Xu Z. Effects of ball milling on microstructure and electrical properties of sol-gel derived $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ piezoelectric ceramics. *Materials and Design*. 2010; 31(9): 4403–4407. Available at: DOI:10.1016/j.matdes.2010.04.041
2. Albaaji AJ., Castle EG., Reece MJ., Hall JP., Evans SL. Effect of ball-milling time on mechanical and magnetic properties of carbon nanotube reinforced FeCo alloy composites. *Materials and Design*. Elsevier Ltd; 2017; 122: 296–306. Available at: DOI:10.1016/j.matdes.2017.02.091
3. Xu Q., Huang DP., Chen M., Chen W., Liu HX., Kim BH. Effect of bismuth excess on ferroelectric and piezoelectric properties of a $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ - BaTiO_3 composition near the morphotropic phase boundary. *Journal of Alloys and Compounds*. 2009; 471(1–2): 310–316. Available at: DOI:10.1016/j.jallcom.2008.03.078
4. Suchanicz J., Lewczuk U. KKDEM. Effect of Ba addition on the structural, dielectric and. *Materials Science-Poland*. 2015; 33(September 2014): 414–417. Available at: DOI:10.1515/msp-2015-0056
5. Suchanicz J., Lewczuk U., Konieczny K. Effect of Ba doping on the structural, dielectric and ferroelectric properties of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramics. *Ferroelectrics*. 2016; 497(1): 85–91. Available at: DOI:10.1080/00150193.2016.1163218
6. Anem S., Rao KS., Rao KH. Investigation of lanthanum substitution in lead-free BNBT ceramics for transducer applications. *Ceramics International*. Elsevier; 2016; Available at: DOI:10.1016/j.ceramint.2016.06.173
7. Xu Q., Chen S., Chen W., Wu S., Lee J., Zhou J., et al. Structure, piezoelectric

- properties and ferroelectric properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ system. *Journal of Alloys and Compounds*. 2004; 381: 221–225. Available at: DOI:10.1016/j.jallcom.2004.02.057
8. Li Q., Wang J., Ma L., Fan H., Li Z. Large electrocaloric effect in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ferroelectric ceramics by La_2O_3 addition. *Materials Research Bulletin*. Elsevier Ltd; 2016; 74: 57–61. Available at: DOI:10.1016/j.materresbull.2015.10.010
 9. Guo F., Yang B., Zhang S., Wu F., Liu D., Hu P., et al. Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition. *Applied Physics Letters*. 2013; 103(18): 182906. Available at: DOI:10.1063/1.4828675
 10. Chen M., Xu Q., Kim BH., Ahn BK., Ko JH., Kang WJ., et al. Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ piezoelectric ceramics. *Journal of the European Ceramic Society*. 2008; 28: 843–849. Available at: DOI:10.1016/j.jeurceramsoc.2007.08.007
 11. Li Q., Wang H., Fan H., Long C., Liu X. Ferroelectric, electromechanical, and dielectric properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ co-doped MnO_2 and La_2O_3 lead-free ceramics. *Journal of Materials Science*. 2013; 49(1): 211–217. Available at: DOI:10.1007/s10853-013-7694-x
 12. McQuade R., Dolgos MR. A review of the structure-property relationships in lead-free piezoelectric $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-(x)\text{BaTiO}_3$. *Journal of Solid State Chemistry*. 2016; : 0–19. Available at: DOI:10.1016/j.jssc.2016.01.008
 13. Yoon MS., Khansur NH., Ur SC. The effect of pre-milling/pre-synthesis process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized $0.94[(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3]-0.06[\text{Ba}(1+x)\text{TiO}_3]$. *Ceramics International*. Elsevier Ltd and Techna Group S.r.l.; 2010; 36(4): 1265–1275. Available at: DOI:10.1016/j.ceramint.2010.01.011
 14. Daniels JE., Jo W., Roedel J., Jones JL. Electric-field-induced phase

- transformation at a lead-free morphotropic phase boundary. Case study in a 93%(Bi_{0.5}Na_{0.5})TiO₃-7% BaTiO₃ piezoelectric ceramic. Appl. Phys. Lett. FIELD Full Journal Title:Applied Physics Letters. 2009; 95(3): 032904/1-032904/3. Available at: DOI:10.1063/1.3182679
15. Naceur H., Megriche A., El Maaoui M. Effect of sintering temperature on microstructure and electrical properties of Sr_{1-x}(Na_{0.5}Bi_{0.5}) x Bi₂Nb₂O₉ solid solutions. Journal of Advanced Ceramics. 2014; 3(1): 17–30. Available at: DOI:10.1007/s40145-014-0089-x
 16. Wang QB., Wang QG., Wan CX. Effect of sintering time on the microstructure and properties of inorganic polyphosphate bioceramics. Science of Sintering. 2010; 42(3): 337–343. Available at: DOI:10.2298/SOS1003337W
 17. Ghasemi B., Khoei AAN. Investigation of the Effect of Milling Time on the Mechanochemical Synthesis of Fe₃Al / Al₂O₃ Nanocomposite. 2012; : 1198–1201.
 18. Hiruma Y., Yoshii K., Nagata H., Takenaka T. Investigation of Phase Transition Temperatures on (Bi_{1/2}Na_{1/2})TiO₃-(Bi_{1/2}K_{1/2})TiO₃ and (Bi_{1/2}Na_{1/2})TiO₃-BaTiO₃ Lead-free Piezoelectric Ceramics by Electrical Measurements. Ferroelectrics. 2007; 346(773557621): 114–119. Available at: DOI:10.1080/00150190601180471
 19. Guggilla P., Batra AK., Currie JR., Aggarwal MD., Alim MA., Lal RB. Pyroelectric ceramics for infrared detection applications. Materials Letters. 2006; 60(16): 1937–1942. Available at: DOI:10.1016/j.matlet.2005.05.086
 20. Islam MR., Galib RH., Sharif A., Hasan M., Zubair MA., Islam MF. Correlation of charge defects and morphology with magnetic and electrical properties of Sr and Ta codoped BiFeO₃. Journal of Alloys and Compounds. Elsevier Ltd; 2016; 688: 1186–1194. Available at: DOI:10.1016/j.jallcom.2016.07.134
 21. Hiruma Y., Nagata H., Takenaka T., Member S. Phase-Transition

- Temperatures and Piezoelectric Properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -. 2007; 54(12): 2493–2499.
22. Kang W-S., Lee S-K., Koh J-H. AC conductivity and dielectric properties of $(\text{Bi,Na})\text{TiO}_3\text{--BaTiO}_3$ lead free ceramics. *Ceramics International*. 2015; 41(5): 6925–6932. Available at: DOI:10.1016/j.ceramint.2015.01.147
 23. Sapper E., Schaab S., Jo W., Granzow T., Rödel J. Influence of electric fields on the depolarization temperature of Mn-doped $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\text{--}x\text{BaTiO}_3$. *Journal of Applied Physics*. 2012; 111(1): 14105. Available at: DOI:10.1063/1.3674275
 24. Cheng SY., Shieh J., Lu HY., Shen CY., Tang YC., Ho NJ. Structure analysis of bismuth sodium titanate-based A-site relaxor ferroelectrics by electron diffraction. *Journal of the European Ceramic Society*. Elsevier Ltd; 2013; 33(11): 2141–2153. Available at: DOI:10.1016/j.jeurceramsoc.2013.03.020
 25. Cai W., Gao J., Fu C., Tang L. Dielectric properties, microstructure and diffuse transition of Ni-doped $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ ceramics. *Journal of Alloys and Compounds*. 2009; 487(1–2): 668–674. Available at: DOI:10.1016/j.jallcom.2009.08.034
 26. Babu MVG., Bagyalakshmi B., Venkidu L., Sundarakannan B. Grain size effect on structure and electrical properties of lead-free $\text{Na}_{0.4}\text{K}_{0.1}\text{Bi}_{0.5}\text{TiO}_3$ ceramics. *Ceramics International*. 2017; 43(15): 12599–12604. Available at: DOI:10.1016/j.ceramint.2017.06.137
 27. Ranjan R., Dviwedi A. Structure and dielectric properties of $(\text{Na}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$: $0 \leq x \leq 0.10$. *Solid State Communications*. 2005; 135: 394–399. Available at: DOI:10.1016/j.ssc.2005.03.053
 28. Martínez FL., Hinojosa J., Doménech G., Fernández-luque FJ., Zapata J., Ruiz R., et al. Dielectric Constant Tunability at Microwave Frequencies and Pyroelectric Behavior. *IEEE transactions on ultrasonics, ferroelectrics, and frequency control*. 2013; 60(8): 1595–1602. Available at:

DOI:10.1109/TUFFC.2013.2740.

29. Rodríguez-Ruiz R., González-Ballesteros R., Flores-Cuautle a., Suaste-Gómez E. Determination of the Pyroelectric Coefficient for $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.935}\text{Ba}_{0.065}\text{TiO}_3$ Piezoelectric Ceramics. *Ferroelectrics*. 2008; 368(1): 216–223. Available at: DOI:10.1080/00150190802368537
30. Patel S., Chauhan A., Kundu S., Madhar NA., Llahi B., Vaish R., et al. Tuning of dielectric, pyroelectric and ferroelectric properties of $0.715\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.065\text{BaTiO}_3\text{-}0.22\text{SrTiO}_3$ ceramic by internal clamping. *AIP Advances*. 2015; 5(8): 87145. Available at: DOI:10.1063/1.4929328
31. Abo, Jiro Kobune M., Nishimura T., Yazaw T., Nakai Y. Effects of manganese addition on pyroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)_{0.94}(\text{BaTiO}_3)_{0.06}$ ceramics. *Integrated Ferroelectrics*. 2006; 80(1): 87–95. Available at: DOI:10.1080/10584580600656502
32. He Y. Heat capacity, thermal conductivity, and thermal expansion of barium titanate-based ceramics. *Thermochimica Acta*. 2004; 419(1–2): 135–141. Available at: DOI:10.1016/j.tca.2004.02.008
33. Setter N., Waser R. Electroceramic materials. *Acta Materialia*. 2000; 48(1): 151–178. Available at: DOI:10.1016/S1359-6454(99)00293-1
34. Guo F., Yang B., Zhang S., Wu F., Liu D., Hu P., et al. Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-}x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition. *Applied Physics Letters*. 2013; 103(2013): 182906. Available at: DOI:10.1063/1.4828675

4 Identification of the Morphotropic Phase Boundary Composition in the $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}x\text{BaTiO}_3$, $0.05 \leq x \leq 0.08$.

Abstract

This chapter investigates the MPB composition in $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}x\text{BaTiO}_3$ ceramics, ($x = 0.05, 0.06, 0.07$, and 0.08) and the effects of the extra barium titanate ($x\text{BT}$) content on the forming of the MPB, microstructure, depolarization temperature, dielectric and pyroelectric properties of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}x\text{BaTiO}_3$ material.

4.1 Experimental

The lead free $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}x\text{BaTiO}_3$ (*NBT-xBT*), ($x = 0.05, 0.06, 0.07$, and 0.08) ceramics were synthesised using a conventional solid-state technique employing the method described in Chapter 2, Fig. 2-2.

The reagent materials used in this study were sodium carbonate (Na_2CO_3), bismuth oxide (Bi_2O_3), barium carbonate (BaCO_3), and Titanium dioxide (TiO_2), and are listed in Chapter 2, Table 2-1.

4.2 Results and discussion

4.2.1 Effects of the extra barium titanate (BT) content on microstructure

Fig.4-1 (a) shows the X-ray diffraction spectra of lead-free $(1-x)$ NBT- $x\text{BT}$, ($0.05 \leq x \leq 0.08$) ceramics powders calcined at 850°C for 3 hrs. Samples A to D presented pure perovskite structure, with no secondary phase detected, demonstrating that all the barium titanate concentrations diffused into the NBT main lattice and formed the new NBT- $x\text{BT}$, ($x = 0.05, 0.06, 0.07$, and 0.08) ceramics [1-3].

Enlargement of the XRD pattern for Samples A, B, and C shows the splitting in the peak $[111]$ into $[003]$ and $[021]$ at $39.0^\circ \leq \theta \leq 41.0^\circ$ (Fig.4-1 (b)), indicating the existence of the rhombohedral (*Rh*) phase. The room temperature (*RT*), XRD

spectra of undoped NBT presented a Rh symmetry with splitting of the [111] peak into [003]/[021] at $38.0^\circ \leq \theta \leq 42.0^\circ$ and a single peak at $45.0^\circ \leq \theta \leq 48.0^\circ$ [1,4–6]. However, Sample D illustrates a single peak in [111] demonstrating tetragonal (*Tr*) phase [2,3,5,6]. Another peak splitting was spotted [200] into [200] and [002] at $45.5^\circ \leq \theta \leq 47.5^\circ$ in Samples B, C, and D (Fig.4-1 (c)). This split refers to the existence of tetragonal phase in the NBT lattice (Fig.4-1 (c)) [4,7–11]; whereas, Sample A shows a single peak [200], meaning that Sample A has a pure Rh phase [2,35,6]. The coexistence of Rh and Tr phases in the Samples B and C ($x=0.06$ and 0.07) confirms that these samples structures are at the MPB area. While, Samples A and D present pure Rh and Tr phases respectively (Fig.4-1 (b and c)).

To determine the stability of the perovskite structure, the Goldschmidt tolerance factor (*t*) relation was calculated using Equation 1-12 in chapter 1 [12-15].

The tolerance factor value of stable perovskite structure is in the range of 0.77-1.10 [14,16,17].

The calculated *t* values of the NBT-xBT ($0.05 \leq x \leq 0.08$) compositions were around 0.974, 0.975, 0.976, and 0.977 respectively suggesting that all samples compositions show stable structure.

Table 4-1 presents the lattice parameters (Å), the *c/a* ratio, the average grain size (μm) and density (gm.cm⁻³) of all the samples. The lattice parameters are “*a* = *b*” and “*c*” vary by increase of the barium content in the samples composition. The (*a*=*b*) parameter shows gradual increase from Sample A to D (Table 4-1). While, the “*c*” parameter exhibits a large increase from Sample A to D; but the ultimate “*c*” value was found in Sample B. Because Sample B has the highest *c* value of all the samples, this could indicate that this Sample has more tetragonality in its structure compared to the others. The *c/a* ratio increased considerably with increased Ba²⁺ from $x=0.05$ to $x=0.07$ from Sample A to C, then decreased significantly to Sample D ($x=0.08$) (Table 4-1).

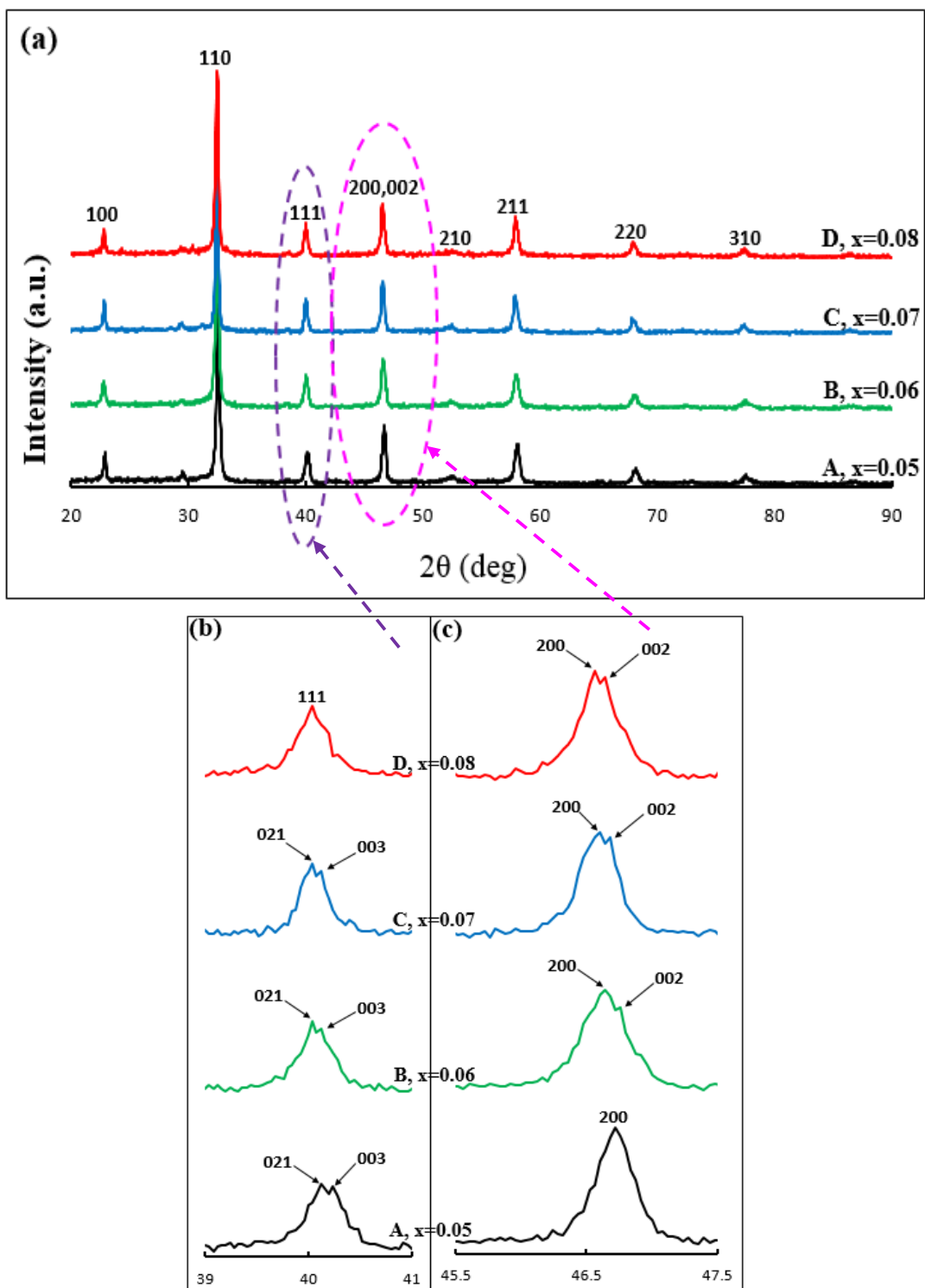


Figure 4-1: (a) XRD patterns of NBT-xBT calcined at different temperature (b) enlargement of [111] peak split into [003] and [021] at 39.0° to 41.0°; (c) enlargement of [200] peak split into [200] and [002] at 45.5° to 47.5°.

Table 4-1: Composition (sample name), lattice parameter, c/a ratio, average grain size and density of all samples in this study.

Composition, (Sample name)	Lattice parameter (Å)		c/a ratio	Average grain size (µm)	Density(ρ) (gm.cm⁻³)
	a=b	c			
NBT-0.05BT, A	5.4960	13.3130	2.424	1.85	5.806
NBT-0.06BT, B	5.5113	13.4744	2.445	1.79	5.757
NBT-0.07BT, C	5.5333	13.4648	2.433	1.64	5.617
NBT-0.08BT, D	5.5664	13.4553	2.417	1.52	5.493

Fig. 4-2 (a to d) illustrates the SEM surface morphology of the samples A, B, C, and D. All the samples display a dense microstructure with an average density of around $5.668 \pm 0.368 \text{ g.cm}^{-3}$. Sample A shows the highest density value whereas Sample D presents the lowest value of all (Table 4-1).

Samples A, B, and D show an obvious granule grain shape with various grain sizes, while it not so clear in Sample C (Fig. 4-2 (c)). The average grain size reduces considerably from Sample A to D (Table 4-1).

The reason behind the reduction in the average grain size may be linked to the extra Ba^{2+} content in the composition of Samples B, C, and D (Table 4-1). In general, Ba^{2+} behaves as an inhibitor of the grain growth in an NBT system. In lead-based ceramics, such as PZT and PLZT (La-containing PZT), a similar effect was also observed when lead was substituted with barium [1,18,19].

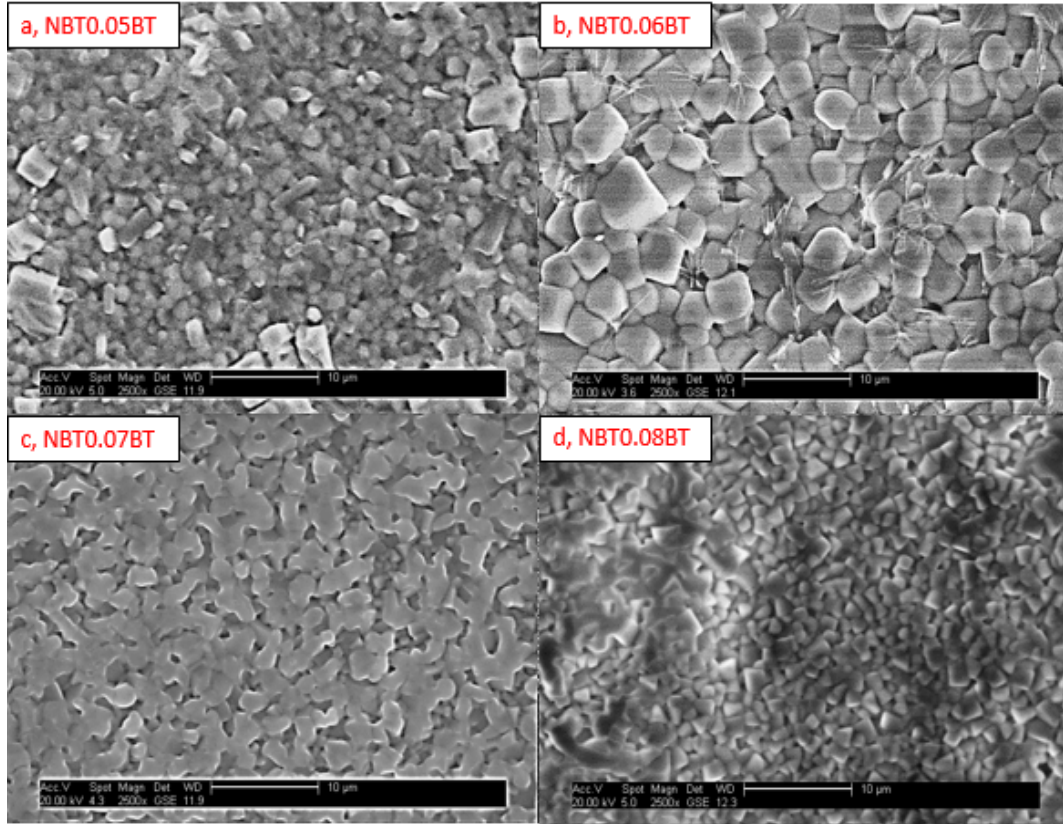


Figure 4-2: SEM surface morphology of the (1-x)NBT-xBT of all samples.

Another technique utilized to confirm the elements that have contributed in each NBT-xBT ($0.05 \leq x \leq 0.08$) composition is energy-dispersive X-ray spectroscopy (*SEM-EDS* or *SEM-EDX*). This analysis technique is used to analyse the sample elements, or their chemical characterisation (Fig 4-3 (a to d)). All the sample compositions were illustrated with the four elements (*Na*, *Bi*, *Ba* and *Ti*) in addition to oxygen.

4.2.2 Effects of the extra barium titanate (BT) content on dielectric properties

Figs 4-4 (a and b) and 4-5 (a and b) illustrate the frequency dependence of the dielectric properties (relative permittivity (ϵ_r) and dielectric loss ($\tan\delta$)) for the unpoled and poled NBT-xBT($0.05 \leq x \leq 0.08$) in frequency range from 80 Hz up to

10 kHz at room temperature (RT). The ϵ_r and the $\tan\delta$ show a strong relationship with both the extra barium titanate concentration (x) and frequency.

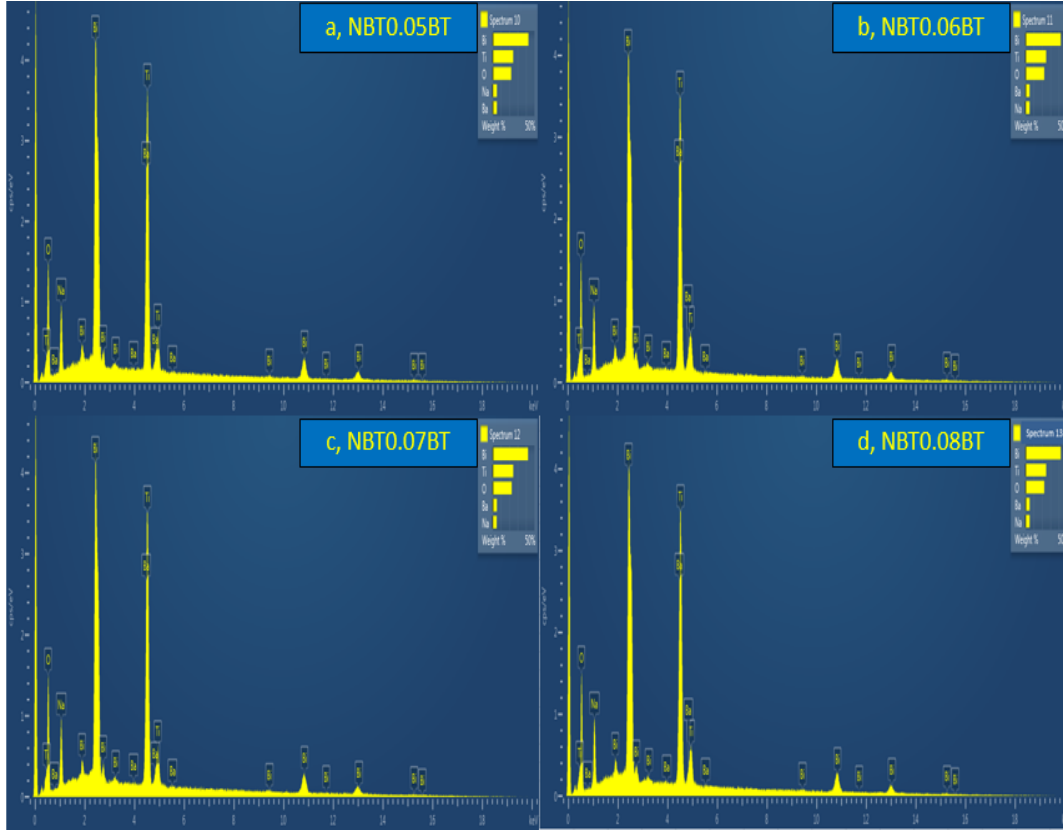


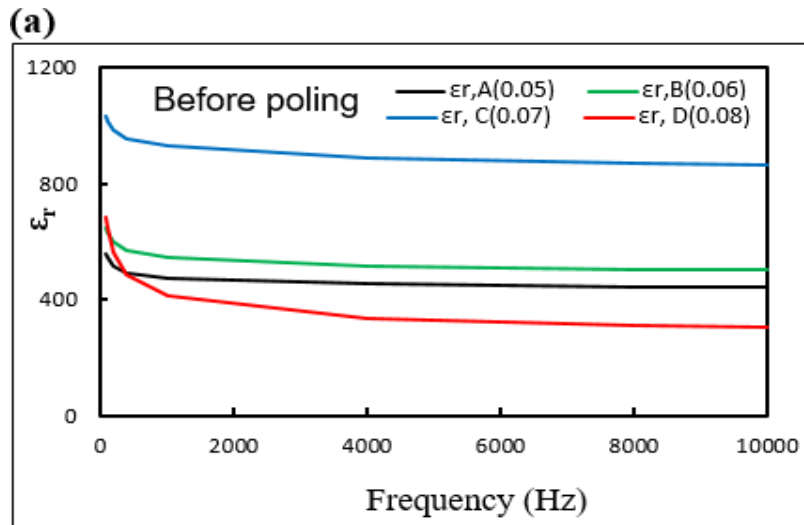
Figure 4-3: The energy dispersive analysis (*SEM-EDS*) of NBT- x BT, ($x=0.05, 0.06, 0.07$, and 0.8) Samples A (a), B (b), C (c), and D (d) respectively.

The dielectric permittivity (ϵ_r) trend, has been observed decreasing with increasing frequency, before and after the poling process for this material as most of dielectric and ferroelectric materials do. This behavior is due to the dipoles in these materials being able to follow the field at low frequency and contribute to the permittivity value. This decreases as frequencies increase and the dipoles start to struggle to follow the changing field [18-21].

The ϵ_r rapidly increased with increased x BT content up to $x=0.07$, then decreased at $x=0.08$ before and after the poling process at RT (Fig 4-4 (a and b)). This

behavior can be interpreted according to the ionic matching relationship and Hume-Rothery rules [10,22], the ionic radius of all elements in the sample compositions are Na^+ (1.39 Å, CN 12) (CN=coordination number), Bi^{3+} (1.31 Å, CN 12), Ba^{2+} (1.61 Å, CN12), and for Ti^{4+} (0.61 Å, CN 6). Thus, the excess of the barium titanate concentration can create A-site vacancies in the NBT-xBT, ($x=0.06$, 0.07, and 0.08) perovskite structure. According to the radius matching, the Ba^{2+} can replace the Na^+ but it is difficult to replace the Bi^{3+} due to the facts that the radius difference between bismuth and barium is more than 15%. Because the barium behaves as a donor this will make the domain wall movement easier, as a result, the dielectric properties of NBT-xBT, ($x=0.06$, 0.07, and 0.08) increased up to $x=0.07$ [1].

In Fig. 4-4 (a, b), Sample C shows the highest $\epsilon_r \sim 1031$ and 482 among all samples before and after poling at RT. Likewise, Sample A shows the lowest ϵ_r both before (~ 559) and after (~ 409) poling at low frequencies (Fig. 4-3 (a, b)). However, at frequencies in the range from 0.5 kHz up to 10 kHz, Sample D exhibits the lowest ϵ_r at both before and after poling (~ 486 and ~ 415) (Fig 4-4 (a and b)).



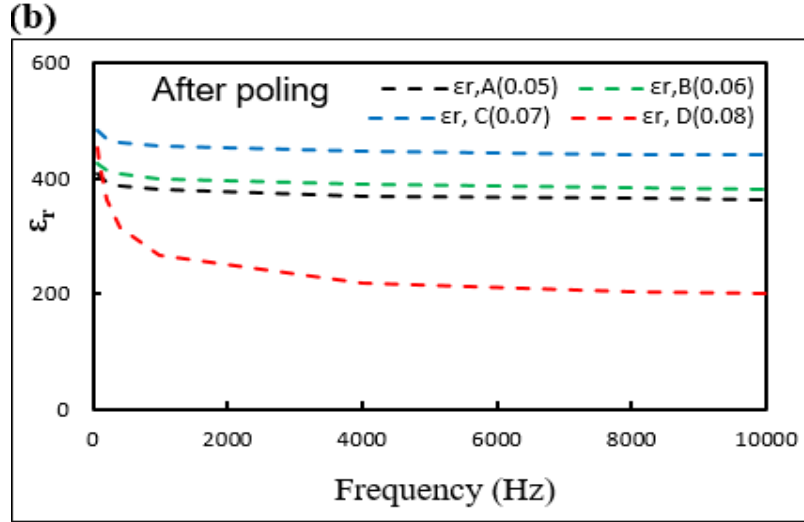


Figure 4-4: the relative permittivity of all samples (a) before and (b) after poling process.

The relationship between the $\tan\delta$ and the frequency before and after the poling process is illustrated in Fig 4-5 (a and b). It can be clearly seen that the $\tan\delta$ of Samples A, B, and C are significantly decreased after poling, but this is not the case with Sample D (Fig 4-5 (a and b)).

Sample D presents the highest $\tan\delta$ than all other samples before and after the poling stage: ~ 0.379 and ~ 0.389 respectively (Fig. 4-4 (a, b)); Sample C demonstrates the lowest loss both before and after the poling process: 0.089 and 0.053 respectively (Fig. 4-5 (a, b)).

The high dielectric loss in Sample D may be because there are some defects or distortions in its structure causing increases in the dielectric loss value of this Sample before and after poling [3,23].

In poled NBT-xBT samples, the reduction in the dielectric properties (ϵ_r and $\tan\delta$) at RT, can be understood due to that the poling field having been induced in the long-range ferroelectric order in these samples [19,23] Similar behaviour was observed in the poled PLZT and PMN materials [19,21,24].

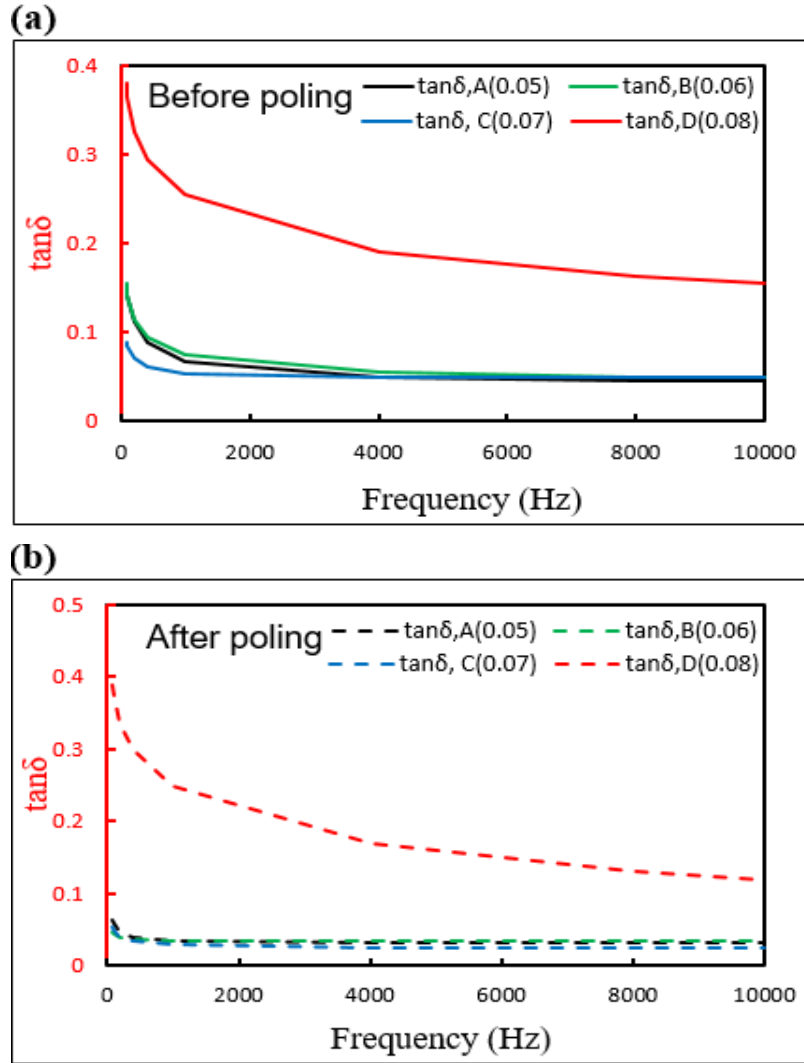


Figure 4-5: the dielectric loss of all samples (a) before and (b) after poling process.

Fig. 4-6 (a-d) presents the change of dielectric properties of poled samples from A to D as a function of temperature from 20 to 150 °C at 1, 10, and 100 (kHz). The relative permittivity (ϵ_r) of all the compositions increases with temperature; this is typical behavior for ferroelectric materials [25].

The ϵ_r demonstrates a significant increase with the increase of Ba^{2+} concentration, with values of 362, 396, 430, and 489, respectively for the Samples A to D at RT and 1 kHz. Therefore, the increment in the Ba^{2+} content

from $x = 0.05$ to $x = 0.08$ can be responsible for the significant increase in the relative permittivity value, as detailed previously [26].

The dielectric loss ($\tan\delta$) also increases with the temperature up to a certain point and then decreases. The $\tan\delta$ value of Sample A is ~ 0.027 at RT and 1 kHz (Fig. 4-6 (a)). It increases to around 0.044, 0.045, and 0.048 for Samples B, C, and D respectively (Fig. 4-6 (b-d)).

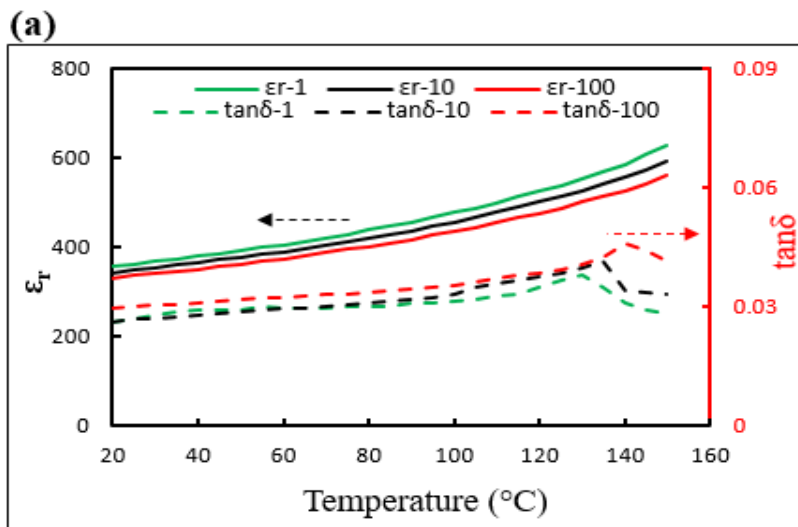
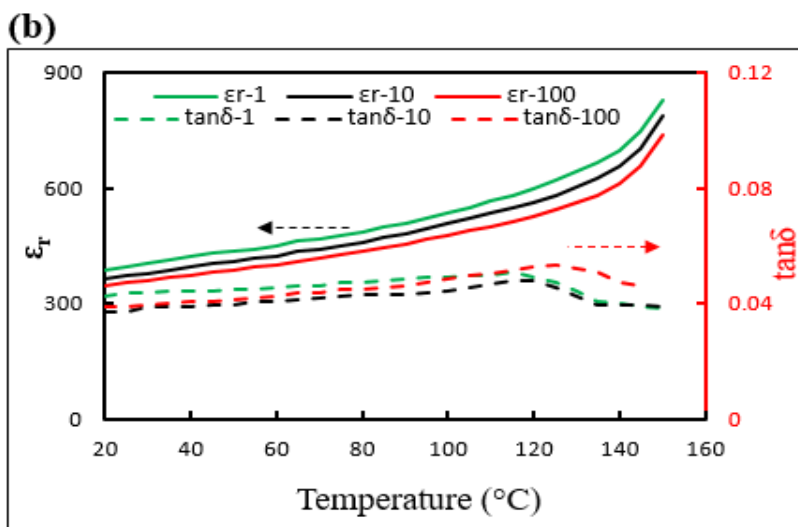
The temperature at which $\tan\delta$ shows a maximum value is known as the depolarization temperature (T_d) [20,37,38]. The $\tan\delta$ values at T_d are around 0.038, 0.051, 0.067, and 0.070, and their corresponding temperatures estimated at ~ 130 , 115, 100 and 120 ($^{\circ}\text{C}$) for Samples A, B, C, and D, respectively (Fig. 4-7). The $\tan\delta$ results at T_d reveal that A also has the lowest value among all samples (Fig. 4-7). The ϵ_r values at T_d are ~ 555 , 582, 730, and 927 for Sample A, B, C, and D, respectively (Fig. 4-6 (a-d)). The ϵ_r values at T_d clearly reveal that the increase in barium concentration has a significant correlation with the dielectric properties but the most dramatic effect on the relative permittivity is the change of temperature at wide temperature range.

4.2.3 Effects of extra barium titanate (BT) content on depolarization temperature

Increasing the xBT in the compositions ($x=0.05$, 0.06, 0.07, and 0.08) of samples A to D can also cause a significant effect on the depolarization temperature (T_d) of the NBT-xBT [26]. However, even though depolarization temperature has been considered an important parameter in pyroelectric study, its origin has not yet been fully understood for NBT-xBT. Thus, it has more than one definition [7,14,29–31], and one of them is the phase transition temperature from ferroelectric (FE) to anti-ferroelectric (AFE) phases or from ferroelectric to relaxor anti-ferroelectric (RAFE) [3,23,27,32].

In this study, the T_d was identified by two methods: (1) Dielectric method, from the dielectric loss peak value vs temperature plots (Fig. 4-7); (2) Pyroelectric method, the pyroelectric coefficient (p) peak value vs temperature plots (Fig. 4-8) [33].

For both methods the T_d is heavily dependent on increasing the Ba^{2+} concentration in the samples (B to D) compositions.



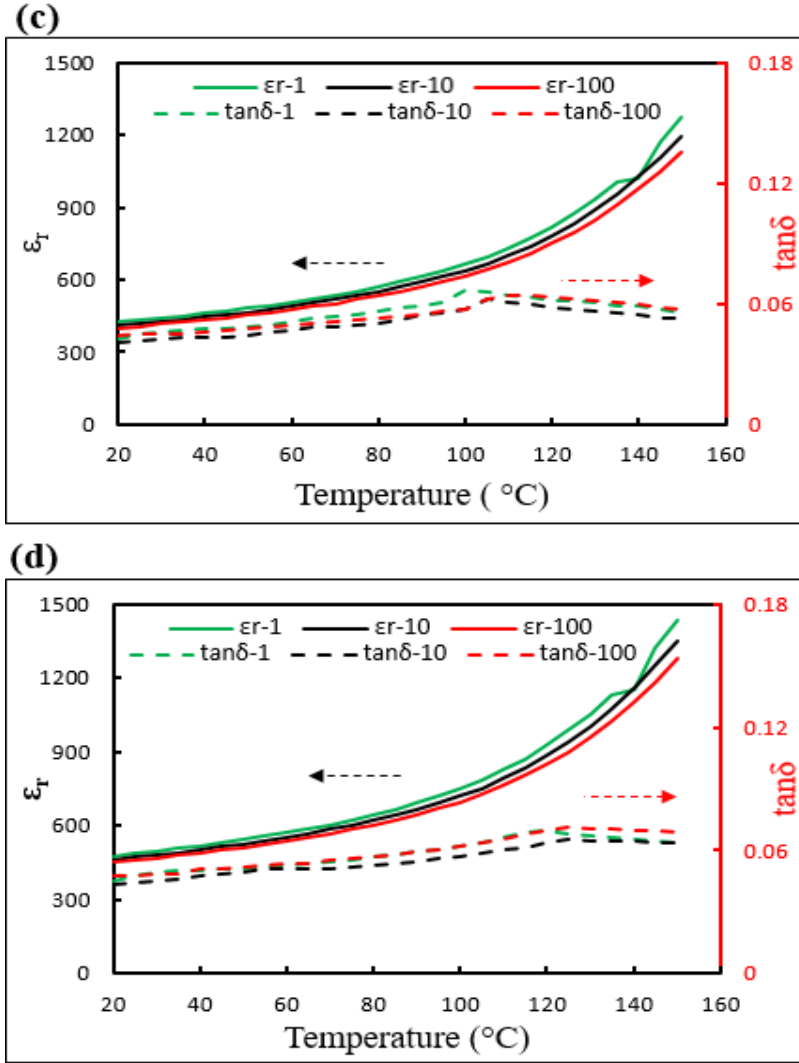


Figure 4-6: the change of the dielectric properties of the NBT-xBT with increase in temperature, (a) NBT-0.05BT; (b) NBT-0.06BT; (c) NBT-0.07BT and (d) NBT-0.08BT.

Fig. 4-7 reveals that T_d decreased from ~ 130 °C in Sample A to around 120 °C for Sample D. However, Sample C presents the lowest T_d which is ~ 100 °C (Fig. 4-7). Furthermore, Sample D illustrates a higher T_d , which is more than 20 °C higher than the T_d for Sample C (Fig. 4-7). This result confirms that with an increase in the BT concentration by more than $x=0.07$, the depolarization temperature will shift towards a higher temperature.

The depolarization temperature can also be obtained from the ultimate pyroelectric coefficient (p) value. It is generally known that the maximum p that can be achieved in this sort of materials is at the phase transition temperature [21,34–36]. In this study, T_d value was only identified for Sample C by this method; it showed a decrease from more than 90 °C to ~ 80.0 °C (Fig. 4-8). However, the exact T_d values could not be identified for Samples A, B, and D by this method due to the upper temperature limit of equipment, so the T_d values for Samples A, B, and D are most likely to be higher than 90 °C (Fig. 4-8).

The decrease in T_d for Samples A to D, is possibly caused by the excess amount of barium. According to Yoon *et al.*, Guo *et al.*, and Li *et al.* [18,27,37] the T_d coincides with phase transition from ferroelectric to a so-called “intermediate” phases. This transition shows a shift of T_d toward lower temperature for samples with excess BT concentration.

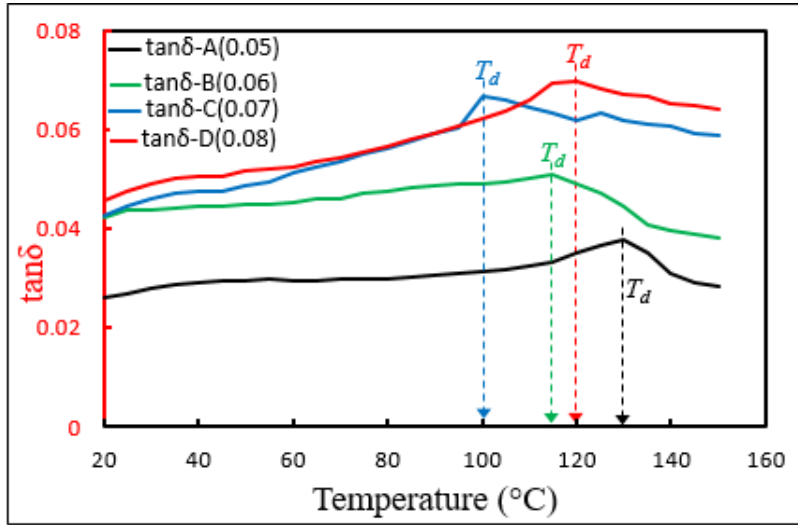


Figure 4-7: the change of the $\tan\delta$ with increase in temperature and the depolarization temperature for each sample of NBT-xBT ($0.05 \leq x \leq 0.08$) materials.

It has been reported that the c/a ratio increase with extra Ba^{2+} content [18], thus, the increase in BT concentration would lead to the improvement of the

tetragonality of BaTiO₃ in NBT-xBT, ($x=0.06, 0.07$ and 0.08) by compensating for the loss in barium during the calcination and sintering stages (Table 4-1) [18]. These extra barium concentrations are more likely to have replaced one of A-site ions rather than B-site [18,37] due to radius similarity (as discussed previously), which may result in the generation of some of the A-site vacancies when Ba²⁺ replaces Na⁺.

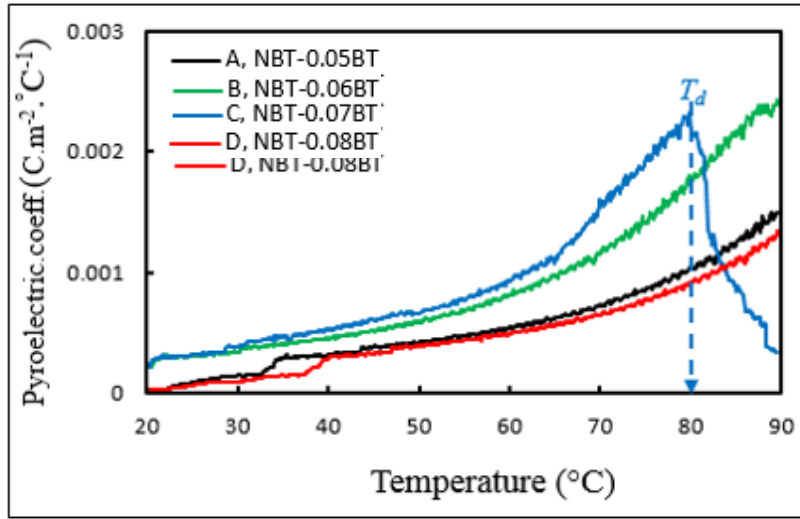


Figure 4-8: The pyroelectric coefficient for NBT-xBT ($0.05 \leq x \leq 0.08$) and the identifying of the depolarization temperature for Sample C.

Comparing T_d values obtained by the two methods, the pyroelectric method shows T_d value for Sample C lower than the dielectric method, which is in agreement with the literature [7].

These vacancies can reduce ferroelectric long-range ordering and weaken the coupling between A-site ions and TiO₆ octahedron, as a result inducing the phase change at a lower temperature [18,37]. The results of this study agree with the literature [26,27]; however, in general the T_d trend is to shift towards a lower temperature with increased BT content from $x=0.05$ up to $x=0.08$.

4.2.4 Effects of extra barium titanate (BT) content on pyroelectric properties

The most efficient way to evaluate a pyroelectric material's performance is to calculate the figure of merits (*FOMs*) that represent the essential parameters for pyroelectric applications [7]. The calculation of the *FOMs* is based on the values of the pyroelectric coefficient, relative dielectric permittivity, dielectric loss and the specific heat [18]. There are several types of *FOMs* depending on the particular type of pyroelectric application, such as infrared or thermal imaging [11,38]. The types of *FOMs* depend on the input of thermal or electrical circuits, current or voltage [7,33,39].

In this study, the pyroelectric coefficient (p) of NBT-xBT ($0.05 \leq x \leq 0.08$) were measured from 20 to 90 °C for Samples A to D. The calculations of the pyroelectric coefficient (p) and *FOMs* were carried out using Equations 1-11 and 1-15 to 1-18 in chapter 1 [9,33, 40,41]:

Fig. 4-8 shows the change of p vs. T for Samples A to D from 20 to 90 °C. Sample B presents the highest p value at both room and depolarization temperatures (Tables 4-2 and 4-3). While in the temperature range from 35 °C to 82 °C, Sample C displays the highest pyroelectric coefficient value with maximum value of p at 80 °C. In contrast, Sample B has the highest p value over the temperature range 83 °C to 90 °C among all other samples (Fig (4-6)). Samples A and D show low pyroelectric coefficient values at both RT and T_d (Tables (4-2 and 4-3)). The low p in both Samples (A and D) can be linked to these samples structures. The XRD results reveal that Samples A and D are located around the MPB (Fig 4-1 (a to c)), therefore, the low p values can most likely be attributed to the effect of the MPB area.

The high pyroelectric coefficient at T_d for Samples B and C may be understood due to the effect of the phase change. The polarization state and also the structure of these Samples (B and C) are possibly changed from ferroelectric (*FE*) rhombohedral (*Rh*) and tetragonal (*Tr*) co-existing (*MPB*) to antiferroelectric (*AFE*) or relaxor antiferroelectric (*RAFE*) tetragonal (*Tr*) phases; these

polarization states and structure changes will substantially enhance the p values of these Samples.

The p , and FOMs F_i , F_v , and F_D values for all samples are listed in Table 4-2 at RT and 1 kHz while, those values at 90 °C or T_d and 1 kHz listed in Table 4-3.

Table 4-2: The pyroelectric coefficient (p) and the FOMS, F_i , F_v , and F_D for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at room temperature and 1 kHz.

Sample name	$p \times 10^{-4}$ (C.m⁻².°C⁻¹) at RT	$F_i \times 10^{-10}$ (m.V⁻²) at 1kHz at RT	F_v (m².C) at 1kHz at RT	F_D (x10⁻⁶ Pa^{-1/2}) at 1kHz at RT
A	0.90	0.32	0.01	3.43
B	3.14	1.12	0.021	9.08
C	3.04	1.09	0.018	8.32
D	0.70	0.24	0.006	1.70

The FOMs F_i , F_v , and F_D values (Tables (4-2 and 4-3)) at both RT and T_d show the same trend as in p . Sample B demonstrates the highest FOMs values while Sample D has the lowest F_i , F_v , and F_D values among all samples in this study (Tables (4-2 and 4-3)). Although, Sample B has a lower pyroelectric coefficient value than PZT (4.14×10^{-4} C.m⁻².°C⁻¹) [9,42], it does; however, show higher F_v (0.021 m².C⁻¹) and F_D (9.08×10^{-6} Pa^{-1/2}) values than PZT (0.008 m².C⁻¹) and (9.01×10^{-6} Pa^{-1/2}) respectively at RT and 1 kHz (Table 4-2) [9,23,25,42].

At 90 °C or T_d , Samples B and C show higher p , F_i , F_v , and F_D values (Table 4-3) than some of lead-free ceramic compositions, such as Na_{0.5}Bi_{0.5}TiO₃-0.07Ba(Zr_{0.055}Ti_{0.945})O₃ (NBT-0.07BZT) (20×10^{-4} C.m⁻².°C⁻¹, 7.33×10^{-10} m.V⁻¹, 0.066 m².C⁻¹, and 33.6×10^{-6} Pa^{-1/2}) [42] respectively.

Table 4-3: The pyroelectric coefficient (p) and the FOMs, F_i , F_v , and F_D for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at 90 °C and 1 kHz.

Sample name	$p \times 10^{-4}$ (C.m⁻².°C⁻¹) at 90°C or T_d	$F_i \times 10^{-10}$ (m.V⁻²) at 1kHz at 90°C or T_d	F_v (m².C) at 1kHz at 90°C or T_d	F_D (x10⁻⁶ Pa^{-1/2}) at 1kHz at 90°C or T_d
A	15.06 at 90°C	5.38 at 90°C	0.13 at 90°C	49.10 at 90°C
B	23.9 at 90°C	8.55 at 90°C	0.19 at 90°C	65.52 at 90°C
C	20.30 at 80°C	7.27 at 80°C	0.13 at 80°C	40.56 at 80°C
D	9.17 at 90°C	3.27 at 90°C	0.05 at 90°C	17.18 at 90°C

The FOMs F_v , and F_D at room and depolarization temperatures with a wide range of frequencies are listed in Tables 4-4, 4-5, 4-6 and 4-7.

In these tables, Sample B illustrates the maximum FOMs F_v , and F_D at both RT and T_d , and at over all the frequency ranges of all the samples. While, Sample D presents the lowest F_v , and F_D values in these temperatures and over the frequency ranges of all samples.

The high F_v , and F_D values in Sample B can be related to its higher p and also to lower dielectric properties (ϵ_r and $\tan\delta$) at room, depolarization temperatures and over a wide range of frequencies.

The F_C values of Samples A to D at RT and at frequency range from 100 Hz to and 1 MHz, were calculated, (Table 4-8). The F_C values reveal strong reliance on the excess in BT content. Generally, the materials suitable for infrared detectors should have a F_C threshold value $\sim 3 \pm 1 \times 10^{-9}$ C. cm⁻². °C⁻¹ [41]. All samples show F_C values lower than the threshold value (Fig. 4-8).

Table 4-4: The FOM, F_V for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at RT and 90 °C or T_d and at frequency 0.1, 10, 100k Hz and 1 MHz.

Sample name	F_V (m².C) at RT			
	0.1kHz	10kHz	100kHz	1MHz
A	0.009	0.010	0.011	0.011
B	0.020	0.024	0.026	0.027
C	0.018	0.022	0.023	0.025
D	0.006	0.006	0.006	0.006

Table 4-5: The FOM, F_V for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at 90 °C or T_d and at frequency 10, 100k Hz and 1 MHz.

Sample name	F_V (m².C) at 90°C or T_d		
	10kHz	100kHz	1MHz
A	0.134	0.145	0.148
B	0.204	0.216	0.221
C	0.140	0.144	0.145
D	0.056	0.057	0.058

Table 4-6: The FOM, F_D for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at RT and at frequency 0.1, 10, 100k Hz and 1 MHz.

Sample name	F_D ($\times 10^{-6} \text{ Pa}^{-1/2}$) at RT			
	0.1kHz	10kHz	100kHz	1MHz
A	2.21	3.45	3.36	2.51
B	8.76	10.12	10.40	7.00
C	7.55	8.79	8.54	6.00
D	0.64	1.78	1.74	1.26

Table 4-7: The FOM, F_D for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at 90 °C or T_d at and at frequency 10, 100k Hz and 1 MHz.

Sample name	F_D ($\times 10^{-6} \text{ Pa}^{-1/2}$) at 90°C or T_d		
	10kHz	100kHz	1MHz
A	48.80	47.61	34.13
B	66.29	65.49	41.85
C	43.13	43.66	31.74
D	18.20	17.44	13.44

However, Rodríguez-Ruiz *et al.*; calculated the F_C value for 0.935Na_{0.5}Bi_{0.5}TiO₃-0.065BaTiO₃ composition at RT and found that the F_C value for this composition is around $1.44 \times 10^{-9} \text{ C. cm}^{-2} \cdot ^\circ\text{C}^{-1}$ [41]. In this study, the F_C values of Samples B and C are higher than those been reported in literature by Rodríguez-Ruiz *et al.*

The high F_C values for Samples B and C can be linked to their higher p values at room temperature.

Table 4-8: The FOM, F_C for the NBT-xBT; A, NBT-0.05BT; B, NBT-0.06BT; C, NBT-0.07BT; and D, NBT-0.08BT at RT and frequency range from 100 Hz to 1 MHz.

Sample name	$F_C \times 10^{-9} \text{ C.cm}^{-2} \cdot ^\circ\text{C}^{-1}$ at RT				
	0.1kHz	1kHz	10kHz	100kHz	1MHz
A	0.44	0.47	0.48	0.49	0.50
B	1.53	1.58	1.63	1.67	1.70
C	1.45	1.54	1.56	1.58	1.56
D	0.33	0.31	0.31	0.32	0.31

4.3 Conclusion

NBT-xBT ($0.05 \leq x \leq 0.08$) ceramics were synthesized by a conventional solid-state route. The pyroelectric properties of these materials were investigated and compared with PZT and some other lead-free ceramics.

The microstructure study using the XRD technique, confirms that the compositions of the Samples B and C ($x = 0.06$ and 0.07) are both at the MPB area, while Samples A and D ($x = 0.05$ and 0.08) are around the MPB region. The lattice parameter values and c/a ratio slightly change with increasing the BT content up to $x = 0.07$, then decreased. The SEM investigation shows the average grain size reduced from 1.85 to 1.52 (μm) with increasing the BT concentration. Moreover, Sample A ($x = 0.05$) presents higher density than all other samples. Both relative permittivity (ϵ_r) and dielectric loss ($\tan\delta$) increase with an increase in BaTiO_3 content.

The T_d was identified by two different methods and decreased from ~ 130 $^\circ\text{C}$ in Sample A ($x = 0.05$) to around 120 $^\circ\text{C}$ in Sample D ($x = 0.08$) with extra Ba^{2+}

content However, Sample C presents the lowest T_d which is around 100 °C according to the dielectric method. The T_d value was identified solely for Sample C (80 °C) according to pyroelectric coefficient method whereas the exact T_d values for Samples A, B and D was not identified by this method.

Sample B has the optimum p , FOMs (F_i , F_v and F_D) at RT and at T_d , and this sample shows higher F_v and F_D values than PZT at RT. In addition, Sample B presents higher p , F_i , F_v and F_D values than NBT-0.07BZT lead-free ceramic material.

This study reveals that the MPB region of NBT-xBT is located at $x=0.06$ and 0.07 BT but the highest improvement of the pyroelectric properties was achieved at $x=0.06$ BT.

4.4 References

1. Chen M., Xu Q., Kim BH., Ahn BK., Ko JH., Kang WJ., et al. Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ piezoelectric ceramics. *Journal of the European Ceramic Society*. 2008; 28: 843–849. Available at: DOI:10.1016/j.jeurceramsoc.2007.08.007
2. Rawat M., Yadav KL., Kumar A., Patel PK., Adhlakha N., Rani J. Structural, dielectric and conductivity properties of Ba^{2+} doped $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramic. *Advanced Materials Letters*. 2012; 3(4): 286–292. Available at: DOI:10.5185/amlett.2012.2322
3. Ranjan R., Dwiwedi A. Structure and dielectric properties of $(\text{Na}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$: $0 \leq x \leq 0.10$. *Solid State Communications*. 2005; 135: 394–399. Available at: DOI:10.1016/j.ssc.2005.03.053
4. Li Q., Wang H., Fan H., Long C., Liu X. Ferroelectric, electromechanical, and dielectric properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ co-doped MnO_2 and La_2O_3 lead-free ceramics. *Journal of Materials Science*. 2013; 49(1): 211–217. Available at: DOI:10.1007/s10853-013-7694-x

5. García JE. Elastic, dielectric and electromechanical properties of (Bi_{0.5}Na_{0.5})TiO₃–BaTiO₃ piezoceramics at the morphotropic phase boundary region. *Journal of Alloys and Compounds*. Elsevier Ltd; 2016; Available at: DOI:10.1016/j.jallcom.2016.08.116
6. Fu P., Xu Z., Chu R., Li W., Zang G., Hao J. Piezoelectric, ferroelectric and dielectric properties of Nd₂O₃-doped (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ lead-free ceramics. *Materials Science and Engineering B: Solid-State Materials for Advanced Technology*. Elsevier B.V.; 2010; 167(3): 161–166. Available at: DOI:10.1016/j.mseb.2010.01.057
7. Anton EM., Jo W., Damjanovic D., Rdel J. Determination of depolarization temperature of (Bi_{1/2}Na_{1/2})TiO₃-based lead-free piezoceramics. *Journal of Applied Physics*. 2011; 110(9): 1–14. Available at: DOI:10.1063/1.3660253
8. Fu P., Xu Z., Chu R., Li W., Zang G., Hao J. Piezoelectric, ferroelectric and dielectric properties of La₂O₃-doped (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ lead-free ceramics. *Materials & Design*. Elsevier Ltd; 2010; 31(2): 796–801. Available at: DOI:10.1016/j.matdes.2009.07.056
9. Martínez FL., Hinojosa J., Doménech G., Fernández-luque FJ., Zapata J., Ruiz R., et al. Dielectric Constant Tunability at Microwave Frequencies and Pyroelectric Behavior. *IEEE transactions on ultrasonics, ferroelectrics, and frequency control*. 2013; 60(8): 1595–1602. Available at: DOI:10.1109/TUFFC.2013.2740.
10. Xu C., Lin D., Kwok KW. Structure, electrical properties and depolarization temperature of (Bi_{0.5}Na_{0.5})TiO₃–BaTiO₃ lead-free piezoelectric ceramics. *Solid State Sciences*. 2008; 10(7): 934–940. Available at: DOI:10.1016/j.solidstatesciences.2007.11.003
11. Xu Q., Huang DP., Chen M., Chen W., Liu HX., Kim BH. Effect of bismuth excess on ferroelectric and piezoelectric properties of a (Na_{0.5}Bi_{0.5})TiO₃–BaTiO₃ composition near the morphotropic phase boundary. *Journal of Alloys and Compounds*. 2009; 471(1–2): 310–316. Available at:

DOI:10.1016/j.jallcom.2008.03.078

12. Hiruma Y., Nagata H., Takenaka T. Formation of Morphotropic Phase Boundary and Electrical Properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--Ba}(\text{Al}_{1/2}\text{Nb}_{1/2})\text{O}_3$ Solid Solution Ceramics. *Japanese Journal of Applied Physics*. 2009; 48(9): 09KC08. Available at: DOI:10.1143/JJAP.48.09KC08
13. Kumari R., Ahlawat N., Agarwal A., Sanghi S., Sindhu M. Structural transformation and investigation of dielectric properties of Ca substituted $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.95}\text{--xBa}_{0.05}\text{Ca}_x\text{TiO}_3$ ceramics. *Journal of Alloys and Compounds*. Elsevier Ltd; 2016; Available at: DOI:10.1016/j.jallcom.2016.11.200
14. Cho J-H., Jeong Y-H., Nam J-H., Yun J-S., Park Y-J. Phase transition and piezoelectric properties of lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--BaTiO}_3$ ceramics. *Ceramics International*. 2014; 40: 8419–8425. Available at: DOI:10.1016/j.ceramint.2014.01.051
15. Le Goupil F., Bennett J., Axelsson AK., Valant M., Berenov A., Bell AJ., et al. Electrocaloric enhancement near the morphotropic phase boundary in lead-free NBT-KBT ceramics. *Applied Physics Letters*. 2015; 107(17): 103–107. Available at: DOI:10.1063/1.4934759
16. Li Z., Yang M., Park JS., Wei SH., Berry JJ., Zhu K. Stabilizing Perovskite Structures by Tuning Tolerance Factor: Formation of Formamidinium and Cesium Lead Iodide Solid-State Alloys. *Chemistry of Materials*. 2016; 28(1): 284–292. Available at: DOI:10.1021/acs.chemmater.5b04107
17. Moure, Carlos OP. Recent advances in perovskites: Processing and properties. *Solid State Chemistry*. 2015; 43: 123–148. Available at: DOI:10.1016/j.progsolidstchem.2015.09.001
18. Yoon MS., Khansur NH., Ur SC. The effect of pre-milling/pre-synthesis process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized $0.94[(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3]\text{--}0.06[\text{Ba}(1+x)\text{TiO}_3]$. *Ceramics International*. Elsevier Ltd and Techna Group S.r.l.; 2010; 36(4):

1265–1275. Available at: DOI:10.1016/j.ceramint.2010.01.011

19. Hiruma Y., Yoshii K., Nagata H., Takenaka T. Investigation of Phase Transition Temperatures on $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 Lead-free Piezoelectric Ceramics by Electrical Measurements. *Ferroelectrics*. 2007; 346(773557621): 114–119. Available at: DOI:10.1080/00150190601180471
20. Hiruma Y., Nagata H., Takenaka T., Member S. Phase-Transition Temperatures and Piezoelectric Properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -. 2007; 54(12): 2493–2499.
21. Kang W-S., Lee S-K., Koh J-H. AC conductivity and dielectric properties of $(\text{Bi},\text{Na})\text{TiO}_3$ - BaTiO_3 lead free ceramics. *Ceramics International*. 2015; 41(5): 6925–6932. Available at: DOI:10.1016/j.ceramint.2015.01.147
22. Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*. 1976; 32(5): 751–767. Available at: DOI:10.1107/S0567739476001551
23. Sapper E., Schaab S., Jo W., Granzow T., Rödel J. Influence of electric fields on the depolarization temperature of Mn-doped $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ - $x\text{BaTiO}_3$. *Journal of Applied Physics*. 2012; 111(1): 14105. Available at: DOI:10.1063/1.3674275
24. Cheng SY., Shieh J., Lu HY., Shen CY., Tang YC., Ho NJ. Structure analysis of bismuth sodium titanate-based A-site relaxor ferroelectrics by electron diffraction. *Journal of the European Ceramic Society*. Elsevier Ltd; 2013; 33(11): 2141–2153. Available at: DOI:10.1016/j.jeurceramsoc.2013.03.020
25. Guggilla P., Batra AK., Currie JR., Aggarwal MD., Alim MA., Lal RB. Pyroelectric ceramics for infrared detection applications. *Materials Letters*. 2006; 60(16): 1937–1942. Available at: DOI:10.1016/j.matlet.2005.05.086
26. Li M., Zhang H., Cook SN., Li L., Kilner JA., Reaney IM., et al. Dramatic

- influence of A-site nonstoichiometry on the electrical conductivity and conduction mechanisms in the perovskite oxide $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Chemistry of Materials*. 2015; 27(2): 629–634. Available at: DOI:10.1021/cm504475k
27. Guo Y., Gu M., Luo H. Antiferroelectric phase and pyroelectric response in $(\text{Na}_{1-z}\text{Bi}_z)\text{Ti}_{1-x}\text{O}_3(1-x)\text{-xBaTi}_3$ ceramics. *Journal of the American Ceramic Society*. 2011; 94(5): 1350–1353. Available at: DOI:10.1111/j.1551-2916.2011.04509.x
 28. Jo W., Daniels J., Damjanovic D., Kleemann W., Rodel J. Two-stage processes of electrically induced-ferroelectric to relaxor transition in $0.94(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-}0.06\text{BaTiO}_3$. *Applied Physics Letters*. 2013; 102(19): 0–4. Available at: DOI:10.1063/1.4805360
 29. Levanyuk AP. Phase transitions and domain structures in thin ferroelectric films. *Phase Transitions*. Taylor & Francis; 2015; 88(7): 682–691. Available at: DOI:10.1080/01411594.2014.986732
 30. Lichtensteiger C., Fernandez-Pena S., Weymann C., Zubko P., Triscone JM. Tuning of the depolarization field and nanodomain structure in ferroelectric thin films. *Nano Letters*. 2014; 14(8): 4205–4211. Available at: DOI:10.1021/nl404734z
 31. Okatan MB., Mantese J V., Alpay SP. Effect of space charge on the polarization hysteresis characteristics of monolithic and compositionally graded ferroelectrics. *Acta Materialia*. Acta Materialia Inc.; 2010; 58(1): 39–48. Available at: DOI:10.1016/j.actamat.2009.08.055
 32. Zhang S., Kouna AB., Aulbach E., Jo W., Granzow T., Ehrenberg H., et al. Lead-free piezoceramics with giant strain in the system $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-BaTiO}_3\text{-K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$. II. Temperature dependent properties. *Journal of Applied Physics*. 2008; 103(3): 34108. Available at: DOI:10.1063/1.2838476
 33. Abo, Jiro Kobune M., Nishimura T., Yazaw T., Nakai Y. Effects of

- manganese addition on pyroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)_{0.94}(\text{BaTiO}_3)_{0.06}$ ceramics. *Integrated Ferroelectrics*. 2006; 80(1): 87–95. Available at: DOI:10.1080/10584580600656502
34. Anem S., Rao KS., Rao KH. Investigation of lanthanum substitution in lead-free BNBT ceramics for transducer applications. *Ceramics International*. Elsevier; 2016; Available at: DOI:10.1016/j.ceramint.2016.06.173
 35. Wang X., Tang X., Chan H. Electromechanical and ferroelectric properties of $(\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3)_{1-x}(\text{Bi}_{1/2}\text{K}_{1/2}\text{TiO}_3)_x$ lead-free piezoelectric ceramics. *Applied physics letters*. 2004; 85(1): 91. Available at: DOI:10.1063/1.1767592
 36. Yao Z., Chu R., Xu Z., Hao J., Li W., Li G. Processing and enhanced electrical properties of $\text{Sr}_{1-x}(\text{K}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_2\text{Nb}_2\text{O}_9$ lead-free piezoelectric ceramics. *Ceramics International*. Elsevier; 2016; 42(9): 10619–10623. Available at: DOI:10.1016/j.ceramint.2016.03.156
 37. Li XJ., Xi ZZ., Long W., Fang PY. Synthesis of antiferroelectric $(\text{Bi}_{0.534}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ ceramics with high phase transition temperature and broad temperature range by a solid-state reaction method. *Chinese Science Bulletin*. 2013; 58(23): 2893–2897. Available at: DOI:10.1007/s11434-013-5972-2
 38. Li Q., Wang J., Ma L., Fan H., Li Z. Large electrocaloric effect in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ferroelectric ceramics by La_2O_3 addition. *Materials Research Bulletin*. Elsevier Ltd; 2016; 74: 57–61. Available at: DOI:10.1016/j.materresbull.2015.10.010
 39. Lau ST., Cheng CH., Choy SH., Lin DM., Kwok KW., Chan HLW. Lead-free ceramics for pyroelectric applications. *Journal of Applied Physics*. 2008; 103(10): 10–13. Available at: DOI:10.1063/1.2927252
 40. Byer RL., Roundy CB. Pyroelectric coefficient direct measurement technique and application to a nsec response time detector. *IEEE Transactions on Sonics and Ultrasonics*. 1972; 19(2): 333–338. Available

at: DOI:10.1109/T-SU.1972.29679

41. Rodríguez-Ruiz R., González-Ballesteros R., Flores-Cuautle a., Suaste-Gómez E. Determination of the Pyroelectric Coefficient for $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.935}\text{Ba}_{0.065}\text{TiO}_3$ Piezoelectric Ceramics. *Ferroelectrics*. 2008; 368(1): 216–223. Available at: DOI:10.1080/00150190802368537
42. Guo F., Yang B., Zhang S., Wu F., Liu D., Hu P., et al. Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition. *Applied Physics Letters*. 2013; 103(2013): 182906. Available at: DOI:10.1063/1.4828675

5 Modifying the A-site of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -0.06 BaTiO_3 by changing its elements contents.

This chapter has been divided into two parts:

- A. Changing the barium content in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -0.06 $\text{Ba}_{1+x}\text{TiO}_3$.
- B. Changing the Na, Bi, and Ba contents of the $\text{N}_x\text{B}_y\text{T}$ -0.06 B_zT .

Abstract

The aims of this chapter are to improve the pyroelectric properties of the NBT-0.06BT ceramics at both room and depolarization temperature, by forming nonstoichiometry compositions through modifying the concentration of the barium (Ba), the sodium and bismuth (Na and Bi) or all the elements (Ba, Na, and Bi) in the A-site of the material. In addition to, control and bring the depolarization temperature down to around room temperature of the new compositions.

5.1 The effects of changing the Ba^{2+} content in the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -0.06 $\text{Ba}_{1+x}\text{TiO}_3$.

The text in this part of chapter 5 is based on a paper published in the Journal of Materials Science: Materials in Electronics. Please see publication 1 in the publication list.

5.1.1 Experimental

All the ceramics samples were synthesised using a conventional solid-state technique employing the method described in Chapter 2, Fig. 2-2, and the raw materials used in this project were powders as same as in the previous chapters.

The amounts of powders were calculated according to the chemical formula of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -0.06 $\text{Ba}_{1+x}\text{TiO}_3$ with $x = 0.00, 0.01, 0.02, \text{ and } 0.03$. Sample compositions are listed in Table 5-1.

5.1.2 Results and discussion

5.1.2.1 Effects of the extra barium on microstructure

Fig. 5-1 shows the XRD patterns of 0.94NBT-0.06B_{1+x}T (NBT-0.06B_{1+x}T) ceramic powders calcined at 850 °C for 3 hrs. Fig. 5-1(a) showed that all ceramic samples have a pure perovskite structure (ABO₃) and no second phase was observed. The absence of other phase indicates that NBT-0.06B_{1+x}T lattices have either absorbed the extra amount of Barium (Ba²⁺) and formed the NBT-0.06B_{1+x}T ceramic solid solutions [1,2] or the amount of the second phase is too small to be tested by XRD. Fig. 5-1 shows, in all the samples, a splitting in the peak [111] into [003] and [021] at 39.0° - 41.0°, indicating the existence of rhombohedral phase (Fig. 5-1(b)) and a splitting in the peak [200] into [200] and [002] at 45.0° - 48.0°, indicating the existence of tetragonal phase (Fig. 5-1(c)). The coexistence of both rhombohedral and tetragonal phases in NBT-0.06B_{1+x}T ceramics proves that the sample structures are at morphotropic phase boundary (MPB), which was consistent with what was reported in literature [3-5]. Fig. 5-1(c) shows that the splitting in peak [200] became quite pronounced for the sample at x = 0.02 as shown in Fig. 5-1 (b). It seems that the composition of NBT-0.06B_{1+x}Ti with x= 0 – 0.03 is still within MPB.

The measurement of the lattice parameters (a, b and c) reveals that the extra Ba²⁺ content has slightly changed a, b and c from a = b = 5.488 Å, c = 13.505 Å to a = b = 5.493 Å, c = 13.505 Å for Samples A to D respectively (Table 5-1). Sample C presents the biggest lattice parameters (a = b = 5.494 Å, c = 13.505 Å).

Comparing the ionic radii of the A-site cations of Na⁺ (1.39 Å), Bi³⁺ (1.31 Å) and Ba²⁺ (1.61 Å) (coordination No. 12) according to Hume-Rothery rules, Ba²⁺ in NBT-0.06B_{1+x}Ti could replace Na⁺ but seems to be difficult to replace Bi³⁺ because the radius difference between Bi³⁺ and Ba²⁺ is more than 15% [5].

Yoon *et al.* reported that the c/a ratio increased with adding more extra Ba²⁺ content and reached the maximum at x=0.02 [5]. Thus, the increase in Ba²⁺ content would lead to the improvement of the tetragonality of BT in NBT-0.06B_{1+x}T by compensating for the loss in Ba during the sintering stage.

However, any extra Ba^{2+} content more than $x=0.02$ would not go to increase the c/a ratio because the c/a ratio was saturated at 0.02, and therefore consequently the extra Ba would precipitate into a secondary phase [5], but in this study the second phase was not identified up to $x = 0.03$, probably due to the amount of the secondary phase being too small to be tested by XRD.

Fig. 5-2 shows the surface morphology of the NBT-0.06 B_{1+x} T ceramics by *SEM*. The average grain size was reduced from 1.7 μm at $x=0.00$ to 1.61, 1.31, 1.52 at $x=0.01$, 0.02 and 0.03, respectively. Increasing Ba^{2+} led to a sharp reduction in the grain size and reached the lowest value at $x=0.02$. In general, Ba^{2+} behaves as an inhibitor of the grain growth in NBT system. In lead-based ceramics, such as PZT and PLZT (La-containing PZT), similar effect was also observed when lead was substituted with barium [1,5,6]. All the samples showed a density $94.63 \pm 0.333 \text{ g/cm}^3$ as shown in Table 5-1. Density measurements revealed that Sample A, B and D at $x=0.0$, 0.01 and 0.03 have a similar density value; however, Sample C, at $x=0.02$ has a higher density.

5.1.2.2 Effects of the extra barium on dielectric properties

Fig. 5-3 shows the temperature dependence of the dielectric properties of poled NBT-0.06 B_{1+x} T from RT up to 150 °C at different frequencies (1, 10 and 100kHz). The relative dielectric permittivity (ϵ_r) and the dielectric loss tangent ($\tan\delta$) show a strong dependence upon Ba content and temperature. The ϵ_r increased with temperature for all samples; however, the ϵ_r showed increasing at $x=0.01$, and 0.02 at room temperature and this can be related to extra Ba^{2+} . The extra Ba at $x=0.01$ compensated the deficiency in Ba in BT side and rectified the tetragonality in NBT.

The excess Ba up to 0.02 can then replace cations in the A-site of the NBT-0.06 B_{1+x} T perovskite structure, so Ba^{2+} will replace Na^+ according to the radius matching rules and the donor behaviour of Ba will make the domain wall motion easier resulting in the increase of the dielectric properties of NBT-0.06 $\text{B}_{1+0.02}$ T [7].

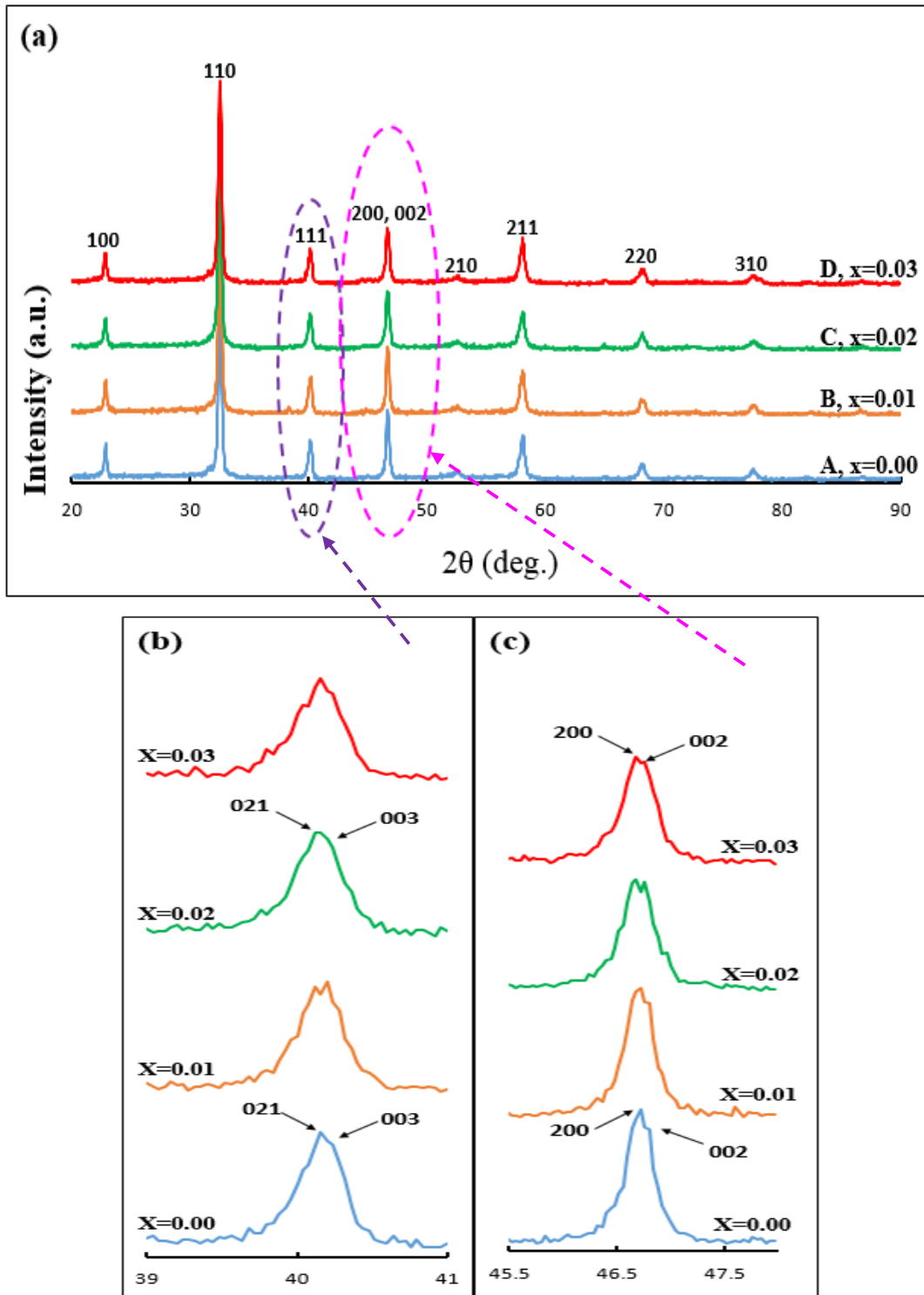


Figure 5-1: XRD patterns of NBT-0.06B_(x+1)TiO₃ ceramics where, (a) $x=0.00, 0.01, 0.02$, and 0.03 ; (b) expansion at 2θ from 39.0° to 41.0° and (c) expansion at 2θ from 45.0° to 48.0°

Table 5-1: The NBT-0.06B_{1+x}T, composition (sample) depending on the extra concentrations of Ba²⁺ from A, x=0.00 to D, x=0.03; samples density (gm.cm⁻³), comparing with the theoretical density (%) which is (p=6 gm.cm⁻³), and the relative permittivity (ϵ_r), dielectric loss (tan δ) both at 1kHz and RT, the depolarization temperature (T_d) value 0.0≤x≤0.03.

Composition (Sample name) 0.94NBT-0.06B _{1+x} T	Lattice parameters (Å)		Density(ρ) gm.cm ⁻³	Compare with theoretical density%	Depolarization temperature(T_d) (°C)	Relative permittivity (ϵ_r) at RT	Dielectric loss (tan δ) at RT
	a=b	c					
NBT-0.06BT (A, x=0.0)	5.488	13.505	5.697	94.95	125	1178	0.042
NBT-0.06B _{1+0.01} T (B, x=0.01)	5.487	13.437	5.661	94.35	85	1468	0.046
NBT-0.06B _{1+0.02} T (C, x=0.02)	5.494	13.505	5.718	95.55	85	1472	0.045
NBT-0.06B _{1+0.03} T (D, x=0.03)	5.493	13.505	5.678	94.63	115	1266	0.040

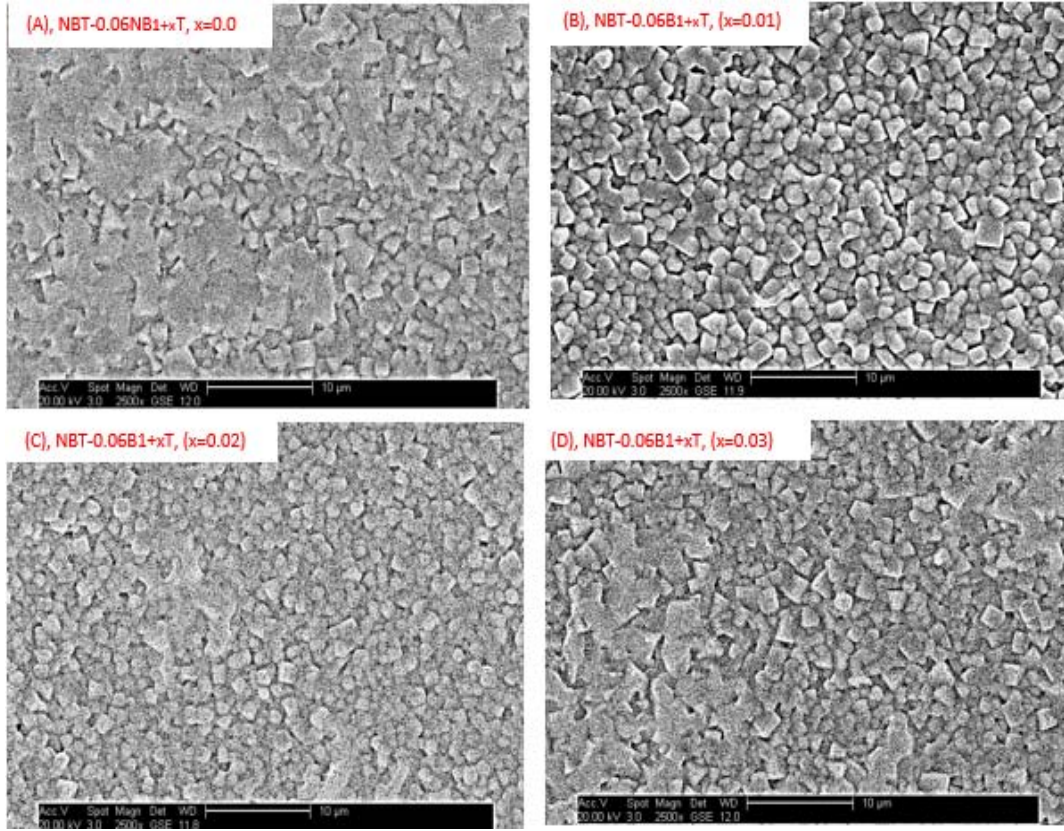


Figure 5-2: The SEM surface morphology, NBT-0.06B_{1+x}T where, (a) $x=0.00$; (b) $x=0.01$; (c) $x=0.02$; (d) $x=0.03$.

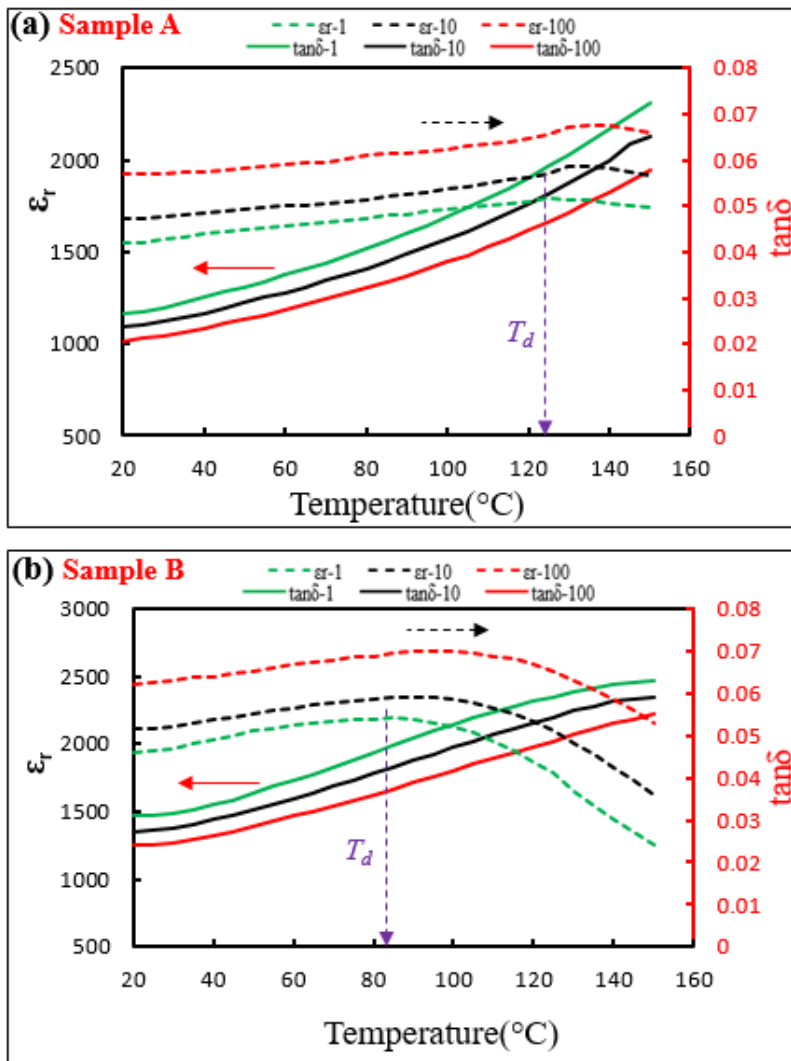
The ϵ_r values at $x=0.01$ and 0.02 were close to 1500 for both compositions whereas, the ϵ_r values at $x = 0.0$ and 0.03 at RT were near 1225 . However, at T_d and 150°C , the ϵ_r for the samples at $x = 0.01$ and 0.02 increased to around 2000 and 2150 (T_d), and above for both compositions 2500 (150°C) respectively. However, the ϵ_r values for the samples at $x = 0.00$ and 0.03 were relatively low which are around 2250 .

5.1.2.3 Effects of extra barium on depolarization temperature

Depolarization temperature (T_d) is a parameter that has not clearly been defined [7], but the European standard on piezoelectric properties has defined it as the reduction of remnant polarization because of temperature and other influences [8]. However, there are other definitions of T_d such as the steep reduction of

remnant polarization [9], or the phase transition temperature from ferroelectric (*FE*) to anti-ferroelectric (*AFE*) or to relaxor anti-ferroelectric or to relaxor [10-14].

In this study, T_d was identified from the measurement of the dielectric loss ($\tan\delta$) vs. temperature. Fig. 5-3 shows that the T_d of the NBT-0.06B_{1+0.00}T was at ~125 °C and decreased to ~85 °C, at x = 0.01 and 0.02, and then rises to ~115 °C, at x = 0.03. The reduction in T_d is probably due to the formation of A-site vacancies with increasing Ba content in NBT-0.06B_{1+x}T structures.



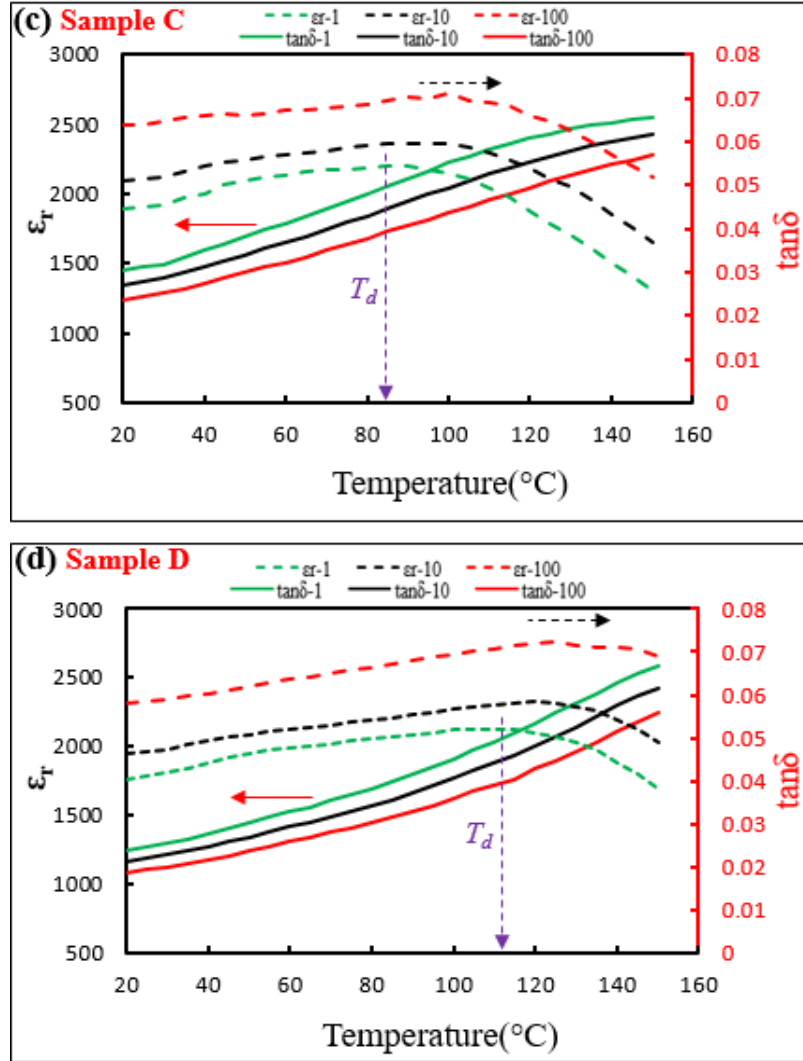


Figure 5-3:The change of the relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) with changing temperature (°C) from RT up to 150°C, for the NBT-0.06B_{1+x}T where 0.0 ≤ x ≤ 0.03 from (a) to (d) in three different frequencies (1, 10 and 100) kHz. The identified of the depolarization temperature (T_d) from the dielectric loss lines at 1kHz.

In ferroelectric NBT-BT perovskite structure, the ferroelectric domain stability is affected by the coupling between ferroelectric (BO₆) and A-site cations, and the stability of the ferroelectric domains will be reduced when vacancies are generated between the octahedral (BO₆) ferroelectric and A-site cations. In this study, Ba²⁺ content at x=0.01-0.02 created A-site vacancies so the stability of the

ferroelectric domain reduced as a result inducing the phase change from ferroelectric (*FE*) to relaxor anti-ferroelectric (*relaxor AFE*) and fast reduction by 40°C in depolarization temperature (T_d) [2,4,8]. With a further increase of Ba^{2+} to $x=0.03$, which is more than Ba^{2+} saturation content ($x=0.02$), the T_d was decreased by only about 10°C, because there were less vacancies in A-site due to minimal (Ba^{2+}/Na^+) replacement and more ferroelectric domain wall stability [4,15,16]. The value of the T_d of NBT-0.06BT in this work is close to that reported in the literature (~123°C) but the depolarization temperature of the NBT-0.06B_{1+x}T, ($0.01 \leq x \leq 0.02$) is lower than 123 °C [17]. Table 5-1 lists the values of relative dielectric permittivity (ϵ_r) and dielectric loss ($\tan\delta$) at RT and depolarization temperatures (T_d) at 1 kHz achieved in this work.

5.1.2.4 Effects of extra barium on pyroelectric properties

The calculation of the figure of merits (*FOMs*) is based on the values of pyroelectric coefficient (p), relative dielectric permittivity (ϵ_r), the dielectric loss tangent ($\tan\delta$) and the specific heat (C_v). There are several numbers of *FOMs* which are more appropriate to certain pyroelectric materials applications [17,18] and are derived from these application requirements.

Pyroelectric coefficient (p) and the *FOMs* were analysed by using the following equations 1-11 and 1—15 to 1-18 in chapter 1 [19-22].

The pyroelectric current of NBT-0.06B_{1+x}T, ($0.00 \leq x \leq 0.03$) ceramics was measured from RT to T_d or 90 °C that is our equipment upper limit.

Table 5-2 shows the pyroelectric coefficient(p) and the figures of merit (*FOMs*) values of the NBT-0.06B_{1+x}T, ($0.00 \leq x \leq 0.03$) at RT, T_d or 90 °C. The p values varied with the Ba^{2+} content and increased from 2.9×10^{-4} (C.m⁻². °C⁻¹) to 3.54×10^{-4} (C.m⁻².°C⁻¹) when x increased from 0.00 to 0.02 at RT. All the samples showed a great increase in p when the measurement temperature increased from 20 °C to T_d or 90 °C. This great increase in p at T_d or 90 °C was caused by the increase of I_p induced by the reorientation of ferroelectric domain and phase transition in MPB. When the temperature rises from RT to T_d , the phase transition from ferroelectric (*FR*) to relaxor antiferroelectric (relaxor *AFR*) started, and thus a sharp change in polarization resulted in a significant increase in p at T_d [20].

The T_d for Sample B ($x=0.01$) and C ($x=0.02$) is below 90°C and for Sample A ($x=0.00$) and D ($x=0.03$) above 90°C , which explained why Sample B and C had a greater increase in p than Sample A and D. According to Anton *et al.* [9], the T_d determination depends on the highest value of the dielectric loss tangent, which may consistently generate higher T_d than other methods such as the thermally stimulated depolarization current; therefore, the T_d for Sample A and D might actually be less than $\sim 125^\circ\text{C}$ and $\sim 110^\circ\text{C}$, as a result that the observed increase in p for Sample A and D could be related to the beginning of the phase transition in these samples.

The increase of Ba content up to $x = 0.02$ reduces the distortion in the perovskite structure due to the replacement of Na^+ ($1.39 \text{ \AA}$) by Ba^{2+} ($1.61 \text{ \AA}$), which can shift the T_d to lower temperature [21-23]. Further increase in Ba content to $x = 0.03$ would lead to the appearance of a secondary phase or the replacement of Na^+ . Thus, the depolarization temperature at $x = 0.03$ shows a slight increase than that at $x = 0.01 - 0.02$ [4,21,23]. Table 5-2 also lists the p value ($4.14 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$) of a typical PZT ceramic measured at RT as a reference. The prepared NBT-0.06B_{1+x}T at $x = 0.01 - 0.03$ in this research show the comparable pyroelectric coefficients ($3.30 - 3.5 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$) [16,18,19].

The values of F_i , F_v , and F_D of the NBT-0.06B_{1+x}T samples ($0.00 \leq x \leq 0.03$) at RT, T_d or 90°C are also shown in Table 5-2. The F_i value increased from $1.04 \times 10^{-10}(\text{m/V})$ ($x = 0.00$) to $1.24 \times 10^{-10}(\text{m/V})$ ($x = 0.02$) at RT and from $1.24 \times 10^{-10}(\text{m/V})$ ($x = 0.02$) to $260 \times 10^{-10}(\text{m/V})$ ($x = 0.02$) at T_d (85°C). The F_i of Sample C ($x = 0.02$) at RT is very close to that for PZT ($1.415 \times 10^{-10}(\text{m/V})$) [24]. However, at T_d (85°C) this sample ($x = 0.02$) shows a much higher p value ($260 \times 10^{-10}(\text{m/V})$) than the best value ($\sim 7.33 \times 10^{-10}(\text{m/V})$) at T_d (50°C) reported by Gue *et al.* [25].

The F_v values at RT and T_d or 90°C increased from $0.99 \times 10^{-2}(\text{m}^2.\text{C}^{-1})$ at $x=0.00$ to $1.05 \times 10^{-2}(\text{m}^2.\text{C}^{-1})$ at $x=0.03$. All these F_v values exceed the value for PZT [19,22,23,25]. F_v values increased at T_d from $0.95 \times 10^{-2} \text{ m}^2/\text{C}$ to $164 \times 10^{-2} \text{ m}^2/\text{C}$ for Sample C ($x = 0.02$).

The values of F_D at RT, T_d or 90°C are shown in Table 5-2. The F_D values increased with extra Ba^{2+} content at RT from $8.6 \times 10^{-6} \text{ Pa}^{-1/2}$ ($x = 0.00$) to 9.2×10^{-6}

$10^{-6} \text{ Pa}^{-1/2}$ ($x=0.03$). Giant values for F_D achieved at T_d for Samples B and C were 674 and 915($\times 10^{-6} \text{ Pa}^{-1/2}$) respectively. F_D for PZT [19,22,23,25] at RT is $9.01 \times 10^{-6} \text{ Pa}^{-1/2}$ and Sample D showed a higher F_D value than PZT (Table 5-2).

Table 5-2 Comparing the pyroelectric coefficients and the figures of merits (F_i , F_v , and F_D) of the NBT-0.06B_{1+x}T ($0.0 \leq x \leq 0.03$) ceramics at frequency 1kHz, at two different temperature RT, T_d or 90 °C with the other lead-free compositions and PZT.

Composition	$p \times 10^{-4}$ $\text{C.m}^{-2}.\text{°C}^{-1}$ at RT or T_d	$F_i \times 10^{-10}$ m.V^{-1}	$F_v \times 10^{-2} \text{m}^2.\text{C}^{-1}$ at f. 1kHz	$F_D \times 10^{-6} \text{Pa}^{-1/2}$ at f. 1kHz
NBT-0.06BT	2.90 at RT	1.04 at RT	0.99 at RT	8.6 at RT
NBT-0.06BT	55.3 at 90°C	19.7 at 90°C	14 at 90°C	75.6 at 90°C
NBT-0.06Ba _{1.01} T	3.47 at RT	1.238 at RT	0.95 at RT	7.7 at RT
NBT-0.06Ba _{1.01} T	601 at 85°C	215 at 85°C	115 at 90°C	674 at 90°C
NBT-0.06Ba _{1.02} T	3.54 at RT	1.244 at RT	0.95 at RT	8.3 at RT
NBT-0.06Ba _{1.02} T	741 at 85°C	260 at 85°C	164 at 85°C	915 at 85°C
NBT-0.06Ba _{1.03} T	3.30 at RT	1.177 at RT	1.05 at RT	9.1 at RT
NBT-0.06Ba _{1.03} T	73.1 at 90°C	26.12 at 90°C	15 at 90°C	83.9 at 90°C

PZT	4.14 at <i>RT</i>	1.415 at <i>RT</i>	0.8 at <i>RT</i>	9.01
NBT-0.07BZT	5.7 at <i>RT</i>	2.03 at <i>RT</i>	2.18 at <i>RT</i>	10.5
NBT-0.07BZT	20.0 at 50°C	7.33 at 50°C	6.60 at 50°C	33.6 at 50°C
NBT-0.07BZT	221 at 87°C	-	-	-
BNKBT	3.25 at <i>RT</i>	1.95 at <i>RT</i>	2.6 at <i>RT</i>	13.43
KNLNTS	1.9 at <i>RT</i>	0.931 at <i>RT</i>	0.7 at <i>RT</i>	11.5

5.1.3 Conclusion

The NBT-0.06B_{1+x}T ceramics with extra Ba content were prepared by using conventional solid-state synthesis route. The microstructure, dielectric, depolarization temperature and pyroelectric properties of these ceramics were dependent upon the Ba²⁺ content. The depolarization temperature shifted to around 85°C with increasing the Ba²⁺ content up to x = 0.02. The pyroelectric coefficient and figures of merits (F_i , F_v and F_D) all increase at RT when Ba²⁺ content increases to x = 0.02. The giant pyroelectric coefficient, 741×10^{-4} (C.m⁻². °C⁻¹), was obtained at T_d when Ba²⁺ content increases to x = 0.02. The results for NBT-0.06B_{1+x}T obtained in this study indicate that NBT-0.06B_{1+x}T are promising candidates for pyroelectric applications in a wide temperature range.

5.1.4 References

1. Xu C., Lin D., Kwok KW. Structure, electrical properties and depolarization temperature of (Bi_{0.5}Na_{0.5})TiO₃–BaTiO₃ lead-free piezoelectric ceramics. Solid State Sciences. 2008; 10(7): 934–940. Available at: DOI:10.1016/j.solidstatesciences.2007.11.003

2. Rawat M., Yadav KL., Kumar A., Patel PK., Adhlakha N., Rani J. Structural, dielectric and conductivity properties of Ba²⁺ doped (Bi_{0.5}Na_{0.5})TiO₃ ceramic. *Advanced Materials Letters*. 2012; 3(4): 286–292. Available at: DOI:10.5185/amlett.2012.2322
3. Chen M., Xu Q., Kim BH., Ahn BK., Ko JH., Kang WJ., et al. Structure and electrical properties of (Na_{0.5}Bi_{0.5})_{1-x}Ba_xTiO₃ piezoelectric ceramics. *Journal of the European Ceramic Society*. 2008; 28: 843–849. Available at: DOI:10.1016/j.jeurceramsoc.2007.08.007
4. Li Q., Wang J., Ma L., Fan H., Li Z. Large electrocaloric effect in (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ lead-free ferroelectric ceramics by La₂O₃ addition. *Materials Research Bulletin*. Elsevier Ltd; 2016; 74: 57–61. Available at: DOI:10.1016/j.materresbull.2015.10.010
5. Yoon MS., Khansur NH., Ur SC. The effect of pre-milling/pre-synthesis process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized 0.94[(Bi_{0.5}Na_{0.5})TiO₃]-0.06[Ba(1+x)TiO₃]. *Ceramics International*. Elsevier Ltd and Techna Group S.r.l.; 2010; 36(4): 1265–1275. Available at: DOI:10.1016/j.ceramint.2010.01.011
6. Hiruma Y., Yoshii K., Nagata H., Takenaka T. Investigation of Phase Transition Temperatures on (Bi_{1/2}Na_{1/2})TiO₃-(Bi_{1/2}K_{1/2})TiO₃ and (Bi_{1/2}Na_{1/2})TiO₃-BaTiO₃ Lead-free Piezoelectric Ceramics by Electrical Measurements. *Ferroelectrics*. 2007; 346(773557621): 114–119. Available at: DOI:10.1080/00150190601180471
7. Cho J-H., Jeong Y-H., Nam J-H., Yun J-S., Park Y-J. Phase transition and piezoelectric properties of lead-free (Bi_{1/2}Na_{1/2})TiO₃-BaTiO₃ ceramics. *Ceramics International*. 2014; 40: 8419–8425. Available at: DOI:10.1016/j.ceramint.2014.01.051
8. Ranjan R., Dwiwedi A. Structure and dielectric properties of (Na_{0.5}Bi_{0.5})_{1-x}Ba_xTiO₃: 0 ≤ x ≤ 0.10. *Solid State Communications*. 2005; 135: 394–399. Available at: DOI:10.1016/j.ssc.2005.03.053

9. Anton EM., Jo W., Damjanovic D., Rdel J. Determination of depolarization temperature of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based lead-free piezoceramics. *Journal of Applied Physics*. 2011; 110(9): 1–14. Available at: DOI:10.1063/1.3660253
10. Guo Y., Gu M., Luo H. Antiferroelectric phase and pyroelectric response in $(\text{Na}_{1-x}\text{Bi}_x)\text{Ti}_{1-x}\text{O}_3$ - $x\text{BaTi}_3$ ceramics. *Journal of the American Ceramic Society*. 2011; 94(5): 1350–1353. Available at: DOI:10.1111/j.1551-2916.2011.04509.x
11. Sapper E., Schaab S., Jo W., Granzow T., Rödel J. Influence of electric fields on the depolarization temperature of Mn-doped $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ - $x\text{BaTiO}_3$. *Journal of Applied Physics*. 2012; 111(1): 14105. Available at: DOI:10.1063/1.3674275
12. Zhang S., Kouna AB., Aulbach E., Jo W., Granzow T., Ehrenberg H., et al. Lead-free piezoceramics with giant strain in the system $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - BaTiO_3 - $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$. II. Temperature dependent properties. *Journal of Applied Physics*. 2008; 103(3): 34108. Available at: DOI:10.1063/1.2838476
13. Jo W., Daniels JE., Jones JL., Tan X., Thomas P a., Damjanovic D., et al. Evolving morphotropic phase boundary in lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 piezoceramics. *Journal of Applied Physics*. 2011; 109(1): 14110. Available at: DOI:10.1063/1.3530737
14. Jo W., Daniels J., Damjanovic D., Kleemann W., Rodel J. Two-stage processes of electrically induced-ferroelectric to relaxor transition in $0.94(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - 0.06BaTiO_3 . *Applied Physics Letters*. 2013; 102(19): 0–4. Available at: DOI:10.1063/1.4805360
15. Ma X., Xue L., Wan L., Yin S., Zhou Q., Yan Y. Synthesis, sintering, and characterization of BNT perovskite powders prepared by the solution combustion method. *Ceramics International*. Elsevier; 2013; 39(7): 8147–8152. Available at: DOI:10.1016/j.ceramint.2013.03.088

16. Li XJ., Xi ZZ., Long W., Fang PY. Synthesis of antiferroelectric $(\text{Bi}_{0.534}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ ceramics with high phase transition temperature and broad temperature range by a solid-state reaction method. *Chinese Science Bulletin*. 2013; 58(23): 2893–2897. Available at: DOI:10.1007/s11434-013-5972-2
17. Xu Q., Huang DP., Chen M., Chen W., Liu HX., Kim BH. Effect of bismuth excess on ferroelectric and piezoelectric properties of a $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ - BaTiO_3 composition near the morphotropic phase boundary. *Journal of Alloys and Compounds*. 2009; 471(1–2): 310–316. Available at: DOI:10.1016/j.jallcom.2008.03.078
18. Patel S., Chauhan A., Kundu S., Madhar NA., Llahi B., Vaish R., et al. Tuning of dielectric, pyroelectric and ferroelectric properties of $0.715\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - 0.065BaTiO_3 - 0.22SrTiO_3 ceramic by internal clamping. *AIP Advances*. 2015; 5(8): 87145. Available at: DOI:10.1063/1.4929328
19. Lau ST., Cheng CH., Choy SH., Lin DM., Kwok KW., Chan HLW. Lead-free ceramics for pyroelectric applications. *Journal of Applied Physics*. 2008; 103(10): 10–13. Available at: DOI:10.1063/1.2927252
20. Guo F., Yang B., Zhang S., Wu F., Liu D., Hu P., et al. Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition. *Applied Physics Letters*. 2013; 103(2013): 182906. Available at: DOI:10.1063/1.4828675
21. Shannigrahi SR., Tay FEH., Yao K., Choudhary RNP. Effect of rare earth (La, Nd, Sm, Eu, Gd, Dy, Er and Yb) ion substitutions on the microstructural and electrical properties of sol-gel grown PZT ceramics. *Journal of the European Ceramic Society*. 2004; 24(1): 163–170. Available at: DOI:10.1016/S0955-2219(03)00316-9
22. Abo, Jiro Kobune M., Nishimura T., Yazaw T., Nakai Y. Effects of manganese addition on pyroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)$

- 0.94 (BaTiO₃)_{0.06} ceramics. *Integrated Ferroelectrics*. 2006; 80(1): 87–95. Available at: DOI:10.1080/10584580600656502
23. Zhu YZ., Lin SP., Zheng Y., Ma DC., Wang B. Improvement of pyroelectric figures of merit in zirconia-doped congruent lithium niobate single crystals. *Journal of Materials Science*. 2016; 51(6): 3155–3161. Available at: DOI:10.1007/s10853-015-9625-5
 24. Wang X., Tang X., Chan H. Electromechanical and ferroelectric properties of (Bi^{1/2}Na^{1/2})TiO₃–(Bi^{1/2}K^{1/2})TiO₃–BaTiO₃ lead-free piezoelectric ceramics. *Applied physics letters*. 2004; 85(1): 91. Available at: DOI:10.1063/1.1767592
 25. Guo F., Yang B., Zhang S., Wu F., Liu D., Hu P., et al. Enhanced pyroelectric property in (1–x)(Bi_{0.5}Na_{0.5})TiO₃–xBa(Zr_{0.055}Ti_{0.945})O₃: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition. *Applied Physics Letters*. 2013; 103(18): 182906. Available at: DOI:10.1063/1.4828675

5.2 Vary the $\text{Na}_{(x)}$, $\text{Bi}_{(y)}$, and $\text{Ba}_{(z)}$ contents of the $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$

The text of this part is established on a paper published in the Journal of Materials Science: Please see publication 2 in the publication list.

5.2.1 Experimental

A solid-state synthesis technique was selected to prepare the stoichiometry 0.94NBT-0.06BT (NBT-0.06BT) and nonstoichiometry 0.94 $\text{Na}_x\text{Bi}_y\text{TiO}_3\text{-}0.06\text{Ba}_z\text{TiO}_3$ ($\text{Na}_x\text{Bi}_y\text{T-}0.06\text{Ba}_z\text{T}$) compositions. The reagents used in this project were same as in the former chapters.

The amounts of powders were calculated according to the chemical formula of 0.94 $\text{Na}_x\text{Bi}_y\text{TiO}_3\text{-}0.06\text{Ba}_z\text{TiO}_3$, with the x, y, and z value for each composition listed in Table 5-3.

5.2.2 Results and discussion

5.2.2.1 Effects of nonstoichiometry composition on microstructure

Fig. 5-4 (a) depicts the XRD spectra of stoichiometry and nonstoichiometry ceramic powders calcined at 850 °C for 3 hrs. All the compositions present a single crystalline perovskite structure with no evidence of any secondary phases indicating that the excess Na^+ , Bi^{3+} , and Ba^{2+} diffused into the NBT-0.06BT main lattice and formed the new nonstoichiometry $\text{N}_x\text{B}_y\text{T-}0.06\text{B}_z\text{T}$ ceramic solid solutions [1,2].

Fig. 5-4 (b) illustrates a splitting of the peak [111] into [003] and [021] at 39.0° to 41.0°, for all the compositions showing the existence of the rhombohedral (*Rh*) phase. This split coincides with that observed in the X-ray diffraction spectra of the unmodified or undoped NBT [1,3].

A similar splitting was identified in all compositions for the [200] peak into [200] and [002] at 46.0° to 48.0° as shown in Fig.5-4 (c), which indicates the presence of tetragonal (*Tr*) phase in the $\text{N}_x\text{B}_y\text{T-}0.06\text{B}_z\text{T}$ lattice [2-4]. The co-existence of both *Rh* and *Tr* phases in the $\text{N}_x\text{B}_y\text{T-}0.06\text{B}_z\text{T}$ ceramics confirms that the

structures of stoichiometry composition (A) is at the MPB and also the nonstoichiometry compositions (B, C, and D) remain at MPB area. Although the stoichiometric state of B, C, and D have been changed by modifying the elements molar concentrations (x, y, and z) in this study as mention before, XRD patterns show no significant changes in the phase structure of nonstoichiometry $N_xB_yT-0.06B_zT$ compositions compared with the stoichiometry composition, which agrees with literature [1,3-5].

According to the ionic matching relationship [6], the ionic radius of all elements in the compositions are Na^+ (1.39 Å, CN 12) (CN=coordination number), Bi^{3+} (1.31 Å, CN 12), Ba^{2+} (1.61 Å, CN12), and for Ti^{4+} (0.61 Å, CN 6). The excess in the elements content will compensate the loss of elements due to evaporation at the calcining and sintering stages and may also substitute other cations in the composition [7]. For instance, the excess in the barium content in Composition D may compensate the deficiency in the Ba^{2+} , which will improve the tetragonality in the $N_{0.5}B_{0.534}TiO_3-0.06B_{1.02}T$ composition [8], simultaneously being more likely to substitute the sodium than replace the bismuth in NBT due to the larger radial difference (>15% for Bi) [1].

To determine the stability of the perovskite structure, Goldschmidt tolerance factor (t) relation was calculated by using Equation 1-12 in chapter 1 [9–12].

The tolerance factor value of stable perovskite structure is in the range of 0.77-0.99 [11]. The average t value which has been calculated for the stoichiometry and nonstoichiometry compositions in this study it is around 0.982, suggesting that all compositions illustrate stable structure.

Table 5-3 illustrates the lattice parameters (Å), the c/a ratio, the average grains size (μm) and samples density ($gm.cm^{-3}$) of all compositions. The lattice parameters are “a = b” and “c” vary by modifying x, y, and z contents. The c parameter shows a slight increase from composition A to D.

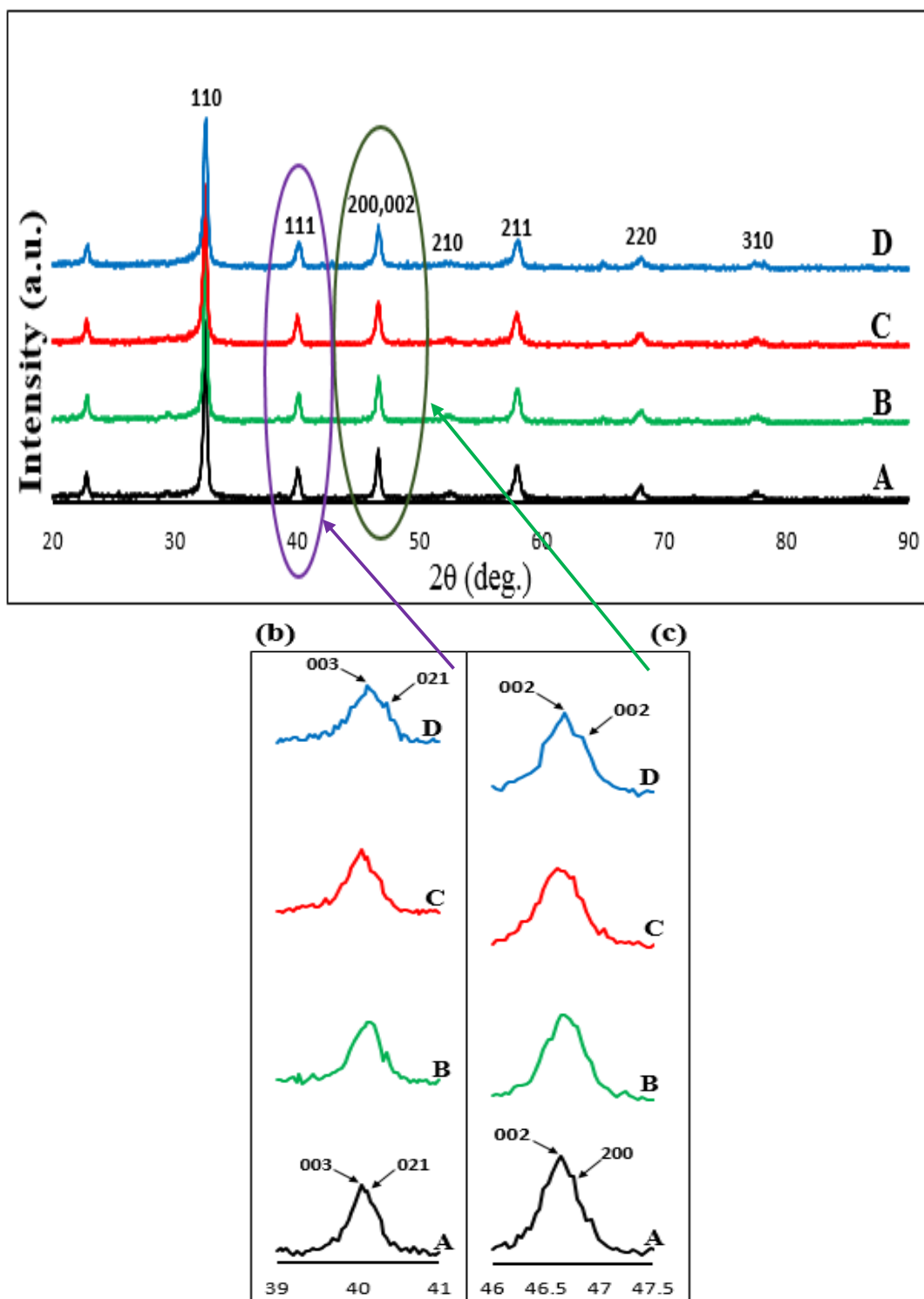


Figure 5-4: (a) XRD patterns of NBT-0.06BT and $N_xB_yT-0.06B_zT$; (b) enlargement of [111] peak split into [021] and [003] at 39.0° to 41.0° ; (c) enlargement of [200] peak split into [200] and [002] at 46.0° to 48.0°

Table 5-3: Lattice parameters (Å), cells volume (Å³), tolerance factor, grain size (μm) and density (gm.cm⁻³) of NBT-0.06 and N_xB_yT-0.06B_zT ceramics.

Composition name	Lattice parameter (Å)		c/a ratio	Average grain size (μm)	Density(ρ) (gm.cm ⁻³)
	a=b	c			
NBT-0.06BT A	5.5113	13.4744	2.4449	1.79	5.757
N _{0.52} B _{0.52} T-0.06BT B	5.4914	13.5048	2.4595	1.67	5.754
N _{0.5} B _{0.534} T-0.06BT C	5.5113	13.4902	2.4516	1.55	5.541
N _{0.5} B _{0.534} T-0.06B _{1.02} T D	5.4957	13.5048	2.4586	1.41	5.704

Compositions B, C, and D have higher c/a ratio than Composition A indicating that the nonstoichiometry compositions B, C, and D have more tetragonality in their structure. This result agrees with the Yoon *et al.*, results [13].

Fig. 5-5 shows the SEM surface morphology of the compositions A, B, C, and D. All the compositions display a dense microstructure with an average density of around $5.689 \pm 0.264 \text{ g.cm}^{-3}$. Although, B, C, and D have nonstoichiometry compositions with excess sodium, bismuth and barium, contents but they present a lower density value than Composition A (Table 5-3). Stoichiometry and nonstoichiometry compositions show a granule grain shape with various grain sizes. The average grain size reduces gradually from Compositions A to D (Table 5-3). The reason behind the reduction in the average grain size may link to the compositional changes that happened during calcining and sintering at high temperature. The loss of Na^+ is more likely higher than that of Bi^{3+} due to the larger volatility of Na^+ . Thus, the composition may shift to a bismuth-nonstoichiometry state after calcining and sintering. Generally, the bismuth behaves as an inhibitor of the grain growth in the NBT structure. Hence, the excess in bismuth content in Composition B can reduce the grain size [3].

Both Compositions C and D are bismuth-nonstoichiometric. Therefore, the effect of the Bi^{3+} on grain size is more pronounced in these compositions. Composition D presents the smallest grain size, which is due to the influence of Bi^{3+} and Ba^{2+} nonstoichiometric (excess content), and both of which, may boost the prevention of the grain growth [1,8,13,14]. In PZT ceramics similar results (grain size reduction) have been reported where lead was substituted with barium [1,8,13,14].

5.2.2.2 Effects of nonstoichiometry composition on dielectric properties

Modifying the stoichiometric state of the starting composition has a big effect on the magnitude of the dielectric properties of the $\text{N}_x\text{B}_y\text{T}-0.06\text{B}_z\text{T}$ material. Fig. 5-6 (a-d) presents the change of the dielectric properties of poled compositions from A to D as a function of temperature from 20 to 150 °C at 1, 10, and 100 (kHz).

The relative permittivity (ϵ_r) of all the compositions increases with temperature, which behaves like a typical ferroelectric material [15].

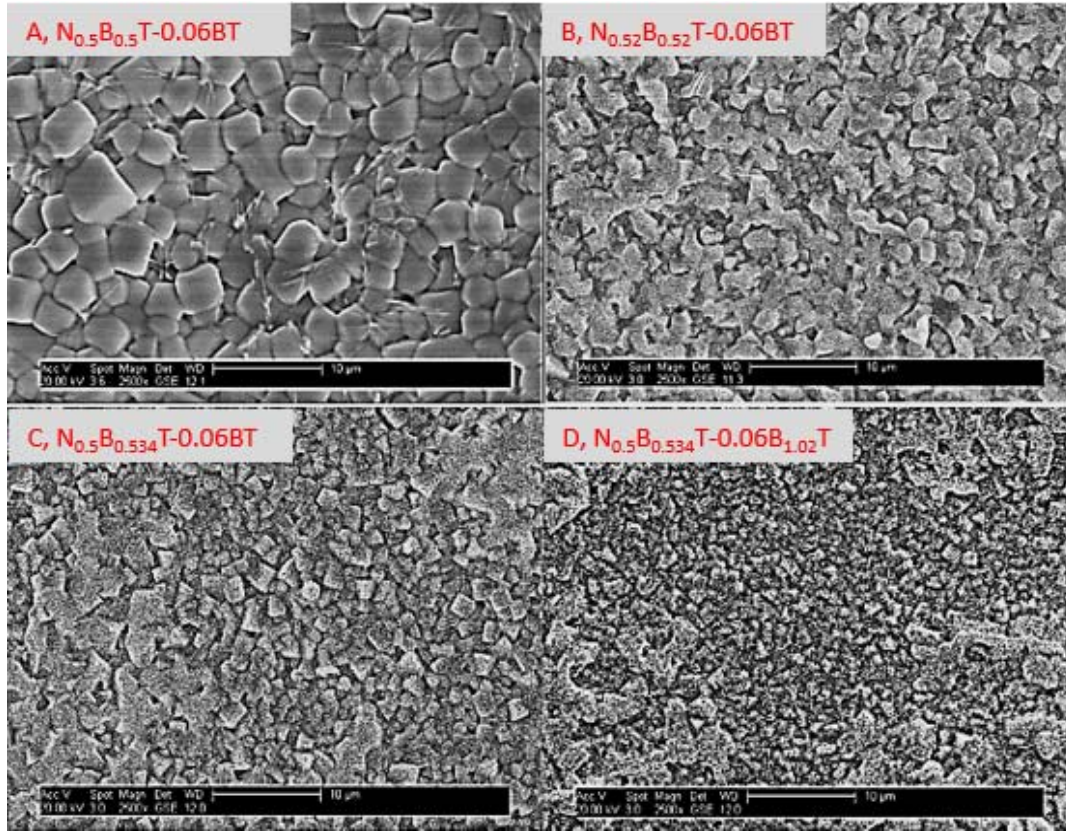
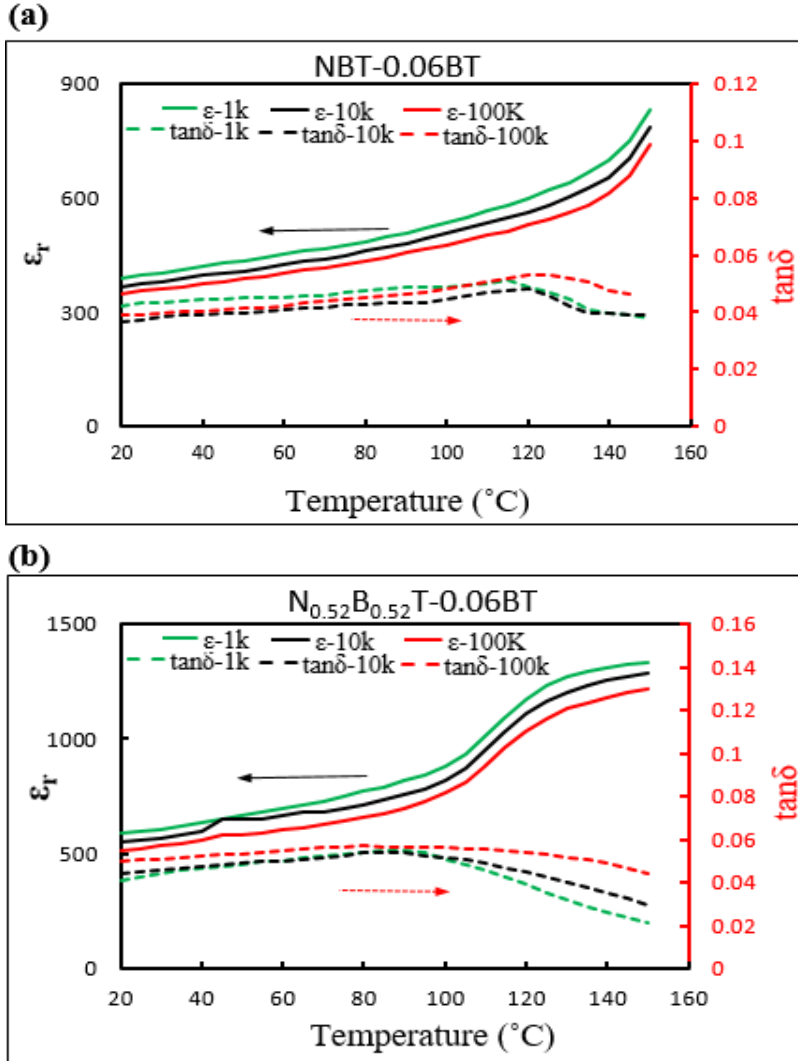


Figure 5-5: SEM surface morphology of NBT-0.06BT and N_xB_yT -0.06B_zT ceramic compositions.

The dielectric loss ($\tan\delta$) also increases with the temperature up to a certain point and then decreases. The $\tan\delta$ value of Composition A is ~ 0.0436 at RT and 1 kHz (Fig. (5-6 (a))). It increases for nonstoichiometry Compositions C and D to around 0.0531 and 0.0561 respectively (Fig. 5-6 (b-d)). However, Composition B presents unexpected dielectric loss value (~ 0.0427) which is the lowest value among all other compositions (Fig. (5-6 (b))).

The temperature at which $\tan\delta$ shows a maximum value is widely known as the depolarization temperature (T_d) [16-18]. The $\tan\delta$ values at T_d are around 0.0510, 0.0548, 0.0599, and 0.0625, and their corresponding temperatures estimated at ~ 115 , 85, 55 and 65 ($^{\circ}\text{C}$) for Compositions A, B, C, and D, respectively (Fig. 5-7). The $\tan\delta$ results at T_d reveal that B shows the lowest value among all other compositions. The ϵ_r values at T_d are ~ 582 , 792, 1055, and 1105 for Compositions A, B, C, and D, respectively (Fig. 5-6 (a-d)). The ϵ_r values at T_d clearly present that the change in the nonstoichiometric state of the composition has a significant effect on the dielectric properties but the dramatic effect is on the relative permittivity at wide temperature range.



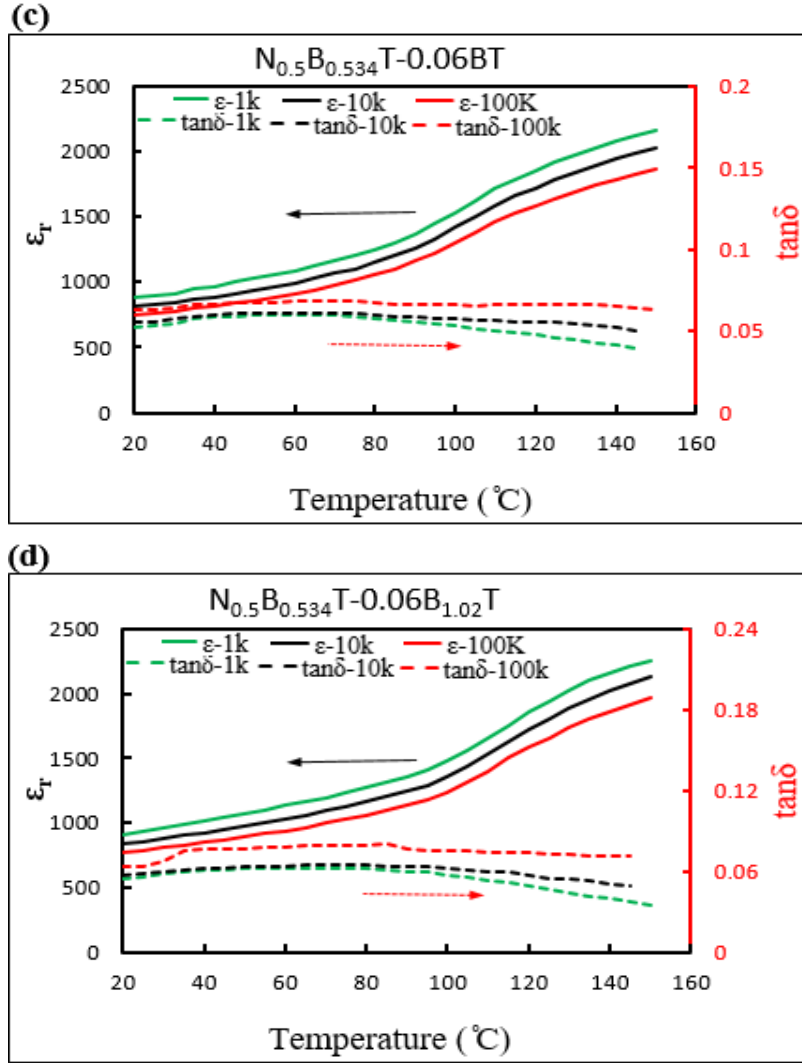


Figure 5-6: Relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) vs temperature for (a) NBT-0.06BT, (b) $N_{0.5}B_{0.5}T-0.06BT$, (c) $N_{0.5}B_{0.534}T-0.06BT$ and (d) $N_{0.5}B_{0.534}T-0.06B_{1.02}T$.

5.2.2.3 Effects of nonstoichiometry composition on depolarization temperature

Changing the stoichiometric state of the composition can also make a large effect on the depolarization temperature (T_d) of the $N_xB_yT-0.06B_zT$ compositions, where the $Na_{0.49}Bi_{0.50}TiO_3$ shows lower T_d than $Na_{0.50}Bi_{0.50}TiO_3$ [7]. Although depolarization temperature is an important parameter in pyroelectric study, but its origin has not been fully understood for NBT-xBT.

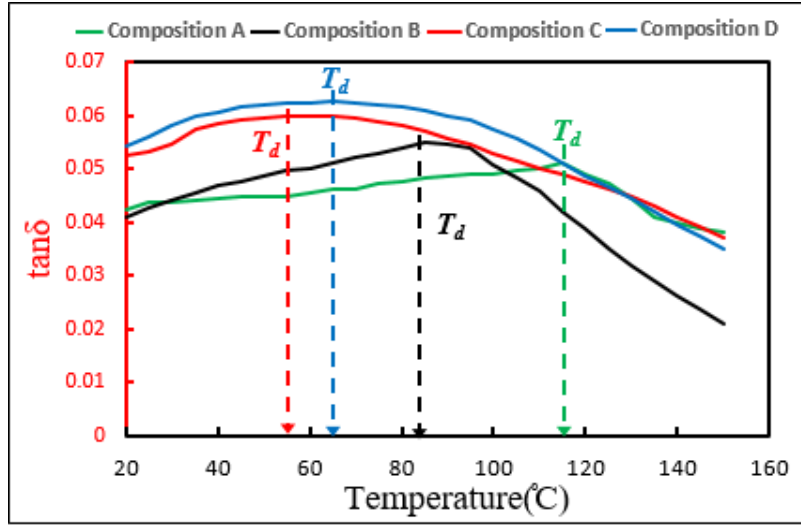


Figure 5-7: The identification of the T_d values of all compositions by dielectric method loss tangent ($\tan\delta$) against temperature ($^{\circ}\text{C}$) for NBT-0.06BT and $\text{N}_x\text{B}_y\text{T}_{1-x-y}$ at 1 kHz.

It has more than one definition [11,16,19-22], which includes the phase transition temperature from ferroelectric (*FE*) to anti-ferroelectric (*AFE*) phases or from ferroelectric to relaxor [17,19,23,24].

In this study, the T_d is subjectively identified by two methods: (1) Dielectric method, from the dielectric loss peak value vs temperature plots (Fig. 5-7); (2) Pyroelectric method, the pyroelectric coefficient (p) peak value vs temperature plots (Fig. 5-8) [25]. For both methods the T_d is strongly dependent on modifying x , y , and z concentrations of the compositions. Fig. 4 reveals that T_d decreased from 115 $^{\circ}\text{C}$ in Composition A to around 55 $^{\circ}\text{C}$ for Composition C respectively. Composition D illustrates a higher T_d , which is more than 10 $^{\circ}\text{C}$ higher than the T_d for Composition C (Fig. 5-7) whereas a shift to lower temperature for Ba^{2+} -nonstoichiometric composition was expected according to our previous study [8].

T_d can also be obtained from the maximum pyroelectric coefficient values. It is widely known that the maximum p can be achieved at the phase transition temperature [26–29].

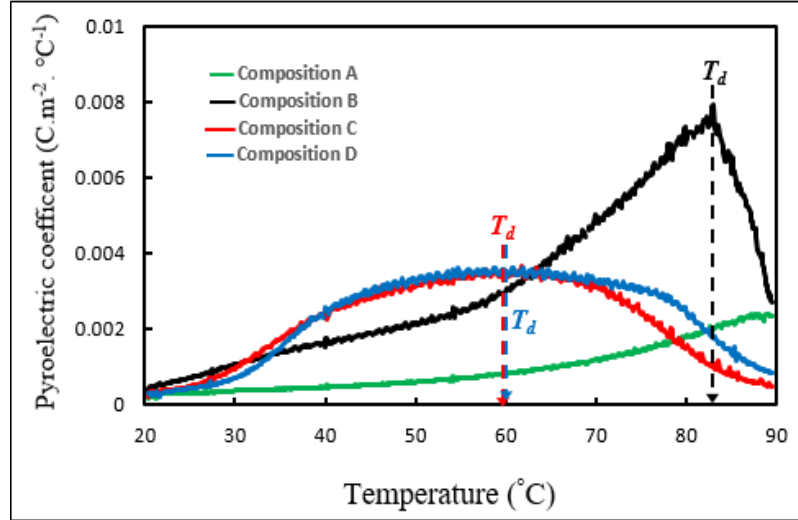


Figure 5-8: Pyroelectric coefficient (p) vs temperature at different x,y, and z contents of NBT-0.06BT and $N_xB_yT-0.06B_zT$ ceramics.

In this study, T_d values identified by this method showed a decrease from more than 90 °C to ~ 82.7, 60.0, and 60.6 °C for Compositions A to D respectively. The exact T_d could not be identified for Composition A by the pyroelectric method due to the upper temperature limit of equipment (Fig. 5-8). In addition, Composition D shows a similar T_d to Composition C although as mentioned above, a lower value with increasing the Ba^{2+} content [8] was expected. The Bi^{3+} -nonstoichiometric (excess content) in Composition D may be the reason for unexpected high T_d in both methods.

The decrease in T_d for nonstoichiometry compositions is probably caused by the excess amount of bismuth and/or deficiency of sodium and also by extra barium concentration in the case of Composition D. According to Yoon *et al.*, Guo *et al.*, and Li *et al.* [13,17,30] the T_d coincides with phase transition from ferroelectric to

a so-called “intermediate phase” phase, and this transition shows a shift of T_d toward lower temperature for compositions with excess Bi^{3+} and/or deficit of Na^+ . Excess Bi^{3+} concentration in the Compositions B, C and D are more likely to replace the A-site ions, Na^+ , Bi^{3+} and Ba^{2+} rather than B-site Ti^{4+} [13,30] as discussed before, which may result in the generation of some of the A-site vacancies when Bi^{3+} replaces Na^+ . These vacancies can reduce ferroelectric long-range ordering and weaken the coupling between A-site ions and TiO_6 octahedron, as a result inducing the phase change at lower temperature [13,30]. Our results agree with the literature but also reveal that the T_d can be reduced and shifted towards lower temperature not only by changing the $\text{Bi}^{3+} / \text{Na}^+$ ratio but also by modifying all the A-site ions (Na^+ , Bi^{3+} , and Ba^{2+}) contents [7,8,17].

Comparing T_d values obtained by the two methods, the pyroelectric method shows T_d values slightly lower than the dielectric method, which is in agreement with the literature [16].

5.2.2.4 Effects of nonstoichiometry composition on pyroelectric properties

Modifying the stoichiometry state of the start composition can significantly affect the pyroelectric coefficient (p) of NBT-0.06BT material. However, the efficient way for evaluating the pyroelectric material performance is to calculate the figure of merits (FOMs) that represent the essential parameters for the pyroelectric applications [16]. The calculation of the FOMs is based on the values of the pyroelectric coefficient, relative dielectric permittivity, dielectric loss and the specific heat [13]. There are several types of FOMs depending on special types of the pyroelectric applications such as infrared or thermal imaging [4,31]. The types of FOMs depend on the input of thermal or electrical circuits, current or voltage [16,25,32].

In this study, the pyroelectric coefficient (p) of NBT-0.06BT and $\text{N}_x\text{B}_y\text{T}-0.06\text{B}_z\text{T}$ were measured from 20 to 90 °C for stoichiometric Composition (A) or T_d for nonstoichiometric Compositions B, C, and D. The calculations of the pyroelectric coefficient (p) and FOMs were carried out using the Equations 1-11 and 1-15 to 1-18 in chapter 1 [14,33-35].

Fig. 5-8 shows the change of p vs. T for all compositions from 20 to 90 °C, with Composition B showing the highest p value at RT. In the temperature range from 33 °C to 70 °C, Compositions C and D have similar pyroelectric coefficient values with a very close maximum value of p . In contrast, Composition B shows a very characteristic peak p value. Generally, pyroelectric materials show one sharp peak at a phase transition temperature as with Composition B. However, it is very evident that the broad flat profiles for Compositions C and D in the temperature range (33 - 70 °C) must be linked to a different compositional structure. The composition of both samples is located at the MPB. At T_d , their structure has been changed to tetragonal with antiferroelectric or relaxor state. However, with the increase of temperature, the structure and polarization states possibly changed from rhombohedral and tetragonal co-existing (*MPB*) ferroelectric to tetragonal ferroelectric and then to tetragonal antiferroelectric or relaxor. This phase transition may give the pyroelectric coefficient with a broad flat peak temperature region.

The p , and FOMs F_i , F_v , and F_D values for all compositions are listed in Table 5-4 at RT while, those values at 90°C or T_d are listed in Table 5-5.

The pyroelectric coefficients of nonstoichiometric compositions vary but are higher than Composition A at RT and T_d .

Composition B shows the optimum p value at both RT and T_d (Tables 5-4 and 5-5). This may be linked to the microstructural change due to the change of the stoichiometric state of this composition. Composition B has a bigger c/a ratio than all other compositions (Table 5-3), indicating Composition B has more tetragonality in its structure than all other compositions [18,29,30,36,37].

Importantly, at RT, the p values for nonstoichiometry compositions are higher than that of PZT and other lead-free compositions (Table 5-4) [1,11,16,38].

The F_i , F_v and F_D show also an increasing trend as p at RT. Compared with PZT and other lead-free compositions (Table 5-4) [13,14,28,34,38], the nonstoichiometry compositions have higher F_i , F_v and F_D values at RT with Composition B showing the highest value at RT and T_d (Tables 5-4 and 5-5) from

this study. The optimum F_V and F_D values (Tables 5-4 and 5-5) was observed for Composition B at both RT and T_d , which can be linked to the lower ϵ_r and the higher p values observed at these temperatures compared to Compositions C and D. Also, the stoichiometry composition A has a better F_D value than C and D due mainly to the increases in ϵ_r and $\tan\delta$ in this nonstoichiometry compositions. The F_C values of stoichiometry and nonstoichiometry compositions at RT and at two frequencies 100 and 1000 (Hz), were calculated, (Table 5-6). The F_C values revealed a strong dependence upon x, y, and z content. Generally, the materials suitable for infrared detectors should have a F_C threshold value $\sim 3 \pm 1 \times 10^{-9} \text{ C. cm}^{-2} \cdot ^\circ\text{C}^{-1}$ [35]. Composition B shows F_C values which are within the threshold range. Compositions A, C, and D, present lower and close to that the Rodríguez-Ruiz *et al.* founded for a $0.935\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.065\text{BaTiO}_3$ composition which is around $1.44 \times 10^{-9} \text{ C. cm}^{-2} \cdot ^\circ\text{C}^{-1}$ [35]. Thus, the composition of Composition B is a promising candidate for this particular pyroelectric application.

Table 5-4: Pyroelectric coefficient (p) and FOMs (F_i , F_V , and F_D) results at RT of NBT-0.06BT and $\text{N}_x\text{B}_y\text{T-}0.06\text{B}_z\text{T}$ in the present study and literature.

Composition name	$p \times 10^{-4} (\text{C.m}^{-2} \cdot ^\circ\text{C}^{-1})$ at RT	$F_i \times 10^{-10} (\text{m.V}^{-1})$ at RT	$F_V (\text{m}^2 \cdot \text{C}^{-1})$ at 1kHz at RT	$F_D \times 10^{-6} \text{ Pa}^{-1/2}$ at 1kHz at RT
NBT-0.06BT A	3.14	1.12	0.021	9.08
$\text{N}_{0.52}\text{B}_{0.52}\text{T-}0.06\text{BT}$ B	6.99	2.50	0.047	16.63
$\text{N}_{0.5}\text{B}_{0.534}\text{T-}0.06\text{BT}$ C	4.77	1.71	0.022	8.32
$\text{N}_{0.5}\text{B}_{0.534}\text{T-}0.06\text{B}_{1.02}\text{T}$ D	4.20	1.50	0.018	6.96

PZT	4.14	1.42	0.008	9.01
NBT-0.065BT	4.60	-	-	-
NBT-0.06BT- 0.002Mn	3.51	-	-	-
NBT-0.07BZT	5.73	2.03	0.022	10.52
BNKBT	3.25	1.95	0.026	13.43
KNLNTS	1.94	0.93	0.007	11.51
NKLBT-0.05BT	3.61	1.27	0.017	-

Table 5-5: Pyroelectric coefficient (p) and FOMs (F_i , F_v , and F_D) results at T_d of NBT-0.06BT and N_xB_yT -0.06B_zT in the present study and literature.

Composition, name	$p \times 10^{-4}$ (C.m ⁻² .°C ⁻¹) at 90°C or T_d	$F_i \times 10^{-10}$ (m.V ⁻¹) at 90°C or T_d	F_v (m ² .C ⁻¹) at 1kHz at 90°C or T_d	$F_D \times 10^{-6}$ (Pa ^{-1/2}) at 1kHz at 90°C or T_d
NBT-0.06BT A	23.91 at 90 °C	8.60 at 90 °C	0.19 at 90 °C	65.51 at 90 °C
N _{0.52} B _{0.52} T- 0.06BT, B	75.33 at 82.7 °C	26.92 at 82.7 °C	0.39 at 82.7 °C	138.72 at 82.7 °C
N _{0.5} B _{0.534} T- 0.06BT, C	35.24 at 60.0 °C	12.61 at 60.0 °C	0.13 at 60.0 °C	52.34 at 60.0 °C
N _{0.5} B _{0.534} T- 0.06B _{1.02} T, D	34.93 at 60.6 °C	12.54 at 60.6 °C	0.12 at 60.6 °C	49.80 at 60.6 °C
NBT-0.07BZT	20.01 at 50°C	7.33 at 50 °C	0.07 at 50 °C	33.62 at 50 °C

NBT-0.07BZT	22.10 at 87 °C	-	-	-
--------------------	-------------------	---	---	---

Table 5-6: The figure of merit F_c , results at room temperature and at 100 and 1000(Hz) of NBT-0.06BT and $N_xB_yT-0.06B_zT$ ceramics.

Composition, name	FOM, $F_c \times 10^{-9} \text{ C. cm}^{-2} \text{ } ^\circ\text{C}^{-1}$ at RT	
	100 Hz	1000 Hz
NBT-0.06BT, A	1.53	1.58
$N_{0.52}B_{0.52}T-0.06BT,$ B	2.58	2.86
$N_{0.5}B_{0.534}T-0.06BT,$ C	1.52	1.60
$N_{0.5}B_{0.534}T-0.06B_{1.02}T,$ D	1.31	1.37

5.2.3 Conclusion

The stoichiometry NBT-0.06BT and nonstoichiometry $N_xB_yT-0.06B_zT$ ceramic compositions were prepared by a conventional solid-state technique. The pyroelectric properties of these compositions were investigated, and their values were better than those in PZT and other lead-free ceramic compositions.

XRD indicates that all compositions phase structure is at the MPB region. The lattice parameter values and c/a ratio slightly change in nonstoichiometry compositions. The average grain size reduces from 1.79 (A) to 1.41 μm (D). Moreover, the stoichiometry composition shows a higher density than the nonstoichiometry compositions. Both relative permittivity (ϵ_r) and dielectric loss ($\tan\delta$) are affected by change the stoichiometric state of the compositions and show an increase with the increase of x, y, and z contents.

The T_d was subjectively identified by two different methods and decreases from $\sim 115^\circ\text{C}$ in Composition A to around 55°C in Composition C, as predicted by the dielectric method. However, the T_d value for Composition C was $\sim 60^\circ\text{C}$ according to pyroelectric coefficient method which questions the accuracy of the two techniques to give a definitive answer. However, it was evident that certain compositions showed much clearer maxima to pinpoint the T_d , compared to others, which suggests the techniques may still be valid.

Composition B has the optimum p at RT and T_d . The F_i , F_v and F_D increase with the increase of Na^+ (x) and Bi^{3+} (y) contents up to $x = y = 0.52$ at both RT and T_d . The F_C shows the optimum values in Composition B. The results presented in this study demonstrate that the nonstoichiometry $\text{N}_{0.52}\text{B}_{0.52}\text{T}-0.06\text{BT}$ composition is a promising material for infrared detectors and other pyroelectric applications in a wide range of temperatures and frequencies.

5.2.4 References

1. Xu C., Lin D., Kwok KW. Structure, electrical properties and depolarization temperature of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{--BaTiO}_3$ lead-free piezoelectric ceramics. *Solid State Sciences*. 2008; 10(7): 934–940. Available at: DOI:10.1016/j.solidstatesciences.2007.11.003
2. Rawat M., Yadav KL., Kumar A., Patel PK., Adhlakha N., Rani J. Structural, dielectric and conductivity properties of Ba^{2+} doped $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramic. *Advanced Materials Letters*. 2012; 3(4): 286–292. Available at: DOI:10.5185/amlett.2012.2322
3. Chen M., Xu Q., Kim BH., Ahn BK., Ko JH., Kang WJ., et al. Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ piezoelectric ceramics. *Journal of the European Ceramic Society*. 2008; 28: 843–849. Available at: DOI:10.1016/j.jeurceramsoc.2007.08.007
4. Li Q., Wang J., Ma L., Fan H., Li Z. Large electrocaloric effect in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ferroelectric ceramics by La_2O_3 addition. *Materials Research Bulletin*. Elsevier Ltd; 2016; 74: 57–61.

Available at: DOI:10.1016/j.materresbull.2015.10.010

5. Search H., Journals C., Contact A., Iopscience M. ($\text{Bi}_{1/2}\text{Na}_{1/2}$) TiO_3 - BaTiO_3 System for Lead-Free Piezoelectric Ceramics. *Jpn. J. Appl. Phys.* 1991; 2236(20/07/1991): 2236–2239.
6. Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*. 1976; 32(5): 751–767. Available at: DOI:10.1107/S0567739476001551
7. Li M., Zhang H., Cook SN., Li L., Kilner JA., Reaney IM., et al. Dramatic influence of A-site nonstoichiometry on the electrical conductivity and conduction mechanisms in the perovskite oxide $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$. *Chemistry of Materials*. 2015; 27(2): 629–634. Available at: DOI:10.1021/cm504475k
8. Balakt AM., Shaw CP., Zhang Q. The effects of Ba^{2+} content on depolarization temperature and pyroelectric properties of lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - 0.06\text{Ba}_{1+x}\text{TiO}_3$ ceramics. *Journal of Materials Science: Materials in Electronics*. 2016; 27: 12947–12954. Available at: DOI:10.1007/s10854-016-5433-1
9. Hiruma Y., Nagata H., Takenaka T. Formation of Morphotropic Phase Boundary and Electrical Properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - \text{Ba}(\text{Al}_{1/2}\text{Nb}_{1/2})\text{O}_3$ Solid Solution Ceramics. *Japanese Journal of Applied Physics*. 2009; 48(9): 09KC08. Available at: DOI:10.1143/JJAP.48.09KC08
10. Kumari R., Ahlawat N., Agarwal A., Sanghi S., Sindhu M. Structural transformation and investigation of dielectric properties of Ca substituted $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.95-x}\text{Ba}_{0.05}\text{Ca}_x\text{TiO}_3$ ceramics. *Journal of Alloys and Compounds*. Elsevier Ltd; 2016; Available at: DOI:10.1016/j.jallcom.2016.11.200
11. Cho J-H., Jeong Y-H., Nam J-H., Yun J-S., Park Y-J. Phase transition and piezoelectric properties of lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3 - \text{BaTiO}_3$ ceramics. *Ceramics International*. 2014; 40: 8419–8425. Available at:

DOI:10.1016/j.ceramint.2014.01.051

12. Le Goupil F., Bennett J., Axelsson AK., Valant M., Berenov A., Bell AJ., et al. Electrocaloric enhancement near the morphotropic phase boundary in lead-free NBT-KBT ceramics. *Applied Physics Letters*. 2015; 107(17): 103–107. Available at: DOI:10.1063/1.4934759
13. Yoon MS., Khansur NH., Ur SC. The effect of pre-milling/pre-synthesis process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized $0.94[(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3]-0.06[\text{Ba}(1+x)\text{TiO}_3]$. *Ceramics International*. Elsevier Ltd and Techna Group S.r.l.; 2010; 36(4): 1265–1275. Available at: DOI:10.1016/j.ceramint.2010.01.011
14. Hiruma Y., Yoshii K., Nagata H., Takenaka T. Investigation of Phase Transition Temperatures on $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 Lead-free Piezoelectric Ceramics by Electrical Measurements. *Ferroelectrics*. 2007; 346(773557621): 114–119. Available at: DOI:10.1080/00150190601180471
15. Guggilla P., Batra AK., Currie JR., Aggarwal MD., Alim MA., Lal RB. Pyroelectric ceramics for infrared detection applications. *Materials Letters*. 2006; 60(16): 1937–1942. Available at: DOI:10.1016/j.matlet.2005.05.086
16. Anton EM., Jo W., Damjanovic D., Rdel J. Determination of depolarization temperature of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based lead-free piezoceramics. *Journal of Applied Physics*. 2011; 110(9): 1–14. Available at: DOI:10.1063/1.3660253
17. Guo Y., Gu M., Luo H. Antiferroelectric phase and pyroelectric response in $(\text{Na}_{1-z}\text{Bi}_z)\text{Ti}_{1-x}\text{O}_3(1-x)-x\text{BaTi}_3$ ceramics. *Journal of the American Ceramic Society*. 2011; 94(5): 1350–1353. Available at: DOI:10.1111/j.1551-2916.2011.04509.x
18. Jo W., Daniels J., Damjanovic D., Kleemann W., Rodel J. Two-stage processes of electrically induced-ferroelectric to relaxor transition in $0.94(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3-0.06\text{BaTiO}_3$. *Applied Physics Letters*. 2013; 102(19): 0–4. Available at: DOI:10.1063/1.4805360

19. Sapper E., Schaab S., Jo W., Granzow T., Rödel J. Influence of electric fields on the depolarization temperature of Mn-doped $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ - $x\text{BaTiO}_3$. *Journal of Applied Physics*. 2012; 111(1): 14105. Available at: DOI:10.1063/1.3674275
20. Levanyuk AP. Phase transitions and domain structures in thin ferroelectric films. *Phase Transitions*. Taylor & Francis; 2015; 88(7): 682–691. Available at: DOI:10.1080/01411594.2014.986732
21. Lichtensteiger C., Fernandez-Pena S., Weymann C., Zubko P., Triscone JM. Tuning of the depolarization field and nanodomain structure in ferroelectric thin films. *Nano Letters*. 2014; 14(8): 4205–4211. Available at: DOI:10.1021/nl404734z
22. Okatan MB., Mantese J V., Alpay SP. Effect of space charge on the polarization hysteresis characteristics of monolithic and compositionally graded ferroelectrics. *Acta Materialia*. Acta Materialia Inc.; 2010; 58(1): 39–48. Available at: DOI:10.1016/j.actamat.2009.08.055
23. Ranjan R., Dwiwedi A. Structure and dielectric properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$: $0 \leq x \leq 0.10$. *Solid State Communications*. 2005; 135: 394–399. Available at: DOI:10.1016/j.ssc.2005.03.053
24. Zhang S., Kounga AB., Aulbach E., Jo W., Granzow T., Ehrenberg H., et al. Lead-free piezoceramics with giant strain in the system $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – BaTiO_3 – $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$. II. Temperature dependent properties. *Journal of Applied Physics*. 2008; 103(3): 34108. Available at: DOI:10.1063/1.2838476
25. Abo, Jiro Kobune M., Nishimura T., Yazaw T., Nakai Y. Effects of manganese addition on pyroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)_{0.94}(\text{BaTiO}_3)_{0.06}$ ceramics. *Integrated Ferroelectrics*. 2006; 80(1): 87–95. Available at: DOI:10.1080/10584580600656502
26. Anem S., Rao KS., Rao KH. Investigation of lanthanum substitution in lead-free BNBT ceramics for transducer applications. *Ceramics International*. Elsevier; 2016; Available at: DOI:10.1016/j.ceramint.2016.06.173

27. Kang W-S., Lee S-K., Koh J-H. AC conductivity and dielectric properties of (Bi,Na)TiO₃–BaTiO₃ lead free ceramics. *Ceramics International*. 2015; 41(5): 6925–6932. Available at: DOI:10.1016/j.ceramint.2015.01.147
28. Wang X., Tang X., Chan H. Electromechanical and ferroelectric properties of (Bi 1/2 Na 1/2) TiO₃–(Bi 1/2 K 1/2) TiO₃–BaTiO₃ lead-free piezoelectric ceramics. *Applied physics letters*. 2004; 85(1): 91. Available at: DOI:10.1063/1.1767592
29. Yao Z., Chu R., Xu Z., Hao J., Li W., Li G. Processing and enhanced electrical properties of Sr_{1-x}(K_{0.5}Bi_{0.5})xBi₂Nb₂O₉ lead-free piezoelectric ceramics. *Ceramics International*. Elsevier; 2016; 42(9): 10619–10623. Available at: DOI:10.1016/j.ceramint.2016.03.156
30. Li XJ., Xi ZZ., Long W., Fang PY. Synthesis of antiferroelectric (Bi_{0.534}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ ceramics with high phase transition temperature and broad temperature range by a solid-state reaction method. *Chinese Science Bulletin*. 2013; 58(23): 2893–2897. Available at: DOI:10.1007/s11434-013-5972-2
31. Xu Q., Huang DP., Chen M., Chen W., Liu HX., Kim BH. Effect of bismuth excess on ferroelectric and piezoelectric properties of a (Na_{0.5}Bi_{0.5})TiO₃–BaTiO₃ composition near the morphotropic phase boundary. *Journal of Alloys and Compounds*. 2009; 471(1–2): 310–316. Available at: DOI:10.1016/j.jallcom.2008.03.078
32. Lau ST., Cheng CH., Choy SH., Lin DM., Kwok KW., Chan HLW. Lead-free ceramics for pyroelectric applications. *Journal of Applied Physics*. 2008; 103(10): 10–13. Available at: DOI:10.1063/1.2927252
33. Byer RL., Roundy CB. Pyroelectric coefficient direct measurement technique and application to a nsec response time detector. *IEEE Transactions on Sonics and Ultrasonics*. 1972; 19(2): 333–338. Available at: DOI:10.1109/T-SU.1972.29679
34. Martínez FL., Hinojosa J., Doménech G., Fernández-luque FJ., Zapata J., Ruiz R., et al. Dielectric Constant Tunability at Microwave Frequencies and

- Pyroelectric Behavior. IEEE transactions on ultrasonics, ferroelectrics, and frequency control. 2013; 60(8): 1595–1602. Available at: DOI:10.1109/TUFFC.2013.2740.
35. Rodríguez-Ruiz R., González-Ballesteros R., Flores-Cuautle a., Suaste-Gómez E. Determination of the Pyroelectric Coefficient for $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.935}\text{Ba}_{0.065}\text{TiO}_3$ Piezoelectric Ceramics. Ferroelectrics. 2008; 368(1): 216–223. Available at: DOI:10.1080/00150190802368537
 36. Craciun F., Galassi C., Birjega R. Electric-field-induced and spontaneous relaxor-ferroelectric phase transitions in $(\text{Na}_{1/2}\text{Bi}_{1/2})_{1-x}\text{Ba}_x\text{TiO}_3$. Journal of Applied Physics. 2012; 112(2012). Available at: DOI:10.1063/1.4770326
 37. Patel S., Chauhan A., Kundu S., Madhar NA., Llahi B., Vaish R., et al. Tuning of dielectric, pyroelectric and ferroelectric properties of $0.715\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.065\text{BaTiO}_3\text{-}0.22\text{SrTiO}_3$ ceramic by internal clamping. AIP Advances. 2015; 5(8): 87145. Available at: DOI:10.1063/1.4929328
 38. Guo F., Yang B., Zhang S., Wu F., Liu D., Hu P., et al. Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-}x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition. Applied Physics Letters. 2013; 103(18): 182906. Available at: DOI:10.1063/1.4828675

6 Doping A-site of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ with $x\text{La}$, $0.0 \leq x \leq 1.0$ (%mole).

This chapter is based on a paper published in the Journal of the European Ceramic Society. Please see publication 3 in the publication list.

Abstract

In this chapter, the pyroelectric properties of A-site (La) doped NBT-0.06BT were investigated in the aim to control and bring down the depolarization temperature to near room temperature and simultaneously, to improve the pyroelectric properties at both RT and T_d . The lanthanum (A-site dopant) was precisely selected according to that the elements with bigger ionic radii than sodium or bismuth can shift the T_d toward low temperature.

6.1 Experimental

A solid-state synthesis route was selected to prepare La^{3+} -doped 0.94NBT-0.06BT composition. The raw materials used in this project were powders and they were the same as in previous chapters. Lithium oxide (La_2O_3), 99.5%, was also used in this work.

The amounts of powders were calculated according to the chemical formula of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3\text{-}x\text{La}_2\text{O}_3$, with $x = 0.0, 0.2\%, 0.5\%$, and 1.0% .

6.2 Results and discussion

6.2.1 Effects of La^{3+} on microstructure

Fig.6-1 (a) shows X-ray diffraction patterns of the La-doped NBT-0.06BT ceramic pellets sintered at 1150°C for 2 hrs. All samples showed a pure perovskite structure (ABO_3), indicating that the NBT-0.06BT lattices have absorbed the La^{3+} content forming a new solid solution, NBT-0.06BT- $x\text{La}$ [1-6].

Lattice parameters ($\text{\AA}$) and c/a ratio of all the samples are given in Table 6-1. Table 6-1 shows that the lattice parameters “ $a = b$ ” and “ c ” are affected by La^{3+} doped. The c/a ratio shows that Sample B has the lowest ratio among all the

samples. La^{3+} can substitute A-site ions in NBT-0.06BT due to the radius similarity according to the Shannon radii [2,3,7-11].

Fig.6-1 (b) shows that a split of the peak [111] into [003] and [021] at 39.0° to 41.0° for all the samples as shown in undoped NBT [8,12-14], indicating the existence of rhombohedral phase. Another split was observed in [200] into [200] and [002] at 46.0° - 48.0° , which indicates the existence of tetragonal phase in NBT lattice (Fig. 1(c)). The coexistence of rhombohedral and tetragonal phases in NBT-0.06BT-xLa ceramics verifies that all the compositions are at morphotropic phase boundary (*MPB*) region. The coexistence of rhombohedral and tetragonal in NBT-xBT at $x = 0.06$ - 0.07 was reported in literature [1,7,9,15]. Therefore, the NBT-0.06BT-xLa phase structure (Sample A-D) is consistent with that reported in literature [1,7,9,15].

Fig. 6-2 exhibits the SEM morphology of all the NBT-0.06BT-xLa ceramic samples. Sample A presents a quite dense structure with a few visible pores. The structures of Samples B, C, and D become denser and no obvious pores can be identified. Sample A presents two distinguishable grain shapes, rod and granule in a wide range of sizes. However, after La^{3+} doping, the granules disappeared and only rods with different sizes existed. The average grain size varies with La^{3+} content and shows a sharp increase firstly from $1.78\ \mu\text{m}$ ($x = 0.0\%$) to $2.85\ \mu\text{m}$ ($x = 0.2\%$) then slightly decrease to $2.71\ \mu\text{m}$ ($x = 0.5\%$) then further to $2.59\ \mu\text{m}$ ($x = 1.0\%$). Sample B presents the biggest grain size among all other samples.

La^{3+} enhances the growth of NBT-0.06BT-xLa grains when it substitutes Na^+ , resulting in A-site vacancies in order to keep charge balance. Generally, the creation of the A-site vacancies is quite beneficial for the mass transportation. This mass transport might be responsible for boosting the grain growth in the NBT-0.06BT-xLa with increasing La^{3+} concentration [2,13].

The densities of Samples B, C, and D (5.84 , 5.79 , and $5.85\ \text{gm.cm}^{-3}$), respectively) are quite similar but higher than that of Sample A ($5.76\ \text{gm.cm}^{-3}$). The higher densities of the doped samples are supported by the SEM pictures (Fig. 6-2).

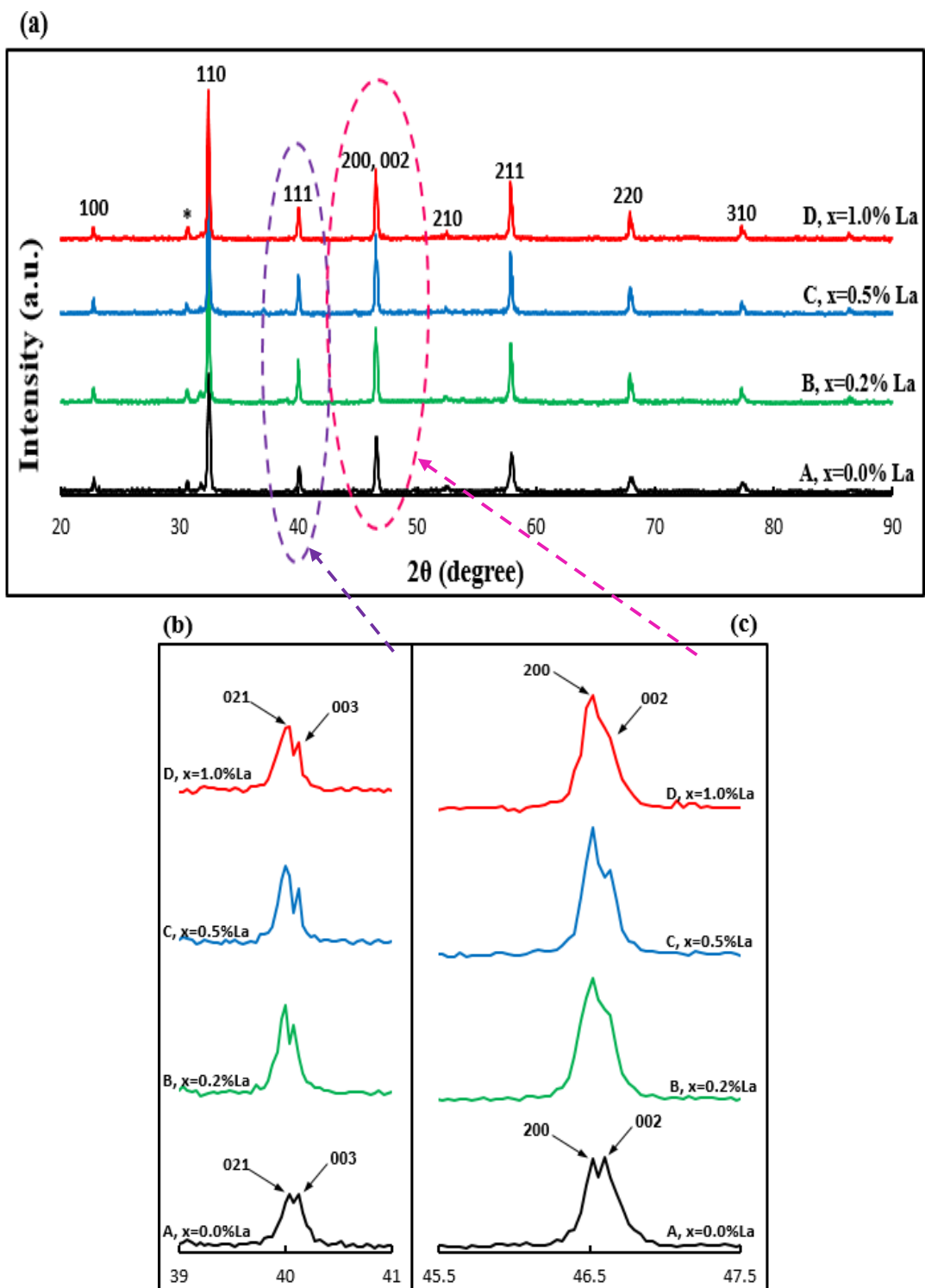


Figure 6-1: (a) X-ray diffraction patterns of NBT-0.06BT-xLa $0.0 \leq x \leq 1.0$ %; (b) enlargement of splitting [111] peak into [003] and [012] at 39.9° to 41.0° ; (c) enlargement of splitting [200] peak into [200] and [002] at 46.0° to 48.0° . *Unidentified peak.

Table 6-1: The lattice parameters ($\text{\AA}$), c/a ratio for NBT-0.06BT and NBT-0.06BT-xLa (%) compositions.

NBT-0.06BT-xLa, sample name	Lattice parameter ($\text{\AA}$)		c/a ratio
	a	c	
NBT-0.0BT, A	5.5113	13.4744	2.4449
NBT-0.0BT-0.002La, B	5.5178	13.4558	2.4386
NBT-0.0BT-0.005La, C	5.5048	13.5061	2.4535
NBT-0.0BT-0.01La, D	5.4876	13.5114	2.4622

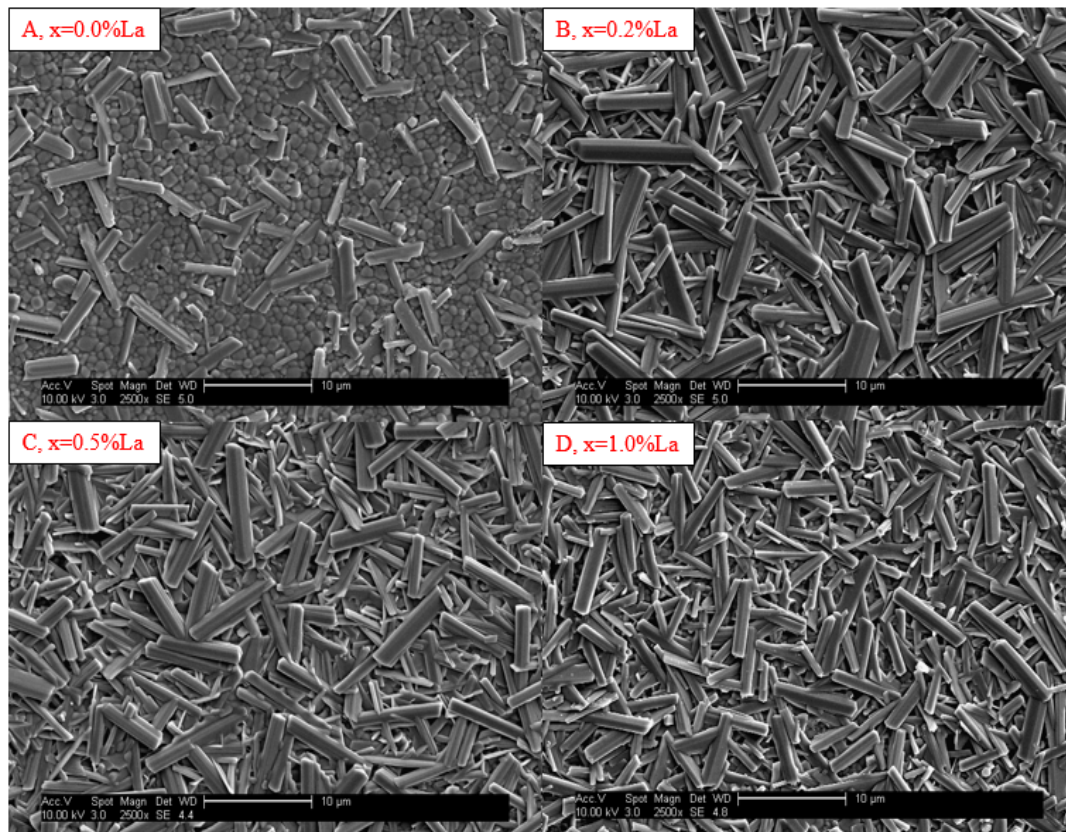


Figure 6-2: SEM morphology of the NBT-0.06BT-xLa $0.0 \leq x \leq 1.0$ (%) ceramics.

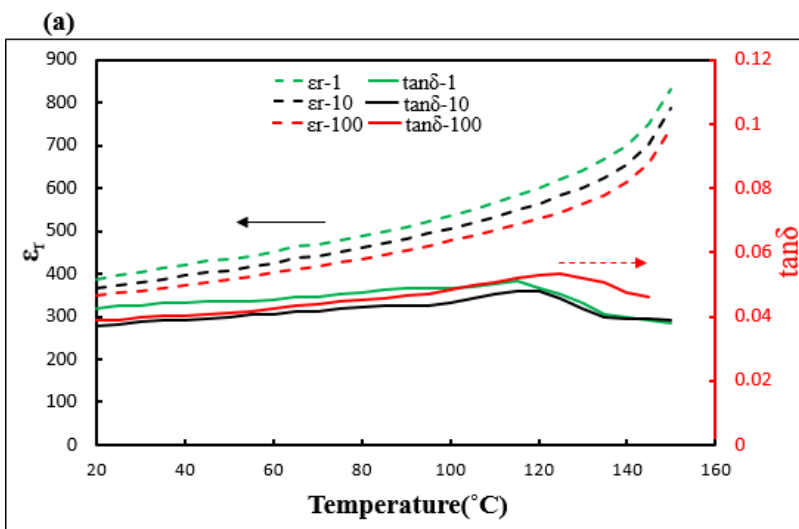
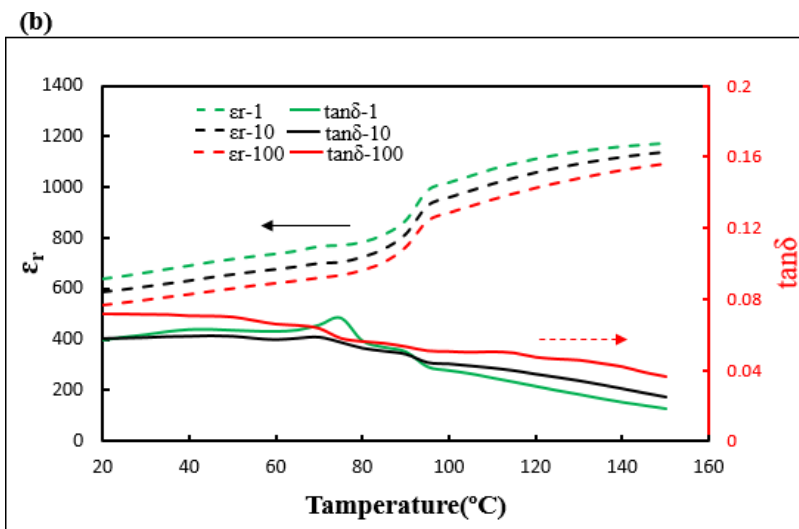
6.2.2 Effects of La^{3+} on dielectric properties

Fig. 6-3 shows the temperature dependence of dielectric properties of poled NBT-0.06BT-xLa, from RT up to 150 °C at 1, 10, and 100 kHz.

The undoped sample shows a relative permittivity (ϵ_r) value of ~ 400 at RT and 1 kHz (Fig. 6-3 (a)) whereas the doped samples present higher ϵ_r values of 600 – 700 (Fig. 6-3 (b to d)). The ϵ_r of all the samples increased with temperature, which is typical for ferroelectric materials [16]. The relative permittivity against temperature demonstrates an obvious declining (Fig 6-4(a)). This declining temperature starts at ~ 70 , ~ 69 and ~ 30 °C for $x = 0.2$, 0.5 and 1.0 (%), respectively but it was not identified for Sample A, (Fig 6-4 (a)) although there is evidence that it may be outside the temperature measurement window. These temperatures are so close to the temperatures where their dielectric losses ($\tan\delta$) show the maximum values which are around 75, 70, and 25 °C for samples B, C, and D, respectively (Fig 6-4(b)). These temperature values can be identified as depolarization temperatures (T_d) (Fig 6-4(b)). The ϵ_r values for doped samples at T_d , (1 kHz) are around 650 for Sample C and ~ 700 for Samples B, D. Sample D shows the highest relative permittivity value ~ 1300 at 150 °C, at which it was around 850 for sample A.

The increase in ϵ_r for doped samples with temperature is because the lattice deformation due to the La^{3+} substitution to Bi^{3+} .

This deformation was identified by XRD (Table 6-1), which makes the ferroelectric domains re-orientating easier during the poling process. Bismuth in NBT-xBT volatiles at high temperature resulting in a higher conductivity or increasing the leakage currents [8]. As a result, La^{3+} addition to NBT-0.06BT leads to the increase of ϵ_r values [2,13]. La^{3+} can also substitute Na^+ , which behaves as a donor, resulting in A-site vacancies and the increase of ϵ_r [2,17].



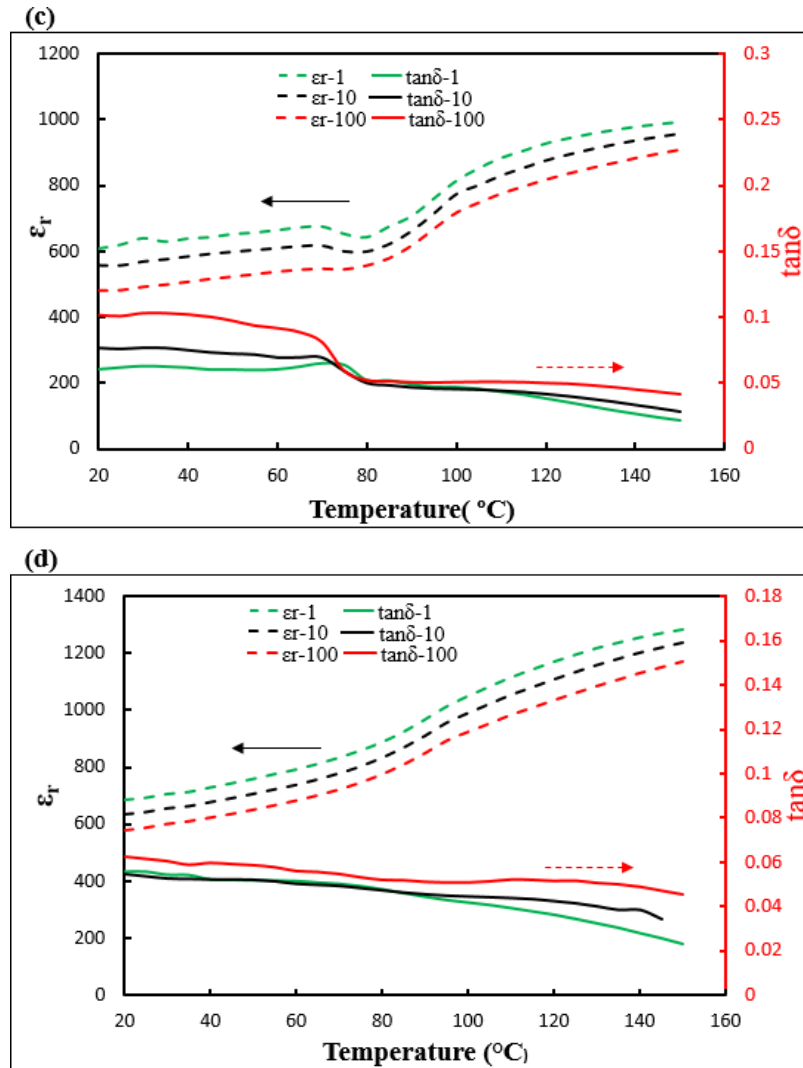


Figure 6-3: Relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) vs temperature for NBT-0.06BT-xLa. a: $x=0.0\%$; b: $x=0.2\%$; c: $x=0.5\%$ and d: $x=1.0\%$, at three different frequencies (1, 10, and 100) kHz.

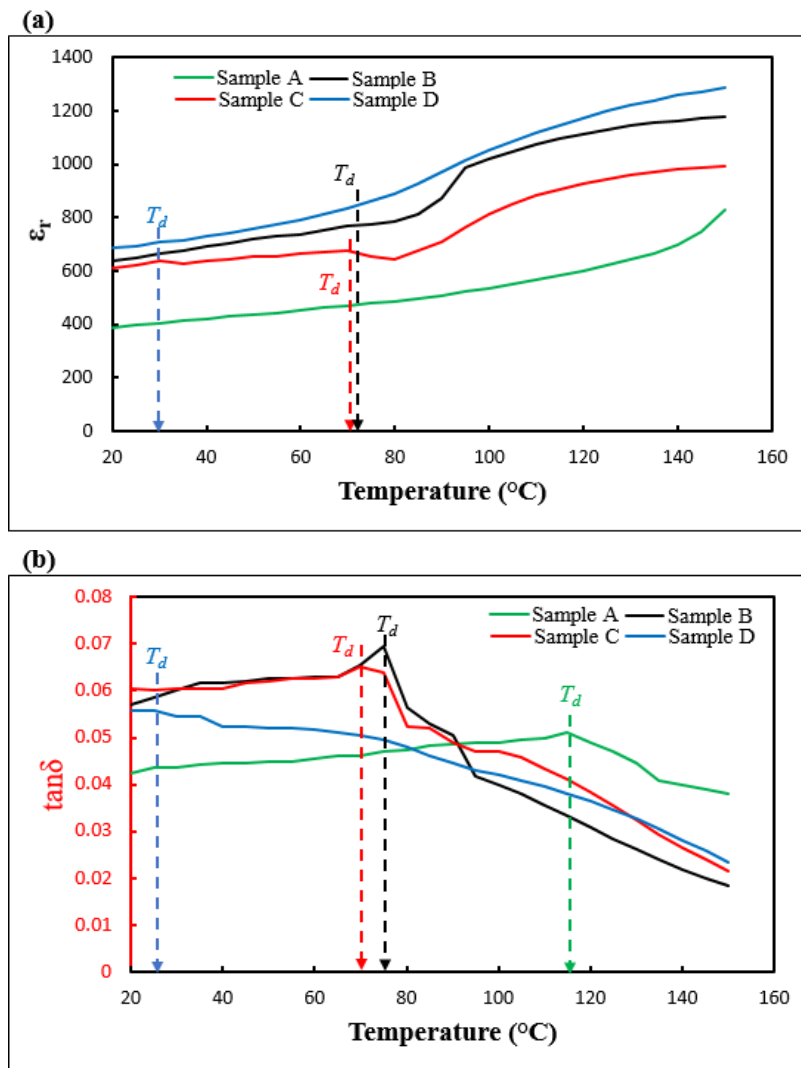


Figure 6-4: (a) the change of the relative permittivity (ϵ_r) and (b) loss tangent ($\tan\delta$) against temperature ($^{\circ}\text{C}$) for NBT-0.06BT-xLa, $0.0 \leq x \leq 1.0$ %, from room temperature up to 150 $^{\circ}\text{C}$ at 1 kHz and T_d value of all samples.

Dielectric losses ($\tan\delta$) of the doped samples are quite similar, which are between 0.055-0.06 at RT and 1 kHz, higher than the undoped sample (~ 0.04). Also, the $\tan\delta$ increased with temperature up to a certain value depending on the dopant content and then decreased. The maximum dielectric loss was observed at T_d , which is ~ 0.07 , ~ 0.065 , and ~ 0.055 for Samples B, C, and D respectively while it is around 0.05 for Sample A.

6.2.3 Effects of dopant La^{3+} on depolarization temperature

The T_d represents one of the important parameters in the pyroelectric study. It has a few definitions, and one of them is the phase transition temperature from ferroelectric (*FE*) to anti-ferroelectric (*AFE*) or to relaxor anti-ferroelectric (*relaxor-AFE*) phases [6,14,18-24].

In this study, the T_d were identified by two methods: 1. Dielectric method, the temperature at dielectric peak (Fig. 6-4 (a, and b)); 2. Pyroelectric method, the temperature at pyroelectric coefficient (p) peak (Fig. 6-5) [3].

The dielectric (permittivity & loss) vs temperature plots in Fig. 6-4 reveal that T_d decreased from 115 °C (Sample A) to around 25 °C ~ 30 °C (Sample D) (Fig. 6-4 (a and b)), which is in agreement with the literature [13,23,25,26]. The T_d values identified from dielectric permittivity for the doped samples are slightly higher than or equal to the T_d identified from the dielectric loss ($\tan\delta$) curves (Fig. 6-4 (b)).

T_d can also be obtained from the ultimate pyroelectric coefficient values. It is known that the maximum p can be achieved at the phase transition temperature [7,14,20,23,25,27-30]. The T_d values identified by this method show a reduction in T_d from > 90 °C to ~ 67.9, ~ 73.5, and ~ 46.8 °C for Samples B-D respectively (Fig. 6-5). Sample C shows an abnormal T_d which is 6.0 °C higher than the T_d of Sample B as it should shift to lower temperature with increasing the dopant content (Fig. 6-5). The exact depolarization temperature could not be identified for Sample A by this method due to the maximum temperature of the equipment being at 90 °C (Fig 6-5).

The reason that T_d shifts to lower temperature with the increase of La^{3+} content might be because La^{3+} (1.36 Å) is larger than Bi^{3+} (1.31 Å). Generally, doping A-site of NBT-0.06BT with larger elements will shift T_d to lower temperature. Therefore, doping Sr, La and other elements in NBT-0.06BT [7,14,30-33] leads the T_d to lower temperatures, whereas, doping NBT-0.06BT with smaller elements such as Dy^{3+} (0.912 Å) [33-35] shifts the T_d value to higher temperature [33,34,36].

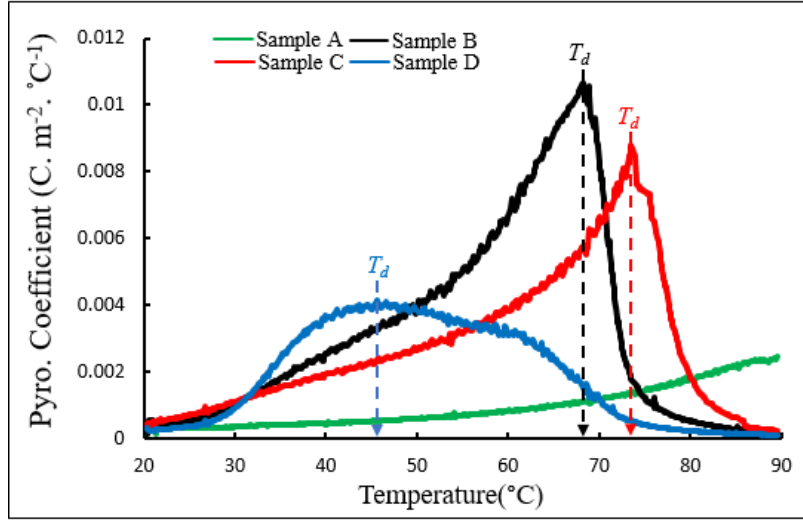


Figure 6-5: Pyroelectric coefficient (p) vs temperature ($^{\circ}\text{C}$) for the NBT-0.06BT- x La ceramics, $0.0 \leq x \leq 1.0$ (%).

6.2.4 Effects of La^{3+} on pyroelectric properties

The pyroelectric coefficient (p) represents an important parameter for selecting the material for pyroelectric applications but improving the performance of a pyroelectric material cannot be achieved by only increasing the p value. Figure of merit (FOM) is another important parameter to be taken into account [3,8].

There are several types of FOMs depending on the special pyroelectric applications such as infrared or thermal imaging [2,5,13].

In this study, the pyroelectric coefficient (p) of NBT-0.06BT- x La, $0.0 \leq x \leq 1.0$ (%) was measured at RT and at 90°C for Sample A or T_d for Samples (B, C, and D). The calculations of FOMs were calculated using Equations (1-11 and 1-15 to 1-18) in chapter 1 [1,4,37-39].

Fig. 6-5 shows the change of p with temperature for NBT-0.06BT- x La from 20 to 90°C . Sample C ($x = 0.5\%$) shows the highest p at RT. Samples B and C show similar profiles differentiated only by their own relative T_d values which coincide with the maximum observed p values for the samples. The T_d value for Sample A clearly lies outside the measurement window so it is difficult to comment on its

likely profile. Sample D presents quite different profile with a broad shape; however, it shows the T_d , without distinguishable sharp peak. This profile may link to its structure and polarization states. Sample D composition is located at MPB. With the increase of temperature, the structure and polarization states possibly changed from rhombohedral and tetragonal co-existing (*MPB*) ferroelectric to tetragonal ferroelectric and then to tetragonal antiferroelectric or relaxer. This phase transition may give the profile of the pyroelectric coefficient a broad and flat shape.

Pyroelectric coefficient (p) and FOMs F_i , F_v , and F_D values for all the samples at RT are listed in Table 6-2 and at 90 °C or T_d in Table 6-3.

The p increased from Samples A to D at RT and a huge increase at T_d . Sample C has the highest p value at RT while Sample B at T_d , which probably links to the microstructure change of these samples. The calculation of c/a ratio reveals that Sample C has a higher ratio which means that Sample C has more tetragonality in its structure than Sample B at RT (Table 6-1).

The huge increase in p at T_d may be attributed to the positive correlation between p and pyroelectric current (I_p), which reaches the maximum at T_d [5]. The large p values obtained at T_d are most likely related to a phase transition. The T_d coincides with the phase transition temperature. At RT and at T_d , the p values for Samples B and C are higher than those of PZT and other lead-free ceramic compositions (Tables 6-2 and 6-3) [7,23,27,40].

The F_i and F_v values show an increase from Samples A to D at RT and a large increase at T_d due to their large p values. Comparing the F_i and F_v values with those of PZT and other lead-free ceramic compositions at RT, the La-doped NBT-0.06BT samples have higher F_i and F_v (Tables 6-2 and 6-3).

F_D values of all doped samples at RT and 90°C or T_d show worse values. The lower F_D values for doped samples may be related to the higher values of both relative permittivity and the dielectric loss which are higher than the undoped sample, though pyroelectric coefficient values of Samples B, C, and D were quite higher than Sample A value.

The F_C values of NBT-0.06BT-xLa at RT and at 33, 100, 1000 (Hz) were calculated. Generally, the materials suitable for infrared detectors should have the FC threshold value at $\sim 3 \pm 1 \times 10^{-9} \text{ C. cm}^{-2} \cdot \text{C}^{-1}$ [38].

Table 6-2: The pyroelectric coefficient and FOM F_i , F_v , and F_D results at room temperature (RT) in this study and in literature.

Composition	$p \times 10^{-4} \text{ C.m}^{-2} \cdot \text{C}^{-1}$ at RT	$F_i \times 10^{-10} \text{ m.V}^{-1}$ at RT	$F_v (\text{m}^2 \cdot \text{C}^{-1})$ at f. 1kHz at RT	$F_D \times 10^{-6} \text{ Pa}^{-1/2}$ at f. 1kHz at RT
NBT-0.06BT	2.14	1.12	0.021	9.08
NBT-0.06BT-0.002La	5.15	1.84	0.032	1.0
NBT-0.06BT-0.005La	7.42	2.65	0.048	1.4
NBT-0.06BT-0.01La	3.60	1.28	0.021	1.4
PZT	4.14	1.415	0.008	9.01
NBT-0.07BZT	5.7	2.03	0.0218	10.5
NBT-0.06BT-0.2Mn	3.5	-	-	-
BNKBT	3.25	1.95	0.026	13.43
KNLNTS	1.9	0.931	0.007	11.5
NKLBT-0.05BT	3.6	1.27	0.017	-

Table 6-3: The pyroelectric coefficient and FOM F_i , F_v , and F_D results at 90 °C or depolarization temperature (T_d) in this study and in literature.

Composition	$p \times 10^{-4} (C.m^{-2}.^{\circ}C^{-1})$ at 90 °C or T_d	$F_i \times 10^{-10}$ (m.V⁻¹) at 90 °C or T_d	$F_v (m^2.C^{-1})$ at f. 1kHz at 90 °C or T_d	$F_D \times 10^{-6} (Pa^{-1/2})$ at f. 1kHz at 90 °C or T_d
NBT-0.06BT	23.9 at 90 °C	8.6 at 90 °C	0.19 at 90 °C	65.5 at 90 °C
NBT-0.06BT- 0.002La	105.4 at 67.9 °C	37.6 at 67.9 °C	0.56 at 67.9 °C	18.2 at 67.9 °C
NBT-0.06BT- 0.005La	86.1 at 73.5 °C	30.8 at 73.5 °C	0.52 at 73.5 °C	15.8 at 73.5 °C
NBT-0.06BT- 0.01La	40.6 at 46.8 °C	14.5 at 46.8 °C	0.22 at 46.8 °C	7.8 at 46.8 °C
NBT-0.07BZT	20.0 at 50 °C	7.33 at 50 °C	0.066 at 50 °C	33.6 at 50 °C
NBT-0.07BZT	22.1 at 87 °C	-	-	-

The composition of Sample C presents F_C values 2.10 ± 0.380 , 2.89 ± 0.398 , and 2.98 ± 0.205 ($\times 10^{-9}$ C.cm⁻². °C⁻¹) at RT and at 33, 100, 1000 (Hz) respectively, which are suitable for infrared detectors. However, Samples A, B, and D show the F_C values less than the threshold value. Rodríguez-Ruiz et al [38]. Investigated the pyroelectric coefficient of 0.935Na0.5Bi0.5TiO3-0.065BaTiO3 ceramics and calculated the F_C of this material, which equals to 1.44×10^{-9} C.cm⁻². °C⁻¹, which is also lower than the threshold value. The high F_C values for Sample C in this work are due to the high p and the lower relative permittivity at RT.

6.3 Conclusion

La-doped lead-free NBT-0.06BT ceramics were prepared using a conventional solid-state technique. The pyroelectric properties of these compositions were investigated and compared with undoped NBT-0.06BT and other lead-free materials including PZT.

All compositions were found being at the morphotropic phase boundary area. The values of lattice parameters and c/a ratio slightly changed with increasing the dopant content. The average grain size, relative permittivity (ϵ_r) and dielectric loss ($\tan\delta$) increase with La content. The T_d was identified by two different ways and decreases from ~ 115 °C in NBT-0.06BT to RT and 46.8 °C in 1.0 % La-doped NBT-0.06BT, according to the dielectric and pyroelectric coefficient methods respectively.

Samples B and C show the optimum p , F_i and F_v values at RT and at T_d respectively. Sample C shows F_C values of 2.10, 2.89, and 2.98 ($\times 10^{-9}$ C.cm⁻². °C⁻¹) at RT at 33, 100 and 1000 (Hz) respectively which are suitable for infrared detectors. The results presented in this study demonstrate that NBT-0.06BT-xLa ($0.2\% \leq x \leq 0.5\%$) ceramics are promising materials for infrared detectors and other pyroelectric applications in a wide temperature range.

6.4 References

- [1] F. Guo, B. Yang, S. Zhang, F. Wu, D. Liu, P. Hu, Y. Sun, D. Wang, W. Cao, Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-}x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition, *Appl. Phys. Lett.* 103 (2013) 182906. doi:10.1063/1.4828675.
- [2] F.L. Martínez, J. Hinojosa, G. Doménech, F.J. Fernández-luque, J. Zapata, R. Ruiz, L. Pardo, Dielectric Constant Tunability at Microwave Frequencies and Pyroelectric Behavior, *IEEE Trans. Ultrason. Ferroelectr. Freq. Control.* 60 (2013) 1595–1602. doi:10.1109/TUFFC.2013.2740.
- [3] M. Abo, Jiro Kobune, T. Nishimura, T. Yazaw, Y. Nakai, Effects of manganese addition on pyroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)_{0.94}(\text{BaTiO}_3)_{0.06}$ ceramics, *Integr. Ferroelectr.* 80 (2006) 87–95. doi:10.1080/10584580600656502.
- [4] Y. Guo, M. Gu, H. Luo, Antiferroelectric phase and pyroelectric response in $(\text{Na}_{1-z}\text{Bi}_z)\text{Ti}_{1-x}\text{O}_3(1-x)\text{-}x\text{BaTi}_3$ ceramics, *J. Am. Ceram. Soc.* 94 (2011) 1350–1353. doi:10.1111/j.1551-2916.2011.04509.x.
- [5] S. Patel, A. Chauhan, S. Kundu, N.A. Madhar, B. Llahi, R. Vaish, K.B.R. Varma, Tuning of dielectric, pyroelectric and ferroelectric properties of $0.715\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}0.065\text{BaTiO}_3\text{-}0.22\text{SrTiO}_3$ ceramic by internal clamping, *AIP Adv.* 5 (2015) 87145. doi:10.1063/1.4929328.
- [6] S.G. Lee, C. Il Kim, B.C. Kim, Dielectric properties of screen-printed $(\text{Ba,Sr,Ca})\text{TiO}_3$ thick films modified with Al_2O_3 for microwave device applications, *J. Eur. Ceram. Soc.* 24 (2004) 157–162. doi:10.1016/S0955-2219(03)00252-8.
- [7] M. Chen, Q. Xu, B.H. Kim, B.K. Ahn, J.H. Ko, W.J. Kang, O.J. Nam, Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ piezoelectric ceramics, *J. Eur. Ceram. Soc.* 28 (2008) 843–849. doi:10.1016/j.jeurceramsoc.2007.08.007.

- [8] J.-H. Cho, Y.-H. Jeong, J.-H. Nam, J.-S. Yun, Y.-J. Park, Phase transition and piezoelectric properties of lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--BaTiO}_3$ ceramics, *Ceram. Int.* 40 (2014) 8419–8425. doi:10.1016/j.ceramint.2014.01.051.
- [9] Q. Li, J. Wang, L. Ma, H. Fan, Z. Li, Large electrocaloric effect in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ferroelectric ceramics by La_2O_3 addition, *Mater. Res. Bull.* 74 (2016) 57–61. doi:10.1016/j.materresbull.2015.10.010.
- [10] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr. Sect. A* 32 (1976) 751–767. doi:10.1107/S0567739476001551.
- [11] C. Xu, D. Lin, K.W. Kwok, Structure, electrical properties and depolarization temperature of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{--BaTiO}_3$ lead-free piezoelectric ceramics, *Solid State Sci.* 10 (2008) 934–940. doi:10.1016/j.solidstatesciences.2007.11.003.
- [12] K.A. Razak, C.J. Yip, S. Sreekantan, Synthesis of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) and Pr doped BNT using the soft combustion technique and its properties, *J. Alloys Compd.* 509 (2011) 2936–2941. doi:10.1016/j.jallcom.2010.11.163.
- [13] S. Anem, K.S. Rao, K.H. Rao, Investigation of lanthanum substitution in lead-free BNBT ceramics for transducer applications, *Ceram. Int.* (2016). doi:10.1016/j.ceramint.2016.06.173.
- [14] M. Rawat, K.L. Yadav, A. Kumar, P.K. Patel, N. Adhlakha, J. Rani, Structural, dielectric and conductivity properties of Ba^{2+} doped $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramic, *Adv. Mater. Lett.* 3 (2012) 286–292. doi:10.5185/amlett.2012.2322.
- [15] S.R. Kanuru, K. Baskar, R. Dhanasekaran, Synthesis, structural, morphological and electrical properties of NBT–BT ceramics for piezoelectric applications, *Ceram. Int.* 42 (2016) 6054–6064. doi:10.1016/j.ceramint.2015.12.162.

- [16] Y. Hiruma, H. Nagata, T. Takenaka, Formation of Morphotropic Phase Boundary and Electrical Properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--Ba}(\text{Al}_{1/2}\text{Nb}_{1/2})\text{O}_3$ Solid Solution Ceramics, *Jpn. J. Appl. Phys.* 48 (2009) 09KC08. doi:10.1143/JJAP.48.09KC08.
- [17] R. Ranjan, A. Dviwedi, Structure and dielectric properties of $(\text{Na}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$: $0 \leq x \leq 0.10$, *Solid State Commun.* 135 (2005) 394–399. doi:10.1016/j.ssc.2005.03.053.
- [18] E.M. Anton, W. Jo, D. Damjanovic, J. Rödel, Determination of depolarization temperature of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based lead-free piezoceramics, *J. Appl. Phys.* 110 (2011) 1–14. doi:10.1063/1.3660253.
- [19] F. Craciun, C. Galassi, R. Birjega, Electric-field-induced and spontaneous relaxor-ferroelectric phase transitions in $(\text{Na}_{1/2}\text{Bi}_{1/2})_{1-x}\text{Ba}_x\text{TiO}_3$, *J. Appl. Phys.* 112 (2012). doi:10.1063/1.4770326.
- [20] W. Jo, J.E. Daniels, J.L. Jones, X. Tan, P. a. Thomas, D. Damjanovic, J. Rödel, Evolving morphotropic phase boundary in lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--BaTiO}_3$ piezoceramics, *J. Appl. Phys.* 109 (2011) 14110. doi:10.1063/1.3530737.
- [21] W.-S. Kang, S.-K. Lee, J.-H. Koh, AC conductivity and dielectric properties of $(\text{Bi},\text{Na})\text{TiO}_3\text{--BaTiO}_3$ lead free ceramics, *Ceram. Int.* 41 (2015) 6925–6932. doi:10.1016/j.ceramint.2015.01.147.
- [22] E. Sapper, S. Schaab, W. Jo, T. Granzow, J. Rödel, Influence of electric fields on the depolarization temperature of Mn-doped $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3\text{--}x\text{BaTiO}_3$, *J. Appl. Phys.* 111 (2012) 14105. doi:10.1063/1.3674275.
- [23] Z. Yao, R. Chu, Z. Xu, J. Hao, W. Li, G. Li, Processing and enhanced electrical properties of $\text{Sr}_{1-x}(\text{K}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_2\text{Nb}_2\text{O}_9$ lead-free piezoelectric ceramics, *Ceram. Int.* 42 (2016) 10619–10623. doi:10.1016/j.ceramint.2016.03.156.
- [24] S. Zhang, A.B. Kounga, E. Aulbach, W. Jo, T. Granzow, H. Ehrenberg, J. Rödel, Lead-free piezoceramics with giant strain in the system

- Bi_{0.5}Na_{0.5}TiO₃–BaTiO₃–K_{0.5}Na_{0.5}NbO₃. II. Temperature dependent properties, J. Appl. Phys. 103 (2008) 34108. doi:10.1063/1.2838476.
- [25] Q. Xu, D.P. Huang, M. Chen, W. Chen, H.X. Liu, B.H. Kim, Effect of bismuth excess on ferroelectric and piezoelectric properties of a (Na_{0.5}Bi_{0.5})TiO₃–BaTiO₃ composition near the morphotropic phase boundary, J. Alloys Compd. 471 (2009) 310–316. doi:10.1016/j.jallcom.2008.03.078.
- [26] H. Search, C. Journals, A. Contact, M. Iopscience, (Bi^{1/2}Na^{1/2}) TiO₃–BaTiO₃ System for Lead-Free Piezoelectric Ceramics, Jpn. J. Appl. Phys. 2236 (1991) 2236–2239.
- [27] M.S. Yoon, N.H. Khansur, S.C. Ur, The effect of pre-milling/pre-synthesis process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized 0.94[(Bi_{0.5}Na_{0.5})TiO₃]-0.06[Ba(1+x)TiO₃], Ceram. Int. 36 (2010) 1265–1275. doi:10.1016/j.ceramint.2010.01.011.
- [28] Y. Hiruma, K. Yoshii, H. Nagata, T. Takenaka, Investigation of Phase Transition Temperatures on (Bi^{1/2}Na^{1/2})TiO₃–(Bi^{1/2}K^{1/2})TiO₃ and (Bi^{1/2}Na^{1/2})TiO₃–BaTiO₃ Lead-free Piezoelectric Ceramics by Electrical Measurements, Ferroelectrics. 346 (2007) 114–119. doi:10.1080/00150190601180471.
- [29] X.J. Li, Z.Z. Xi, W. Long, P.Y. Fang, Synthesis of antiferroelectric (Bi_{0.534}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ ceramics with high phase transition temperature and broad temperature range by a solid-state reaction method, Chinese Sci. Bull. 58 (2013) 2893–2897. doi:10.1007/s11434-013-5972-2.
- [30] W. Cao, W. Li, T. Zhang, J. Sheng, Y. Hou, Y. Feng, Y. Yu, W. Fei, High-Energy Storage Density and Efficiency of (1– x)[(0.94 NBT-0.06 BT)]- x ST Lead-Free Ceramics, Energy Technol. 3 (2015) 1198–1204. doi:10.1002/ente.201500173.
- [31] P. Fu, Z. Xu, R. Chu, W. Li, G. Zang, J. Hao, Piezoelectric, ferroelectric and dielectric properties of La₂O₃-doped (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ lead-free ceramics, Mater. Des. 31 (2010) 796–801.

doi:10.1016/j.matdes.2009.07.056.

- [32] Q. Li, H. Wang, H. Fan, C. Long, X. Liu, Ferroelectric, electromechanical, and dielectric properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ co-doped MnO_2 and La_2O_3 lead-free ceramics, *J. Mater. Sci.* 49 (2013) 211–217. doi:10.1007/s10853-013-7694-x.
- [33] J. Shi, W. Yang, Piezoelectric and dielectric properties of Dy_2O_3 -doped $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ceramics, *J. Alloys Compd.* 472 (2009) 267–270. doi:10.1016/j.jallcom.2008.04.038.
- [34] X. Wang, H.L.W. Chan, C.L. Choy, Piezoelectric and dielectric properties of CeO_2 -added $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ceramics, *Solid State Commun.* 125 (2003) 395–399. doi:10.1016/S0038-1098(02)00816-5.
- [35] Q.C. Peng Fu, Zhijun Xu, Ruiqing Chu, Wei Li, Qian Xie, Yanjie Zhang, Effect of Dy_2O_3 on the structure and electrical properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free piezoelectric ceramics, *J. Alloys Compd.* 508 (2010) 546–553. doi:10.1016/j.jallcom.2010.08.117.
- [36] Y.J. Dai, S. Zhang, T.R. Shrout, X.W. Zhang, Piezoelectric and ferroelectric properties of Li-doped $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ - BaTiO_3 lead-free piezoelectric ceramics, *J. Am. Ceram. Soc.* 93 (2010) 1108–1113. doi:10.1111/j.1551-2916.2009.03535.x.
- [37] F. Guo, B. Yang, S. Zhang, F. Wu, D. Liu, P. Hu, Y. Sun, D. Wang, W. Cao, Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - $x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition, *Appl. Phys. Lett.* 103 (2013) 182906. doi:10.1063/1.4828675.
- [38] R. Rodríguez-Ruiz, R. González-Ballesteros, a. Flores-Cuautle, E. Suaste-Gómez, Determination of the Pyroelectric Coefficient for $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.935}\text{Ba}_{0.065}\text{TiO}_3$ Piezoelectric Ceramics, *Ferroelectrics.* 368 (2008) 216–223. doi:10.1080/00150190802368537.

- [39] C.P. Shaw, S. Gupta, S.B. Stringfellow, A. Navarro, J.R. Alcock, R.W. Whatmore, Pyroelectric properties of Mn-doped lead zirconate-lead titanate-lead magnesium niobate ceramics, *J. Eur. Ceram. Soc.* 22 (2002) 2123–2132. doi:10.1016/S0955-2219(02)00018-3.
- [40] S.T. Lau, C.H. Cheng, S.H. Choy, D.M. Lin, K.W. Kwok, H.L.W. Chan, Lead-free ceramics for pyroelectric applications, *J. Appl. Phys.* 103 (2008) 10–13. doi:10.1063/1.2927252.

7 Doping B-site of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ with xTa, $0.0 \leq x \leq 1.0$ (%mole).

This chapter is based on a paper published in the Journal of Ceramics International. Please see publication 4 in the publication list.

Abstract

The main objective of this chapter is, by doping Tantalum (Ta), to bring the depolarization temperature (T_d) of NBT-0.06BT down and to observe the pyroelectric properties of these compositions in both room and depolarization temperatures. Ta as B-site dopant was carefully chosen due to that the elements with bigger ionic radius than titanium may move the T_d toward low temperature.

7.1 Experimental

Ta⁵⁺-doped 0.94NBT-0.06BT ceramics were prepared by a solid-state synthesis route. The raw materials used in this project were powders as they previously mentioned before, in addition to tantalum oxide (Ta_2O_3), 99.0%.

The amounts of powders were calculated according to the chemical formula of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3\text{-}x\text{Ta}$, where $x = 0.0\%$ (Sample A), 0.2% (Sample B), 0.5% (Sample C), and 1.0% (Sample D).

7.2 Results and discussion

7.2.1 Effects of Ta on Microstructure

Fig. 7-1 (a) depicts XRD patterns of the Ta-doped NBT-0.06BT ceramics powders calcined at 850 °C for 3 hrs. All samples (A to D) showed a single crystalline perovskite phase without any detectable secondary phase, demonstrating that the Ta⁵⁺ diffused into NBT-0.06BT lattice and formed new NBT-0.06BT-xTa solid solutions. The different contents of the dopant did not cause a significant change to the phase structure of NBT-0.06BT.

The enlargement of the X-ray diffraction spectra of all samples illustrates the splitting in the peak [111] into [003] and [021] at 39.0° - 41.0° (Fig.7-1 (b)), indicating the existence of the rhombohedral phase. The XRD spectra of a pure

NBT presented a rhombohedral symmetry with splitting of the [111] peak into [003]/[021] at 38.0° - 42.0° at room temperature (*RT*) [1,2].

The split of the peak [200] into [200] and [002] at 46°- 48° was observed, which refers to the existence of tetragonal phase in the NBT lattice [2-7] (Fig. 7-1(c)). The coexistence of rhombohedral and tetragonal phases in the NBT-0.06BT-xTa ceramics confirms that all sample structures are at the MPB area. The position of the MPB of perovskite structure, such as NBT-0.06BT, can be determined according to Hiruma *et al.* [8] by calculating Goldschmidt tolerance factor (*t*) of the second part (BaTiO₃) of this composition, and for our Ta-doped sample, by calculating the (x_{MPB}) value of the (BaTaTiO₃) using the equations 1-12 and 1-19 in chapter 1[8–10].

Therefore, the result reveals that the MPB position moves from $x_{MPB} = 0.0600$ in Sample A to $x_{MPB} = 0.0619$ in Sample D, (Table 7-1). These results reveal that Samples C and D may slightly move away from the 0.0600, indicates that the high concentration of the Ta⁵⁺ shifts the MPB position towards Ba-rich end (Table 7-1).

Table 7-1 shows the calculation of the MPB positions, lattice parameters (Å), the *c/a* ratio, the average grain size, samples density, and compare with the theoretical density of undoped and doped samples (A-D). The lattice parameters “*a* = *b*” and “*c*” have been affected by Ta⁵⁺ dopant. The *c* parameter shows an obvious increase from 13.4744 in Sample A to 13.5114 in Sample D. The calculations of the *c/a* ratio reveal that Samples B, C, and D have higher ratio than Sample A, indicating that the doped samples are more tetragonal in the structure than the undoped sample.

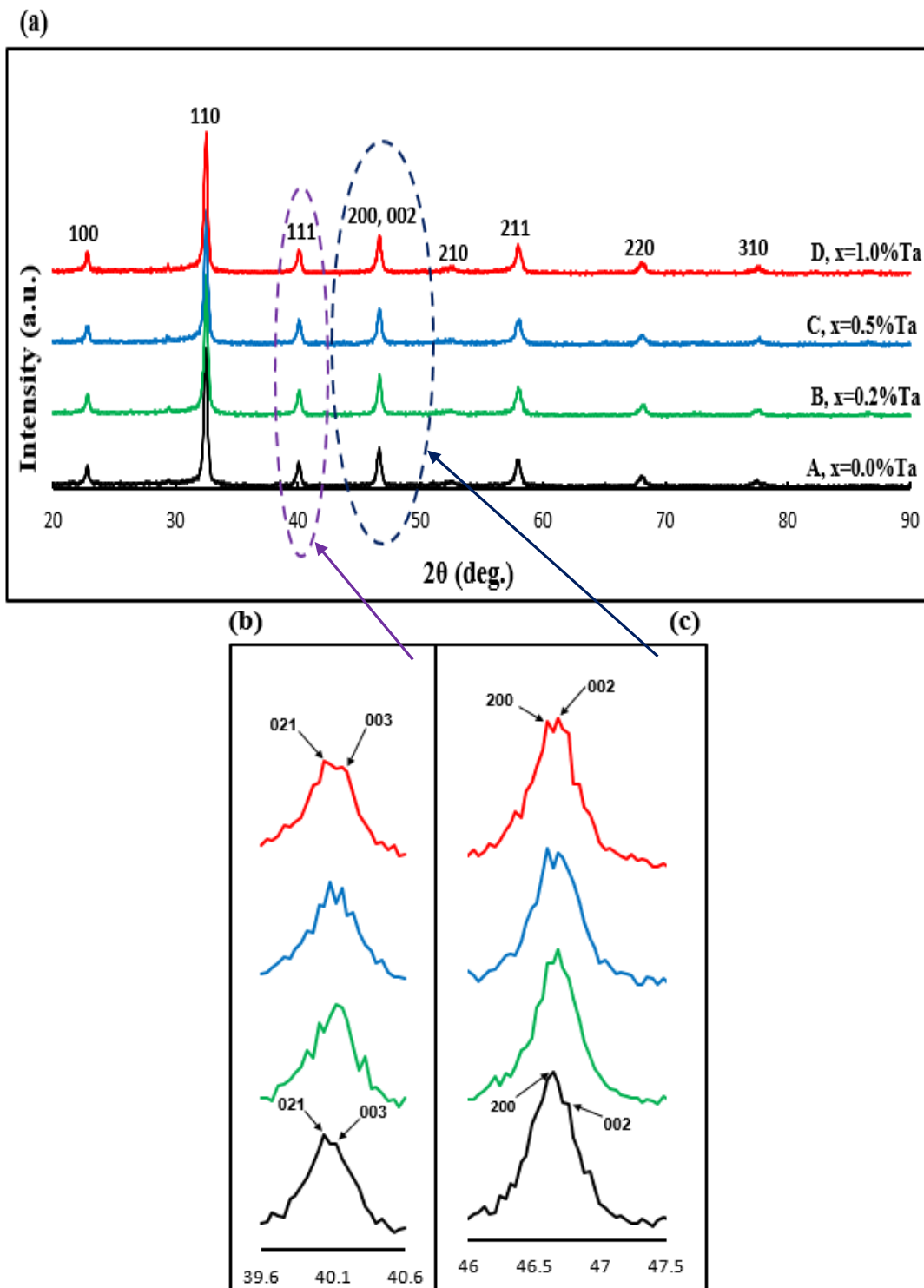


Figure 7-1: (a) X-ray diffraction patterns of NBT-0.06BT- x Ta, $0.0 \leq x \leq 1.0\%$. (b) enlargement of splitting [111] peak into [003] and [021] at $39.6^\circ - 40.6^\circ$. (c) enlargement of splitting [200] peak into [200] and [002] at $46.0^\circ - 47.5^\circ$.

Table 7-1: The positions of the morphotropic phase boundary (*MPB*), the lattice parameters (Å), c/a ratio, the average grain size (μm), samples density (gm.cm⁻³), and comparison with the theoretical density (%) which is (ρ = 6 gm.cm⁻³).

Sample name NBT-0.06BT- xTa (%)	The Morphotropic phase boundary (<i>MPB</i>) position	Lattice parameter (Å)		c/a ratio	Average grain size(μm)	Density(ρ) gm.cm⁻³	Compare with theoretical density%
		a = b	c				
Sample A, 0.0%	0.06	5.511	13.474	2.4449	1.82	5.757	95.95
Sample B, 0.2%	0.0604	5.473	13.490	2.4578	1.78	5.867	97.80
Sample C, 0.5%	0.0609	5.505	13.506	2.4536	1.74	5.872	97.90
Sample D, 1.0%	0.0619	5.500	13.511	2.4601	1.62	5.823	97.00

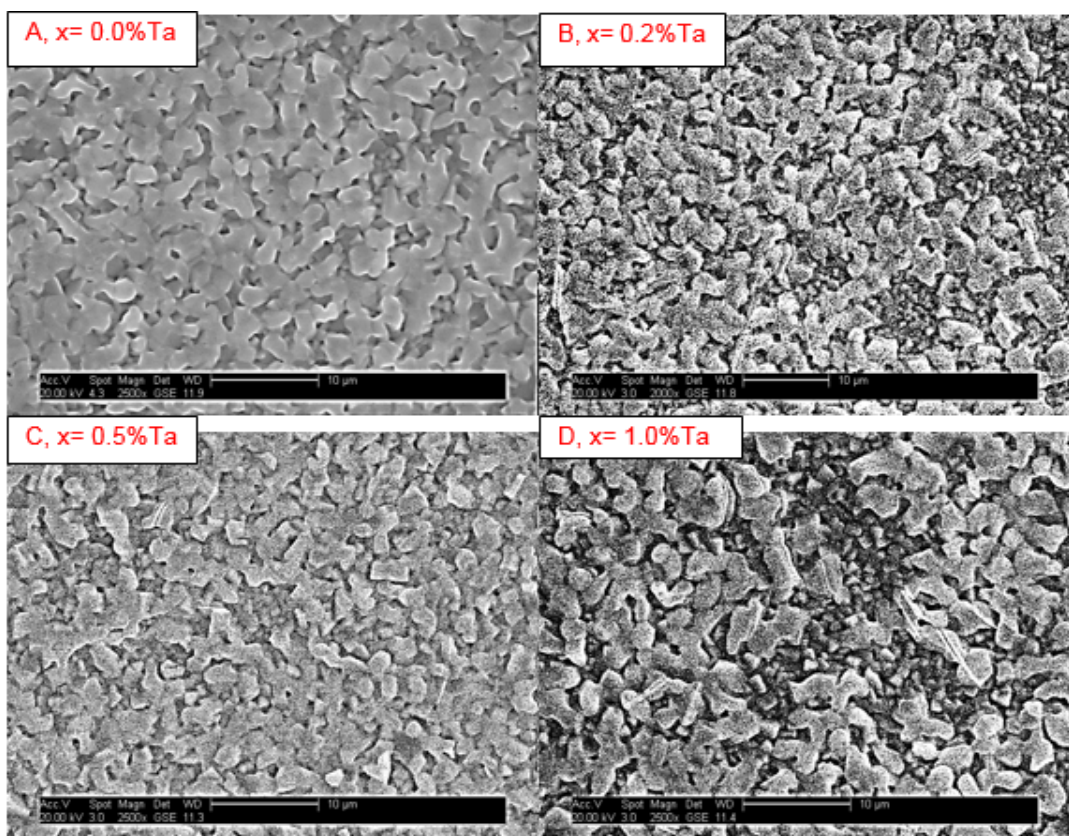


Figure 7-2: SEM surface morphology of the NBT-0.06BT-xTa, $0.0 \leq x \leq 1.0$ % ceramics.

Comparing the ionic radius of Ta^{5+} with the A- and B-sites ionic radii according to the Shannon effective radii and the ionic radius relations [11], the ionic radius of A-site ions are Na^+ (1.39 Å, CN12) (CN=coordination number), Bi^{3+} (1.31 Å, CN12) and Ba^{2+} (1.61 Å, CN12) [12-15]. The B-site ion is Ti^{4+} (0.605 Å, CN6), therefore, it can assume that the Ta^{5+} (0.64 Å, CN6) ions [4,6,7,12,16] substitute the B-site ions of the NBT-0.06BT lattice but not entering A-site because the big radius difference between A-site ions and the Ta^{5+} .

Fig.7-2 shows the scanning electron microscope (SEM) images of the sample surfaces of the NBT-0.06BT-xTa ceramics. All samples display a dense microstructure with an average density around $5.8298 \pm 0.138 \text{ g/cm}^3$. The Samples B, C, and D show a quite similar density, higher than Sample (A).

Sample C presents the highest density value among all other samples (Table 7-1). The average grain size of all samples decreases from $\sim 1.82 \mu\text{m}$ in Sample A to $\sim 1.62 \mu\text{m}$ in Sample D (Table 7-1). The microstructures of Samples B, C, and D become slightly inhomogeneous with increasing the dopant content [16]. The small grains aggregated and were surrounded by large grains.

The reduction of grain size in doped samples is due to the creation of cation vacancies in A-site. Ta^{5+} replaces Ti^{4+} due to the radius analogy. However, there is a valence difference between them. Thus, the Ta^{5+} behaves as a donor, and in order to maintain the charge balance in the system, A-site vacancies form. These A-site vacancies may locate at the grain boundaries due to the thermodynamic stability of the system. The grain growth is restricted by these A-site vacancies. Thus, the Ta^{5+} can act as an inhibitor. As a result doping NBT-BT system with donor elements prevents the growth of the grains [17,18].

7.2.2 Effects of Ta on dielectric properties

Fig. 7-3 (a to d) shows the temperature dependence of the dielectric properties of poled NBT-0.06BT-xTa samples from RT to 150°C at three different frequencies of 1, 10, and 100 kHz. The relative permittivity (ϵ_r) of all samples increases with temperature, which behaves like a typical ferroelectric material [19].

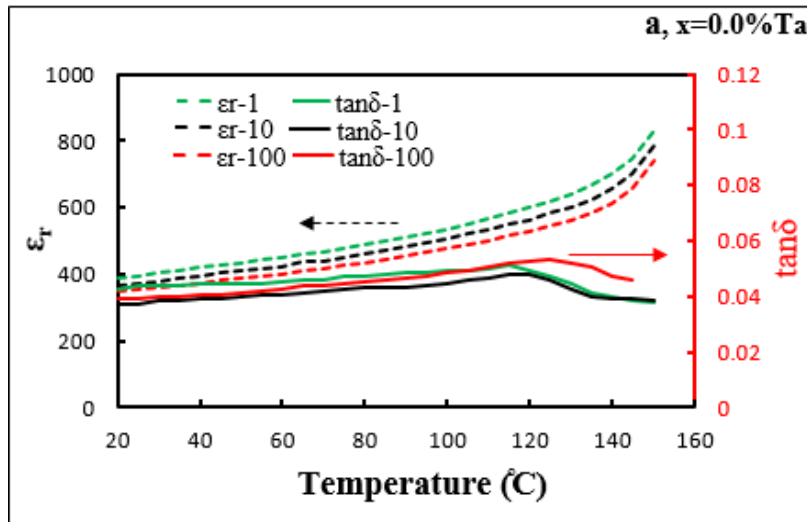
The undoped sample shows a relative permittivity (ϵ_r) value of ~ 396 at RT and at 1 kHz (Fig. 7-3(a)). However, the doped samples (Fig. 7-3 (b to d)) illustrate much higher ϵ_r values that are around 870, 1082 and 1006 for Sample B, C and D respectively.

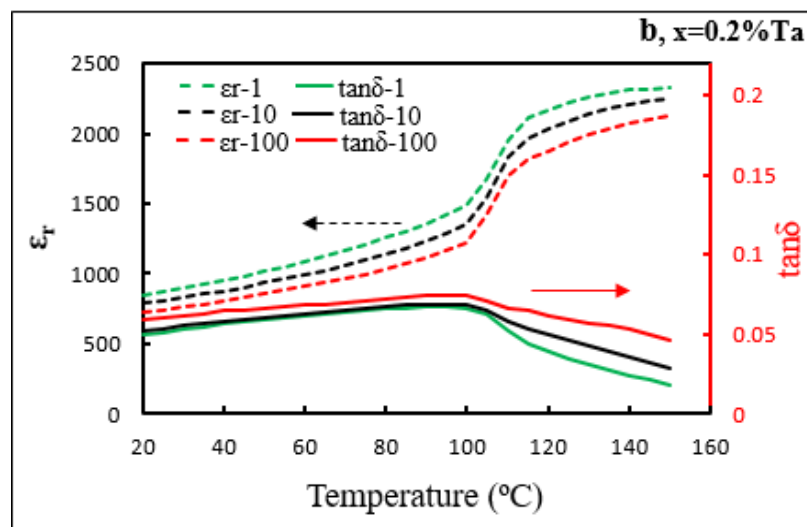
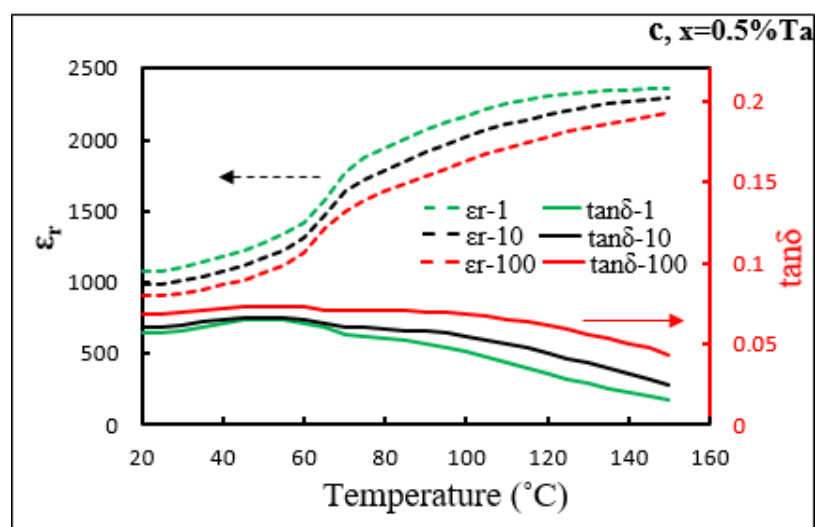
Samples B, C, and D show a sharp increase in ϵ_r with temperature except in Sample A. This sudden rising in ϵ_r starts at $\sim 100^\circ\text{C}$, $\sim 60^\circ\text{C}$, and $\sim 70^\circ\text{C}$ for Samples B, C, and D respectively. The ϵ_r values at these temperatures for the doped samples are around 1487, 1424, and 1367 respectively.

The dielectric loss ($\tan\delta$) of undoped sample is ~ 0.044 at RT and 1 kHz and after doping, it increases to around 0.051, 0.057, and 0.056 for Samples B, C, and D respectively. All doped samples show a close $\tan\delta$ value. With the increase of

temperature, the $\tan\delta$ value increases to the maximum at the temperature widely known as the depolarization temperature (T_d) [3,20,21]. The T_d for Sample A is $\sim 115^\circ\text{C}$ while it is around 90°C , 50°C and 50°C for Samples B, C, and D respectively. The dielectric loss values of Samples A, B, C, and D at T_d are ~ 0.051 , 0.067 , 0.065 , and 0.064 respectively. Obviously, the doped samples show higher $\tan\delta$ values than undoped sample at T_d .

The temperatures that the ϵ_r value shows a sudden increasing (~ 100 , ~ 60 , and $\sim 70^\circ\text{C}$) in Samples B, C, and D are close to the T_d , (90 , 50 and 50°C), which were identified from the $\tan\delta$ peaks. Thus, these temperatures can also be considered as T_d .





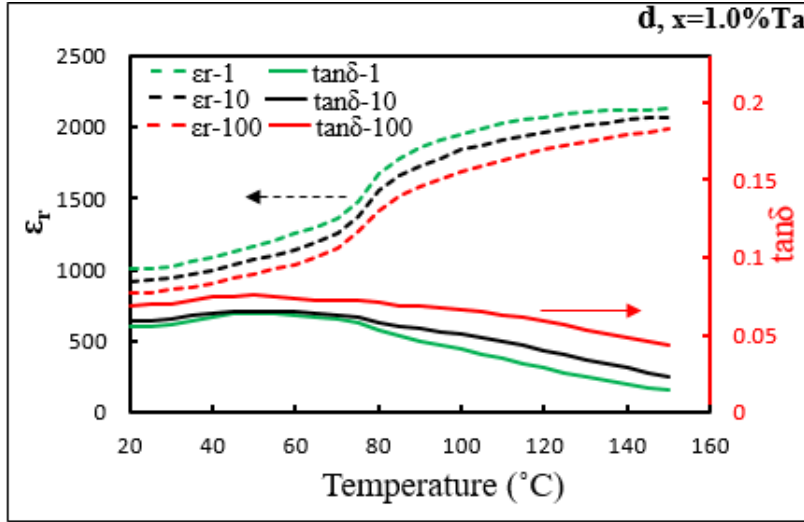


Figure 7-3: The change of the relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) with temperature for Samples A to D at three different frequencies (1, 10, and 100) kHz.

7.2.3 Effects of Ta on depolarization temperature

Depolarization temperature (T_d) is an important parameter in pyroelectric study. Its origin has not been fully understood for NBT-xBT [3,22], and it has a few definitions [9]. One of the definitions is the steep reduction of remnant polarization [3,6]. However, Jo *et al.* reported that the T_d could be the phase transition temperature from ferroelectric to relaxor [23].

In this study, the T_d could be identified by two methods: (1) Dielectric method, the temperature at dielectric peak (Fig. 7-4 (a), and (b)); (2) Pyroelectric method, the temperature at pyroelectric coefficient (p) peak (Table 7-2) [24].

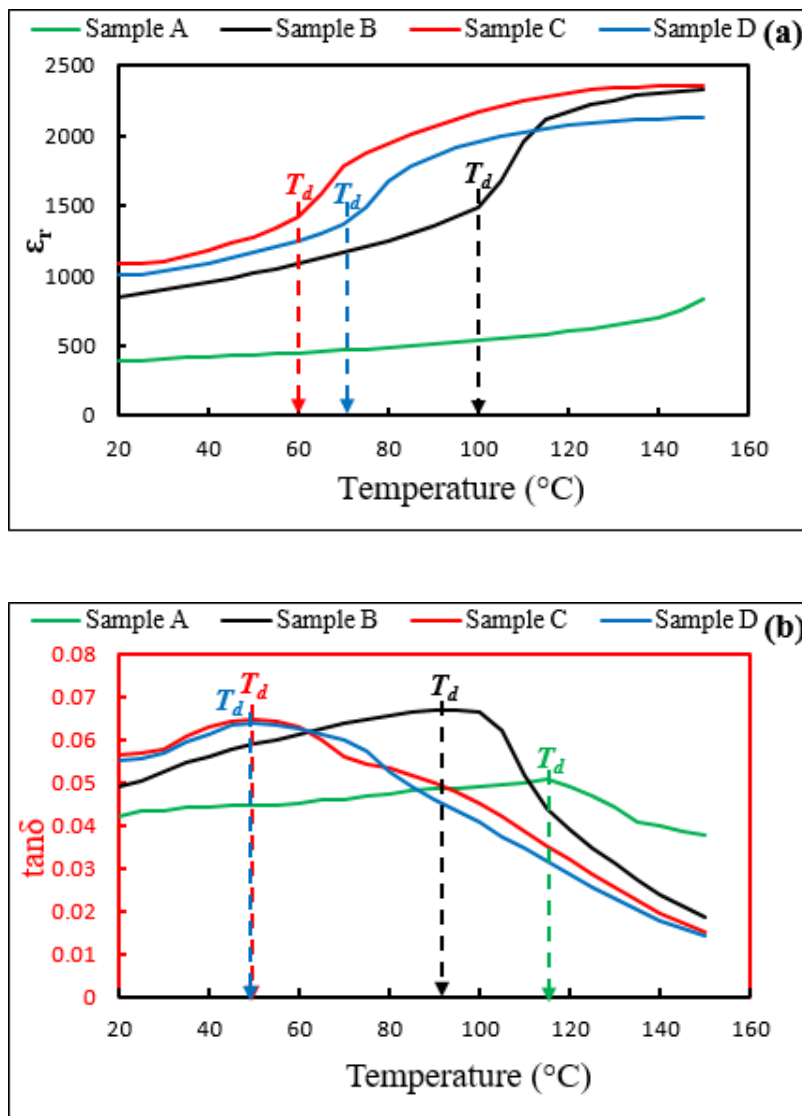


Figure 7-4: The change of the relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) with temperature for Samples A-D at 1 kHz, and the identification of the depolarization temperature (T_d).

The dielectric (permittivity and loss) vs temperature plots in Fig.7-4 reveal that T_d decreased after doping Ta^{5+} from 115°C (Sample A) to around 70°C or 50°C (Sample D) (Fig. 7-4 (a) and (b)).

Table 7-2: The depolarization temperature (T_d) obtained by two methods in this work and others.

Compositions (sample name)	f (kHz)	Dielectric method		Pyroelectric method
		T_d (°C) by ϵ_r	T_d (°C) by $\tan\delta$	
NBT-0.06BT (Sample A)	1	-	115	More than 90
NBT-0.06BT-0.002Ta (Sample B)	1	100	90	78.8
NBT-0.06BT-0.005Ta (Sample C)	1	60	50	49.1
NBT-0.06BT-0.01Ta (Sample D)	1	70	50	56.9

The ϵ_r curves for doped samples show the T_d values at 100 °C, 60 °C and 70 °C in Samples B, C and D respectively; however, it was not identified in Sample A (Fig.7-4 (a)). These depolarization temperatures are slightly higher than the T_d that was identified from the dielectric loss ($\tan\delta$) curves for the same samples (Fig. 7-4 (b)). Sample D shows an abnormal depolarization temperature, which is more than 10 °C higher than the T_d for Sample C whereas it should shift to lower temperature with increasing the dopant content.

The second method to obtain the T_d is from the maximum pyroelectric coefficient values. It is widely known that the maximum p can be achieved at the phase transition temperature [25–28]. NBT-0.06BT shows two phase-transition temperatures. Firstly, at depolarization temperature (T_d) which is between 100 °C - 165 °C [3,28–30]. Secondly, at T_m which is between 225 °C – 292 °C [3,28–30].

In this study, the lower phase transition temperature was utilised to identify the T_d and they were found being 78.8 °C, 49.1 °C, and 56.9 °C for Samples B, C, and D, respectively. Unfortunately, T_d could not be obtained for Sample A by pyroelectric method due to the upper temperature limit of equipment being 90 °C (Table 7-2). In addition, Sample D shows an abnormal T_d , which is more than 8 °C higher than the T_d of Sample C whereas, it should shift toward lower temperature with increasing the Ta content. This can link to the position of the MPB area in this sample, which is moved to 0.0619 (Ba-rich). Thus, the excess in the Ba²⁺ content could be responsible for the shift in T_d value toward higher temperature. Although the MPB of Sample C moves to the Ba-rich end due to the same reason, the MPB position is closer to 0.0600 (Table 7-1).

Comparing the depolarization temperature results obtained by the two methods, the pyroelectric method shows T_d values lower than the dielectric method, which is in agreement with the results reported by Anton *et al.* [3]. Doping the B-site of the NBT-0.06BT with elements which have a bigger ionic radius than Ti⁴⁺ may be responsible for the decrease of the T_d to lower temperature. These elements consumed a larger space in oxygen octahedral than the elements with smaller ionic radii. Therefore, it may reduce the degree of freedom for B-site ion moving in the TiO₆ octahedra. As a result, it weakens the ferroelectric properties [31] of the NBT-0.06BT, and shifts the phase transition from ferroelectric (*FE*) to antiferroelectric (*AFE*) [4,20,22,23,32,33] or intermediate phase [3,30,34] at lower temperature. Thus, undoped NBT-0.06BT [28] showed T_d at higher temperature than B-site doped with bigger radii elements such as NBT-0.06BT-Nd [35]; NBT-0.06Ba(ZrTi)O₃ [33]; NBT-0.06Ba(MnTi)O₃ [36].

7.2.4 Effects of Ta on pyroelectric properties

Pyroelectric coefficient (p) is defined as the change in the spontaneous polarization by fluctuations in temperature [37]. In addition, its value at certain temperature is considered as one of the important parameters while selecting the material for pyroelectric applications. However, the efficient way for evaluating the pyroelectric material performance can be achieved by calculating the figure

of merits (*FOMs*) that represent the essential parameters for the pyroelectric applications [3].

The calculation of the *FOMs* is based on the values of the pyroelectric coefficient, relative dielectric permittivity, dielectric loss and the specific heat [37]. There are several types of *FOMs* depending on special types of the pyroelectric applications such as infrared or thermal imaging [7,34].

The types of *FOMs* depend on the input of thermal or electrical circuits, current or voltage. Therefore, for infrared applications that rely on the current responsivity, F_i is the relevant *FOM*. Similarly, to enlarge the pyroelectric voltage, the more suitable *FOM* is F_v that characterizes to the high voltage (v) detectivity. Likewise, F_D is the *FOM* of the high and specific detectivity. F_C is a *FOM* of the infrared detector materials. These figure-of-merits have been used to characterize and select the materials for thermal and infrared applications as sensors or transducers [2,24,38].

In this study, the pyroelectric coefficient (p) of NBT-0.06BT- x Ta was measured from RT to T_d for doped samples (B, C, and D) or 90 °C for undoped Sample (A).

The measurements of the pyroelectric coefficient (p) and *FOMs* were carried out using the Equations 1-14 to 1-18 in chapter 1 [5,39,40].

Fig. 7-5 shows the change of p vs. temperature for NBT-0.06BT- x Ta at a wide temperature range from RT to 90 °C. Sample B ($x=0.2$ %) shows the highest p at RT (Table 7-3). At a temperature range from 30 °C to 52 °C, Sample C ($x=0.5$ %) presents the highest pyroelectric coefficient of $\sim 109.0 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ at T_d (~ 49.1 °C). At temperature range between 53 °C to 60 °C, Sample D ($x=1.0$ %) shows a highest p value which is around $76.1 \times 10^{-4} \text{ C. m}^{-2} \cdot ^\circ\text{C}^{-1}$, at T_d (~ 56.9 °C). At temperature range from 60 °C up to 90 °C Sample B illustrates the maximum pyroelectric coefficient value which is around $146.1 \times 10^{-4} \text{ C. m}^{-2} \cdot ^\circ\text{C}^{-1}$, at T_d (~ 78.8 °C).

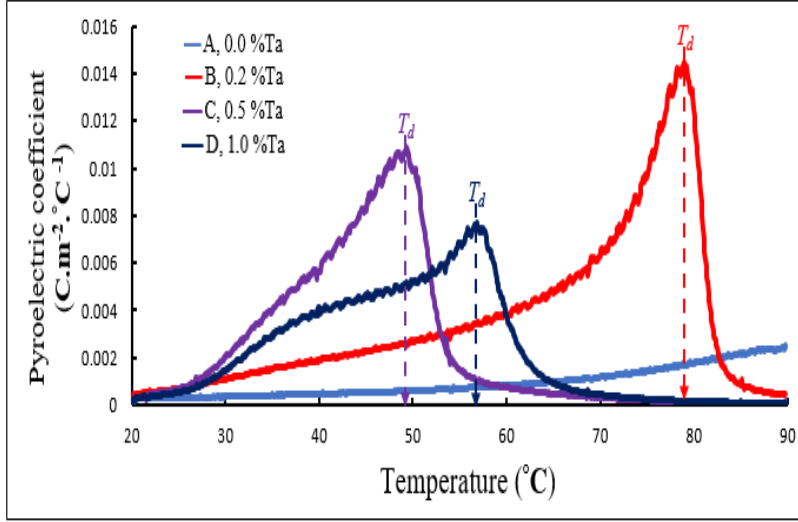


Figure 7-5: The change of pyroelectric coefficient (p) as a function of Ta5+ content and temperature ($^{\circ}\text{C}$) for the NBT-0.06BT- x Ta, $0.0 \leq x \leq 1.0$ %.

Table 7-3 and 7-4 list the pyroelectric coefficient(p) values and FOMs of all samples at RT and T_d respectively. The p increased from Sample A to Sample D at RT and a huge increase at T_d . Sample B shows the maximum p value at RT and T_d , which may link to two factors: (1) the microstructure changes of this sample. The measurement of c/a ratio reveals that Sample B has a bigger ratio (~ 2.4578) than Sample C (~ 2.4536), which means that Sample B is more tetragonal in its structure than Sample C. (2) the position of the MPB in the composition of this sample. The tolerance factor calculation reveals that the x_{MPB} value is 0.0604 which means that the composition of Sample B is in the MPB area. The huge improvements in the p values at T_d may be attributed to the positive correlation between the pyroelectric coefficient (p) and pyroelectric current (I_p), which reaches the maximum at T_d . In pyroelectric materials, the increase of temperature will alter the lattice spacing of the nonsymmetrical ions location, which varies the spontaneous polarization of the pyroelectric material. The variation of the spontaneous polarization generates the I_p [36]. So the optimum current (I_p) and coefficient (p) values appear at T_d because the maximum change of the spacing appears at T_d [36].

Furthermore, the great increase in p at T_d for Sample B may be because the composition of this sample is at MPB, which makes the reorientation of ferroelectric domains easier and results in a sharp change in polarization. This effect appears gradually but with the highest value at T_d . Thus, the pyroelectric coefficient shows a great enhancement at this temperature [12]. It has been reported that the optimum pyroelectric coefficient value of (1-x)NBT-xBT materials can be achieved at phase transition temperature [21,28,34,41]. Hence, the ultimate p values obtained at T_d in this study relates to the phase transition. The T_d coincides with the phase transition temperature as mentioned before. At RT, the p values for doped samples are higher than that of PZT and other lead-free compositions (Tables 7-3 and 7-4) [3,6,9,42].

The FOM, F_i values of the NBT-0.06BT-xTa samples at RT and 90 °C or T_d are listed in Tables 3 and 4. The F_i values increased from Samples A to D at RT. While Sample B ($x = 0.2 \%$) presents the highest value (Table 3). The comparison between the F_i values at RT and value of PZT and other lead-free compositions [27] reveal that the doped Samples have higher F_i values than other lead-free compositions as well as PZT at RT (Table 3). F_i values show further improvement for all samples at 90°C or T_d .

The F_v increases with Ta^{5+} content and reaches a maximum at $x=0.2\%$ at RT. Table 4 presents the F_v results at 90°C or T_d . The F_v values increase for Sample A to Sample D. Sample B also presents the best F_v value at T_d . Again, the F_v values for all samples in this study are higher than that of PZT and other lead-free compositions [5,43].

The F_D results show poor values at both RT and T_d . The lower F_D values for doped samples may be related to the higher values of both relative permittivity and the dielectric loss that are higher than the undoped sample, though pyroelectric coefficient values of Samples B, C, and D were quite higher than Sample A value.

Table 7-5 illustrates the F_C values of the NBT-0.06BT-xTa, at RT and at three frequencies, 33, 0.1, 1000 (Hz). The F_C values revealed a strong dependence upon Ta^{5+} dopant content. In general, the materials suitable for infrared detectors

should have the F_C threshold value at $\sim 3 \pm 1 \times 10^{-9} \text{ C. cm}^{-2} \cdot ^\circ\text{C}^{-1}$ [39]. The F_C of only NBT-0.06BT-0.002Ta (Sample B) shows the suitable values for infrared detectors. Rodríguez-Ruiz *et al.* [39]. investigated the pyroelectric coefficient of $0.935\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.065BaTiO_3 ceramics and calculated the F_C of this material that equals to $1.44 \times 10^{-9} \text{ C.cm}^{-2} \cdot ^\circ\text{C}^{-1}$. The high F_C values for Sample B are due to the high p and the lower relative permittivity at RT.

Table 7-3: The pyroelectric coefficient and FOMs F_i , F_v , and F_D results of the NBT-0.06BT-xTa, $0.0 \leq x \leq 1.0$ %, at RT in the present work and in literature.

Composition	$p \times 10^{-4} (\text{C.m}^{-2} \cdot ^\circ\text{C}^{-1})$ at RT	$F_i \times 10^{-10} (\text{m.V}^{-1})$ at RT	$F_v (\text{m}^2 \cdot \text{C}^{-1})$ at 1kHz at RT	$F_D \times 10^{-6} (\text{Pa}^{-1/2})$ at 1kHz at RT
NBT-0.06BT	3.14	1.12	0.021	9.08
NBT-0.06BT- 0.002Ta	7.14	2.55	0.033	1.29
NBT-0.06BT- 0.005Ta	6.97	2.43	0.025	1.04
NBT-0.06BT- 0.01Ta	5.32	1.90	0.021	0.85
PZT	4.14	1.415	0.008	9.01
NBT-0.07BZT	5.7	2.03	0.0218	10.5
NBT-0.06BT- 0.002Mn	3.5	-	-	-
BNKBT	3.25	1.95	0.026	13.43
KNLNTS	1.9	0.931	0.007	11.5
NKLBT-0.05BT	3.6	1.27	0.017	-

Table 7-4: The pyroelectric coefficient and FOMs F_i , F_v , and F_D results of the NBT-0.06BT-xTa, $0.0 \leq x \leq 1.0$ %, at 90 °C or T_d in the present work and in literature.

Composition	$p \times 10^{-4}$ (C.m ⁻² .°C ⁻¹) at 90°C or T_d	$F_i \times 10^{-10}$ (m.V ⁻¹) at 90°C or T_d	F_v (m ² .C ⁻¹) at 1kHz at 90°C or T_d	$F_D \times 10^{-6}$ (Pa ^{-1/2}) at 1kHz at 90°C or T_d
NBT-0.06BT	23.9 at 90 °C	8.6 at 90 °C	0.19 at 90 °C	65.5 at 90 °C
NBT-0.06BT- 0.002Ta	146.1 at 79°C	52.2 at 79 °C	0.48 at 79 °C	19.7 at 79 °C
NBT-0.06BT- 0.005Ta	109.0 at 49 °C	38.0 at 49 °C	0.34 at 49°C	14.0 at 49 °C
NBT-0.06BT- 0.01Ta	76.1 at 57 °C	27.2 at 57 °C	0.25 at 57 °C	10.4 at 57 °C
NBT-0.07BZT	20.0 at 50°C	7.33 at 50 °C	0.066 at 50 °C	33.6 at 50 °C
NBT-0.07BZT	221 at 87 °C	-	-	-

Table 7-5: The figure of merit, F_c in different frequencies 33, 100, and 1 Hz at RT.

Sample name NBT-0.06BT-xTa%	FOM, F_c (x10 ⁻⁹ C. cm ⁻² °C ⁻¹) at RT		
	33Hz	0.1Hz	1kHz
Sample A, 0.0%	-	1.53	1.58
Sample B, 0.2%	2.26	2.31	2.42
Sample C, 0.5%	1.93	1.97	2.10

Sample D, 1.0%	1.56	1.60	1.68
-----------------------	------	------	------

7.3 Conclusion

The NBT-0.06BT-xTa ceramics were synthesized by a conventional solid-state route. The pyroelectric properties of these materials were investigated and compared with undoped NBT-0.06BT, other lead-free and PZT ceramics.

The XRD study proves that the compositions of the undoped and doped are both at or near the MPB region. The lattice parameter values and c/a ratio slightly change with increasing the dopant content. The SEM investigation shows the average grain size reduced from 1.82 to 1.62 (μm) with increasing the Ta^{5+} content. Moreover, the doped samples present higher density than the undoped sample. Both relative permittivity (ϵ_r) and dielectric loss ($\tan\delta$) increase with Ta content.

The T_d was identified by two different methods and decreased from $\sim 115^\circ\text{C}$ in undoped Sample A to around 70°C (from ϵ_r) or 50°C (from $\tan\delta$) in doped Sample D, according to the dielectric method. However, the T_d values for Samples B, C, and D, are 78.8 , 49.1 , and 56.9°C respectively according to pyroelectric coefficient method.

Sample B has the optimum p at RT and at T_d . The F_i and F_v increase with the increase of Ta^{5+} content up to $x = 0.2\%$ at both RT and at T_d in a wide range of frequency. The F_c shows higher values in Sample B. Results presented in this work demonstrate that NBT-0.06-xTa ceramics at $0.2\% \leq x \leq 0.5\%$ are promising materials for infrared detectors and other pyroelectric applications in a wide temperature.

7.4 References

- [1] M. Chen, Q. Xu, B.H. Kim, B.K. Ahn, J.H. Ko, W.J. Kang, O.J. Nam, Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ piezoelectric

- ceramics, J. Eur. Ceram. Soc. 28 (2008) 843–849. doi:10.1016/j.jeurceramsoc.2007.08.007.
- [2] Q. Li, H. Wang, H. Fan, C. Long, X. Liu, Ferroelectric, electromechanical, and dielectric properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ co-doped MnO_2 and La_2O_3 lead-free ceramics, J. Mater. Sci. 49 (2013) 211–217. doi:10.1007/s10853-013-7694-x.
- [3] E.M. Anton, W. Jo, D. Damjanovic, J. Rdel, Determination of depolarization temperature of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based lead-free piezoceramics, J. Appl. Phys. 110 (2011) 1–14. doi:10.1063/1.3660253.
- [4] P. Fu, Z. Xu, R. Chu, W. Li, G. Zang, J. Hao, Piezoelectric, ferroelectric and dielectric properties of La_2O_3 -doped $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ceramics, Mater. Des. 31 (2010) 796–801. doi:10.1016/j.matdes.2009.07.056.
- [5] F.L. Martínez, J. Hinojosa, G. Doménech, F.J. Fernández-luque, J. Zapata, R. Ruiz, L. Pardo, Dielectric Constant Tunability at Microwave Frequencies and Pyroelectric Behavior, IEEE Trans. Ultrason. Ferroelectr. Freq. Control. 60 (2013) 1595–1602. doi:10.1109/TUFFC.2013.2740.
- [6] C. Xu, D. Lin, K.W. Kwok, Structure, electrical properties and depolarization temperature of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{--BaTiO}_3$ lead-free piezoelectric ceramics, Solid State Sci. 10 (2008) 934–940. doi:10.1016/j.solidstatesciences.2007.11.003.
- [7] Q. Xu, D.P. Huang, M. Chen, W. Chen, H.X. Liu, B.H. Kim, Effect of bismuth excess on ferroelectric and piezoelectric properties of a $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{--BaTiO}_3$ composition near the morphotropic phase boundary, J. Alloys Compd. 471 (2009) 310–316. doi:10.1016/j.jallcom.2008.03.078.
- [8] Y. Hiruma, H. Nagata, T. Takenaka, Formation of Morphotropic Phase Boundary and Electrical Properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--Ba}(\text{Al}_{1/2}\text{Nb}_{1/2})\text{O}_3$ Solid Solution Ceramics, Jpn. J. Appl. Phys. 48 (2009) 09KC08. doi:10.1143/JJAP.48.09KC08.
- [9] J.-H. Cho, Y.-H. Jeong, J.-H. Nam, J.-S. Yun, Y.-J. Park, Phase transition and piezoelectric properties of lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--BaTiO}_3$ ceramics, Ceram. Int. 40 (2014) 8419–8425.

doi:10.1016/j.ceramint.2014.01.051.

- [10] F. Le Goupil, J. Bennett, A.K. Axelsson, M. Valant, A. Berenov, A.J. Bell, T.P. Comyn, N.M. Alford, Electrocaloric enhancement near the morphotropic phase boundary in lead-free NBT-KBT ceramics, *Appl. Phys. Lett.* 107 (2015) 103–107. doi:10.1063/1.4934759.
- [11] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, *Acta Crystallogr. Sect. A.* 32 (1976) 751–767. doi:10.1107/S0567739476001551.
- [12] K.A. Razak, C.J. Yip, S. Sreekantan, Synthesis of (Bi_{0.5}Na_{0.5})TiO₃ (BNT) and Pr doped BNT using the soft combustion technique and its properties, *J. Alloys Compd.* 509 (2011) 2936–2941. doi:10.1016/j.jallcom.2010.11.163.
- [13] L.Y. Liu, M.K. Zhu, Y.D. Hou, H. Yan, R.P. Liu, Abnormal piezoelectric and dielectric behavior of 0.92Na(0.5)Bi(0.5)TiO₃-0.08BaTiO₃ induced by La doping, *J. Mater. Res.* 22 (2007) 1188–1192. doi:10.1557/Jmr.2007.0173.
- [14] C. Ma, X. Tan, Phase diagram of unpoled lead-free – ceramics, *Solid State Commun.* 150 (2010) 1497–1500. doi:10.1016/j.ssc.2010.06.006.
- [15] R. McQuade, M.R. Dolgos, A review of the structure-property relationships in lead-free piezoelectric (1-x)Na_{0.5}Bi_{0.5}TiO₃-(x)BaTiO₃, *J. Solid State Chem.* (2016) 0–19. doi:10.1016/j.jssc.2016.01.008.
- [16] N. Petnoi, P. Bomlai, S. Jiansirisomboon, A. Watcharapasorn, Effects of Nb-doping on the micro-structure and dielectric properties of (Bi_{0.5}Na_{0.5})TiO₃ ceramics, *Ceram. Int.* 39 (2013) S113–S117. doi:10.1016/j.ceramint.2012.10.045.
- [17] P. Guggilla, A.K. Batra, J.R. Currie, M.D. Aggarwal, M.A. Alim, R.B. Lal, Pyroelectric ceramics for infrared detection applications, *Mater. Lett.* 60 (2006) 1937–1942. doi:10.1016/j.matlet.2005.05.086.
- [18] M.R. Islam, R.H. Galib, A. Sharif, M. Hasan, M.A. Zubair, M.F. Islam, Correlation of charge defects and morphology with magnetic and electrical properties of Sr and Ta codoped BiFeO₃, *J. Alloys Compd.* 688 (2016) 1186–1194. doi:10.1016/j.jallcom.2016.07.134.

- [19] P. Guggilla, A.K. Batra, D. Aggarwal, B. Penn, R.B. Lal, Pyroelectric Ceramics for Infrared Detection Applications, (n.d.).
- [20] Y. Guo, M. Gu, H. Luo, Antiferroelectric phase and pyroelectric response in $(\text{Na}_{1-x}\text{Bi}_x)\text{TiO}_3$ ceramics, *J. Am. Ceram. Soc.* 94 (2011) 1350–1353. doi:10.1111/j.1551-2916.2011.04509.x.
- [21] W. Jo, J. Daniels, D. Damjanovic, W. Kleemann, J. Rödel, Two-stage processes of electrically induced-ferroelectric to relaxor transition in $0.94(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – 0.06BaTiO_3 , *Appl. Phys. Lett.* 102 (2013) 0–4. doi:10.1063/1.4805360.
- [22] E. Sapper, S. Schaab, W. Jo, T. Granzow, J. Rödel, Influence of electric fields on the depolarization temperature of Mn-doped $(1-x)\text{Bi}_{1/2}\text{Na}_{1/2}\text{TiO}_3$ – $x\text{BaTiO}_3$, *J. Appl. Phys.* 111 (2012) 14105. doi:10.1063/1.3674275.
- [23] S. Zhang, A.B. Kouna, E. Aulbach, W. Jo, T. Granzow, H. Ehrenberg, J. Rödel, Lead-free piezoceramics with giant strain in the system $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ – BaTiO_3 – $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$. II. Temperature dependent properties, *J. Appl. Phys.* 103 (2008) 34108. doi:10.1063/1.2838476.
- [24] M. Abo, Jiro Kobune, T. Nishimura, T. Yazaw, Y. Nakai, Effects of manganese addition on pyroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)_{0.94}(\text{BaTiO}_3)_{0.06}$ ceramics, *Integr. Ferroelectr.* 80 (2006) 87–95. doi:10.1080/10584580600656502.
- [25] S. Anem, K.S. Rao, K.H. Rao, Investigation of lanthanum substitution in lead-free BNBT ceramics for transducer applications, *Ceram. Int.* (2016). doi:10.1016/j.ceramint.2016.06.173.
- [26] W.-S. Kang, S.-K. Lee, J.-H. Koh, AC conductivity and dielectric properties of $(\text{Bi},\text{Na})\text{TiO}_3$ – BaTiO_3 lead free ceramics, *Ceram. Int.* 41 (2015) 6925–6932. doi:10.1016/j.ceramint.2015.01.147.
- [27] X. Wang, X. Tang, H. Chan, Electromechanical and ferroelectric properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ – $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ – BaTiO_3 lead-free piezoelectric ceramics, *Appl. Phys. Lett.* 85 (2004) 91. doi:10.1063/1.1767592.
- [28] Z. Yao, R. Chu, Z. Xu, J. Hao, W. Li, G. Li, Processing and enhanced electrical properties of $\text{Sr}_{1-x}(\text{K}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_2\text{Nb}_2\text{O}_9$ lead-free piezoelectric ceramics, *Ceram. Int.* 42 (2016) 10619–10623.

- doi:10.1016/j.ceramint.2016.03.156.
- [29] J. Rödel, W. Jo, K.T.P. Seifert, E.M. Anton, T. Granzow, D. Damjanovic, Perspective on the development of lead-free piezoceramics, *J. Am. Ceram. Soc.* 92 (2009) 1153–1177. doi:10.1111/j.1551-2916.2009.03061.x.
 - [30] Y. Hiruma, K. Yoshii, H. Nagata, T. Takenaka, Investigation of Phase Transition Temperatures on $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 Lead-free Piezoelectric Ceramics by Electrical Measurements, *Ferroelectrics*. 346 (2007) 114–119. doi:10.1080/00150190601180471.
 - [31] W. Jo, J.E. Daniels, J.L. Jones, X. Tan, P. a. Thomas, D. Damjanovic, J. Rödel, Evolving morphotropic phase boundary in lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 piezoceramics, *J. Appl. Phys.* 109 (2011) 14110. doi:10.1063/1.3530737.
 - [32] N.B. Do, H.B. Lee, C.H. Yoon, J.K. Kang, J.S. Lee, I.W. Kim, Effect of Ta-Substitution on the Ferroelectric and Piezoelectric Properties of $\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{TiO}_3$ Ceramics, *Trans. Electr. Electron. Mater.* 12 (2011) 64–67. doi:10.4313/TEEM.2011.12.2.64.
 - [33] R. Ranjan, A. Dviwedi, Structure and dielectric properties of $(\text{Na}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$: $0 \leq x \leq 0.10$, *Solid State Commun.* 135 (2005) 394–399. doi:10.1016/j.ssc.2005.03.053.
 - [34] X.J. Li, Z.Z. Xi, W. Long, P.Y. Fang, Synthesis of antiferroelectric $(\text{Bi}_{0.534}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ ceramics with high phase transition temperature and broad temperature range by a solid-state reaction method, *Chinese Sci. Bull.* 58 (2013) 2893–2897. doi:10.1007/s11434-013-5972-2.
 - [35] Q. Li, J. Wang, L. Ma, H. Fan, Z. Li, Large electrocaloric effect in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ferroelectric ceramics by La_2O_3 addition, *Mater. Res. Bull.* 74 (2016) 57–61. doi:10.1016/j.materresbull.2015.10.010.
 - [36] S. Patel, A. Chauhan, S. Kundu, N.A. Madhar, B. Llahi, R. Vaish, K.B.R. Varma, Tuning of dielectric, pyroelectric and ferroelectric properties of $0.715\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - 0.065BaTiO_3 - 0.22SrTiO_3 ceramic by internal

- clamping, *AIP Adv.* 5 (2015) 87145. doi:10.1063/1.4929328.
- [37] M.S. Yoon, N.H. Khansur, S.C. Ur, The effect of pre-milling/pre-synthesis process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized $0.94[(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3]-0.06[\text{Ba}(1+x)\text{TiO}_3]$, *Ceram. Int.* 36 (2010) 1265–1275. doi:10.1016/j.ceramint.2010.01.011.
- [38] S.T. Lau, C.H. Cheng, S.H. Choy, D.M. Lin, K.W. Kwok, H.L.W. Chan, Lead-free ceramics for pyroelectric applications, *J. Appl. Phys.* 103 (2008) 10–13. doi:10.1063/1.2927252.
- [39] R. Rodríguez-Ruiz, R. González-Ballesteros, a. Flores-Cuautle, E. Suaste-Gómez, Determination of the Pyroelectric Coefficient for $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.935}\text{Ba}_{0.065}\text{TiO}_3$ Piezoelectric Ceramics, *Ferroelectrics*. 368 (2008) 216–223. doi:10.1080/00150190802368537.
- [40] R.L. Byer, C.B. Roundy, Pyroelectric coefficient direct measurement technique and application to a nsec response time detector, *IEEE Trans. Sonics Ultrason.* 19 (1972) 333–338. doi:10.1109/T-SU.1972.29679.
- [41] F. Craciun, C. Galassi, R. Birjega, Electric-field-induced and spontaneous relaxor-ferroelectric phase transitions in $(\text{Na}_{1/2}\text{Bi}_{1/2})_{1-x}\text{Ba}_x\text{TiO}_3$, *J. Appl. Phys.* 112 (2012). doi:10.1063/1.4770326.
- [42] F. Guo, B. Yang, S. Zhang, F. Wu, D. Liu, P. Hu, Y. Sun, D. Wang, W. Cao, Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition, *Appl. Phys. Lett.* 103 (2013) 182906. doi:10.1063/1.4828675.
- [43] F. Guo, B. Yang, S. Zhang, F. Wu, D. Liu, P. Hu, Y. Sun, D. Wang, W. Cao, Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition, *Appl. Phys. Lett.* 103 (2013) 182906. doi:10.1063/1.4828675.

8 Co-doping A and B sites of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 with different concentrations of xLa and yTa.

This chapter is divided into two sections:

- A. Doping the $x\text{La-NBT-0.06BT-yTa}$ with various concentrations of lanthanum, $0.0 \leq x \leq 1.0$ (%mole); but the tantalum content is fixed on $y=0.2$ (%mole).
- B. Doping the $x\text{La-NBT-0.06BT-yTa}$ with altered concentrations of tantalum, $(0.0 \leq y \leq 1.0 \text{ (%mole)})$, while the content lanthanum is specified on $x = 0.5$ (%mole).

Abstract

The aim of the present chapter is to improve the pyroelectric properties of NBT-0.06BT by co-doping the A&B sites with different concentrations of La^{3+} and Ta^{5+} at both RT and T_d , and at the same time to bring the depolarization temperature down these compositions to around RT.

8.1 (A) Co-doping A&B sites of NBT-0.06BT with different concentrations of lanthanum oxide ($x\text{La}_2\text{O}_3$), $0.0 \leq x \leq 1.0$ and tantalum oxide ($y\text{Ta}_2\text{O}_3$) is $y=0.2$.

This part of is based on a paper published in the Journal of Alloys and Compounds. Please see publication 5 in the publication list.

8.1.1 Experimental

La^{3+} and Ta^{5+} doped 0.94NBT-0.06BT (NBT-0.06BT) ceramics were prepared by a solid-state synthesis technique. The raw materials used in this study were lithium oxide (La_2O_3), 99.5%, tantalum oxide (Ta_2O_3), 99.0%, bismuth oxide (Bi_2O_3), 99.999%, sodium carbonate (Na_2CO_3), 99.5%, barium carbonate (BaCO_3), 99.98%, and Titanium dioxide (TiO_2), 99.8% (all Sigma- Aldrich).

The amounts of powders were calculated according to the chemical formula $x\text{La}_2\text{O}_3$ - $0.94(\text{Na Bi})_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 - $y\text{Ta}_2\text{O}_3$, where $x = y = 0.0\%$ (Sample A);

$x = y = 0.2\%$ (Sample B); $x = 0.5\%$, $y = 0.2\%$ (Sample C); and $x = 1.0\%$, $y = 0.2\%$ (Sample D).

8.1.2 Results and discussion

8.1.2.1 Effects of Ta and La On Microstructure

Fig. 8-1 (a) depicts XRD patterns of the doped NBT-0.06BT ceramic powders calcined at 850 °C for 3 hrs. All samples (A-D) show a single perovskite phase without any detectable secondary phase, demonstrating that both dopants (La^{3+} and Ta^{5+}) diffused into NBT-0.06BT main lattice and formed new $x\text{La-NBT-0.06BT-yTa}$, solid solutions. The different concentrations of the dopant did not cause a significant change to the phase structure of NBT-0.06BT.

Fig. 8-1 (b) shows a split of the peak [111] into [003] and [021] at 39.0° to 41.0° for all the samples indicating the existence of rhombohedral (*Rh*) phase. This split is in agreement with the phase structure of undoped NBT [1,2]. Another split was observed in [200] into [200] and [002] at 46.0°- 47.5°, which indicates the existence of tetragonal (*Tr*) phase in NBT lattice (Fig. 8-1 (c)). The coexistence of both *Rh* and *Tr* phases in $x\text{La-NBT-0.06BT-yTa}$ ceramics verifies that all the compositions are at morphotropic phase boundary (*MPB*) region. In undoped NBT-*x*BT the co-existence of *Rh* and *Tr* at $x = 0.06\text{-}0.07$ was reported in literature [3-5]. Thus, the phase structure of the doped $x\text{La-NBT-0.06BT-yTa}$ (Samples B, C, and D) are remained in the MPB and consistent with that reported in literature [3-7].

According to Shannon effective radii [8], for the comparison between the La^{3+} and the Ta^{5+} ionic radius with the A-site Na^+ (1.39 Å, CN12) (CN=coordination number), Bi^{3+} (1.31 Å, CN12) and Ba^{2+} (1.61 Å, CN12) [9-12]. And B-site Ti^{4+} (0.605 Å, CN6) ionic radii, it can be assumed that the La^{3+} (1.36 Å, CN12) may substitute A-site ions due to the radius similarity. While, the Ta^{5+} (0.64 Å, CN6) ions [13-14] can substitute the B-site ions of the NBT-0.06BT.

The calculation of the Goldschmidt tolerance factor (*t*) [15] which helps to determine the stability of the perovskite structure by using Equations 1-12 in chapter 1 [6,7,15,16]:

The t value of stable perovskite structures is in the range of 0.77-0.99 [16]. The calculated t values for all samples compositions in this study is around 0.976, which means that all samples compositions illustrate stable structure.

Table 8-1 illustrates the lattice parameters ($\text{\AA}$), c/a ratio and average grain size of all samples. The lattice parameters “ $a=b$ ” and “ c ” are affected by La^{3+} and Ta^{5+} doped. The c parameter shows a clear increase from Sample A to Sample D (Table 8-1). The calculations of the c/a ratio reveal that the doped samples (B, C, and D) have higher ratio than undoped sample (A), indicating that Samples B, C, and D have more tetragonality in their structure.

Fig. 8-2 shows the SEM morphology of the ceramic samples. In general samples A-D show quite dense structures with a few observable pores in Sample A, which appear to diminish with increased doping and further densification. Sample A presents two distinguishable granular and rod-shaped grains, in a wide range of sizes. In the co-doped samples only, a granular morphology was observed. The average grain size varies with La^{3+} and Ta^{5+} contents and shows increase from Sample A to Sample D (Table 8-1). The reason behind the growth of grain in size can be linked to dopants effect. La^{3+} enhances the growth of the grains in NBT-0.06BT when it substitutes Na^{+} and/or Ba^{2+} resulting in A-site vacancies will create in order to keep charge balance [1,17,18]. Generally, creation of the A-site vacancies is quite beneficial for the mass transportation. This mass transport might be responsible for boosting the grain growth in the NBT-0.06BT with increasing La^{3+} concentration [18,19].

Ta^{5+} may affect the composition in a contrary way to La^{3+} . The Ta^{5+} behaves as an inhibitor to the grains growth in NBT-0.06BT due to the valence difference between Ta^{5+} and Ti^{4+} [13,14,20]. As a result, A-site vacancies will be created. These A-site vacancies may locate at the grain boundaries due to the thermodynamic stability of the system, which prevents the growth of grains [20-22].

The average grains size firstly only shows a slight increase for sample B compared to the undoped sample.

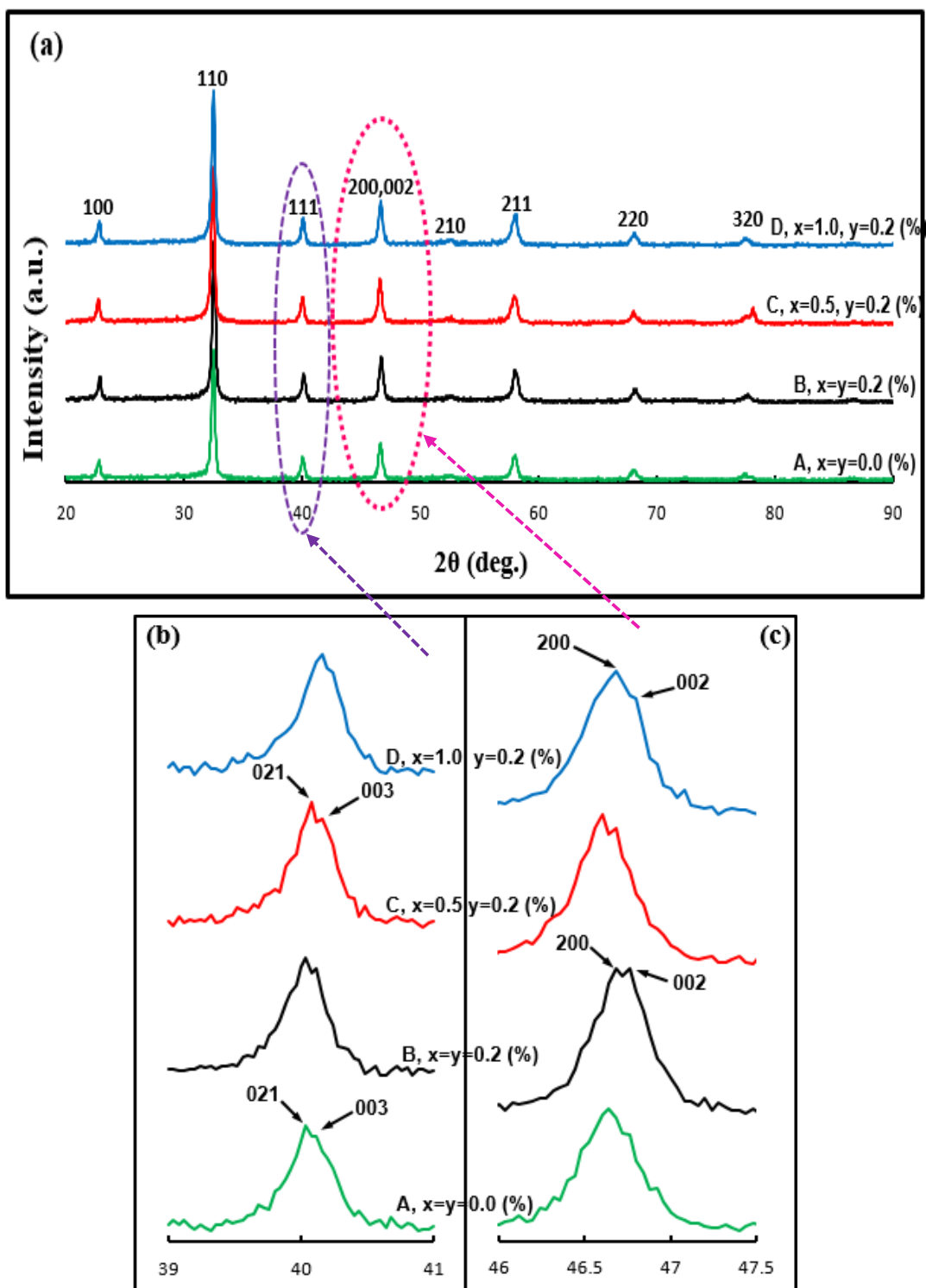


Figure 8-1: (a) XRD patterns of NBT-0.06BT and xLa-NBT-0.06BT-yTa; (b) enlargement of [111] peak split into [003] and [021] at 39.0°-41.0°; (c) enlargement of [200] peak split into [200] and [002] at 46.0°- 47.5°.

Table 8-1: Lattice parameters (Å), c/a ratio and average grain size values of all NBT-0.06BT and xLa-nbt-0.06BT-yTa ceramic compositions.

Sample name, xLa-NBT-0.06BT-yTa	Lattice parameter (Å)		c/a ratio	Average grain size (μm)
	a	c		
A, NBT-0.06BT	5.511	13.474	2.445	1.78
B, 0.002La-NBT-0.06BT-0.002Ta	5.511	13.490	2.446	1.80
C, 0.005La-NBT-0.06BT-0.002Ta	5.494	13.505	2.458	2.05
D, 0.01La-NBT-0.06BT-0.002Ta	5.498	13.505	2.455	2.11

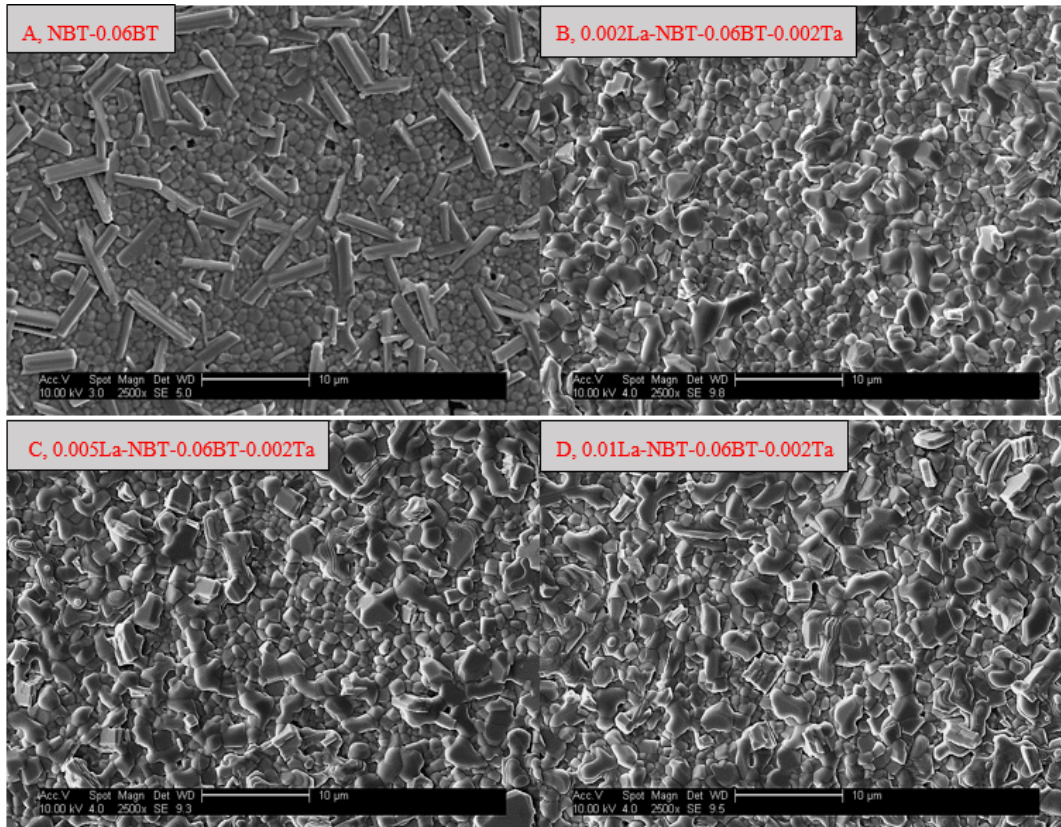


Figure 8-2: SEM morphology of NBT-0.06BT and xLa-NBT-0.06BT-yTa ceramics.

This is possibly due to a competing dopant cancelling effect. However, with increased La^{3+} and fixed Ta^{5+} concentrations, the effects of La^{3+} became more pronounced, and the average grains size is clearly enlarged in Sample D (Fig. 8-2).

8.1.2.2 Effects of La and Ta on dielectric properties

Fig. 8-3 (a-d) shows the change of the dielectric properties of poled undoped and doped NBT-0.06BT as a function of temperature in a wide temperature range from 20 up to 150 °C at 1, 10, and 100 kHz.

Sample A shows a relative permittivity (ϵ_r) of ~ 396 at RT and 1 kHz (Fig. 8-3 (a)). However, Samples B, C, and D (Fig. 8-3 (b-d)) present much higher ϵ_r values as shown in Table 8-2. Sample C shows the lowest ϵ_r value among all other samples. The ϵ_r of all the samples increases with temperature, which behaves like a typical ferroelectric material [22]. Samples B, and C show a pronounced inflexion in ϵ_r with temperature while it is not recognized in Samples A, and D (Fig. 8-3(a-d)), although there is evidence that they may appear outside the temperature measurement window.

The dielectric loss ($\tan\delta$) of the undoped sample is around 0.044 at RT and 1 kHz, and although there is a significant increase to ~ 0.062 for Samples B, Samples C and D have similar values as Sample A (Table 8-2). The $\tan\delta$ value shows a gradual decrease in the doped samples with increasing La^{3+} content from Samples B, C, and D at RT. With increasing the temperature, the $\tan\delta$ value increases to a maximum value at the temperature that is widely known as the depolarization temperature (T_d) [23-25]. The T_d for Sample A is ~ 115 °C while it is around 45, 40 and 45 °C for Samples B, C, and D respectively. The dielectric loss values at T_d are ~ 0.051 , 0.066, 0.052, and 0.045 for Samples A, B, C, and D respectively (Fig. 8-4). Also, the relative permittivity values at T_d are around 582, 1209, 721, and 1112 for samples A to D respectively. Obviously, the doped samples show higher ϵ_r values than undoped sample at T_d , (Fig. 8-4).

8.1.2.3 Effects of La and Ta on depolarization temperature

In this study, the T_d is successfully identified by two methods: (1) Dielectric method ($\tan\delta$ vs temperature plots in Fig. 8-4); (2) Pyroelectric method (temperature vs pyroelectric coefficient (p) plots in Fig. 8-5 (b)).

The dielectric method reveals that T_d decreased after doping with La^{3+} and Ta^{5+} from 115 °C (Sample A) to around 40 °C for Sample C as mentioned in 8.1.3.2. Sample D shows an unexpected depolarization temperature which is more than 5 °C higher than the T_d for Sample C whereas it should shift to lower temperature with increasing the A and B sites dopant content (Fig. 8-4).

The second method to obtain the T_d is from the maximum pyroelectric coefficient(p) value. It is widely known that at phase transitions, maximum p values can be observed [1,18,20,26-29].

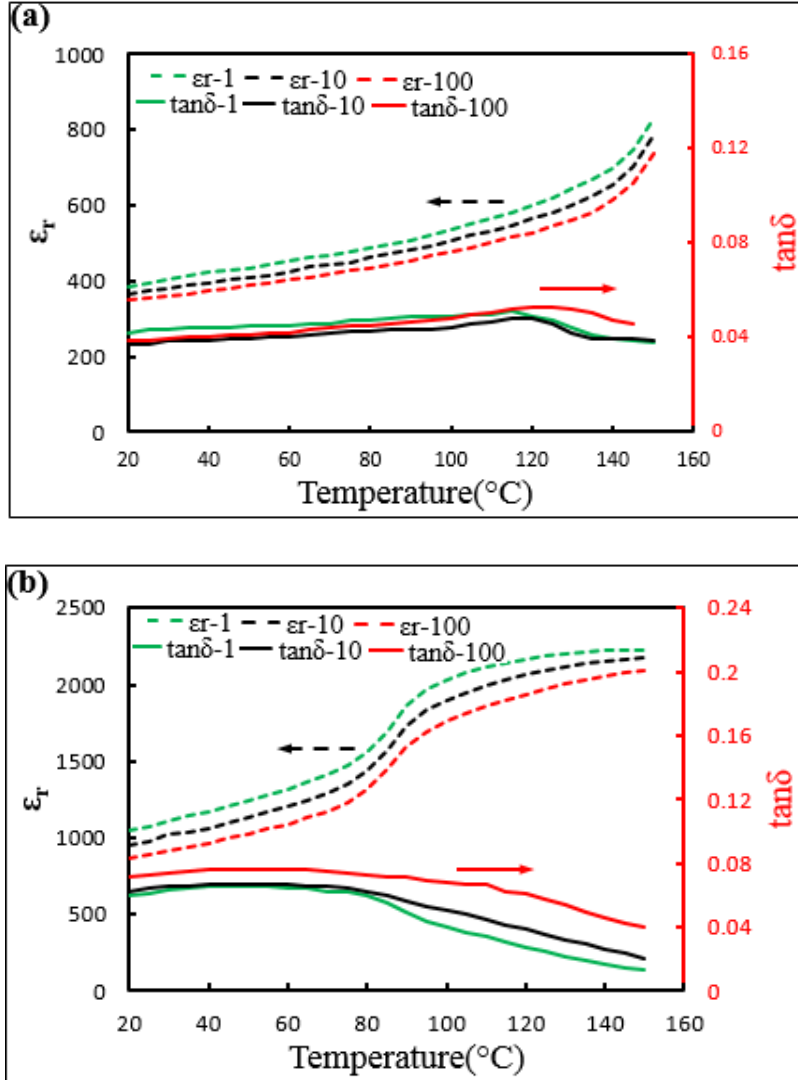
In this study, the lower phase transition (*FR* to *relaxor AFE*) temperature of the NBT-0.06BT [23,29-31] was utilised to identify the T_d with observed values of 61, 55, and 33 °C for Samples B, C, and D, respectively. Unfortunately, the exact T_d could not be identified for Sample A by this method due to the upper temperature limit of equipment being at 90 °C (Fig. 8-5 (b)).

The reason behind the observed decrease in the T_d might be attributed to two factors. Firstly: the generation of A-site vacancies due to La^{3+} replacement of Na^+ and/or Ba^{2+} [1,17]. The ferroelectric domain stability is affected by the coupling between A-site cations and ferroelectric (TiO_6).

This stability decreases with the increase of A-site dopant content [18]. Doping with B-site donor can also create A-site vacancies, which will maintain the charge neutrality in the structure [20,34,35].

Secondly: the reduction of the degree of freedom for B-site ion movement in the TiO_6 octahedra due to doping with B-site ions which have a bigger ionic radius, such as the Ta^{5+} (0.64 Å) for Ti^{4+} (0.605 Å) [13,14,34]. The Ta^{5+} will occupy a larger space in oxygen octahedral than the Ti^{4+} due to the difference in the ionic radii. As a consequence of this, the ferroelectric properties become weakened

[20,34,35]. As a result of both effects, these induce the phase transition from ferroelectric (*FE*) to relaxor anti-ferroelectric (*relaxor AFE*) to be at lower depolarization temperature [4,18,20,29,36,37].



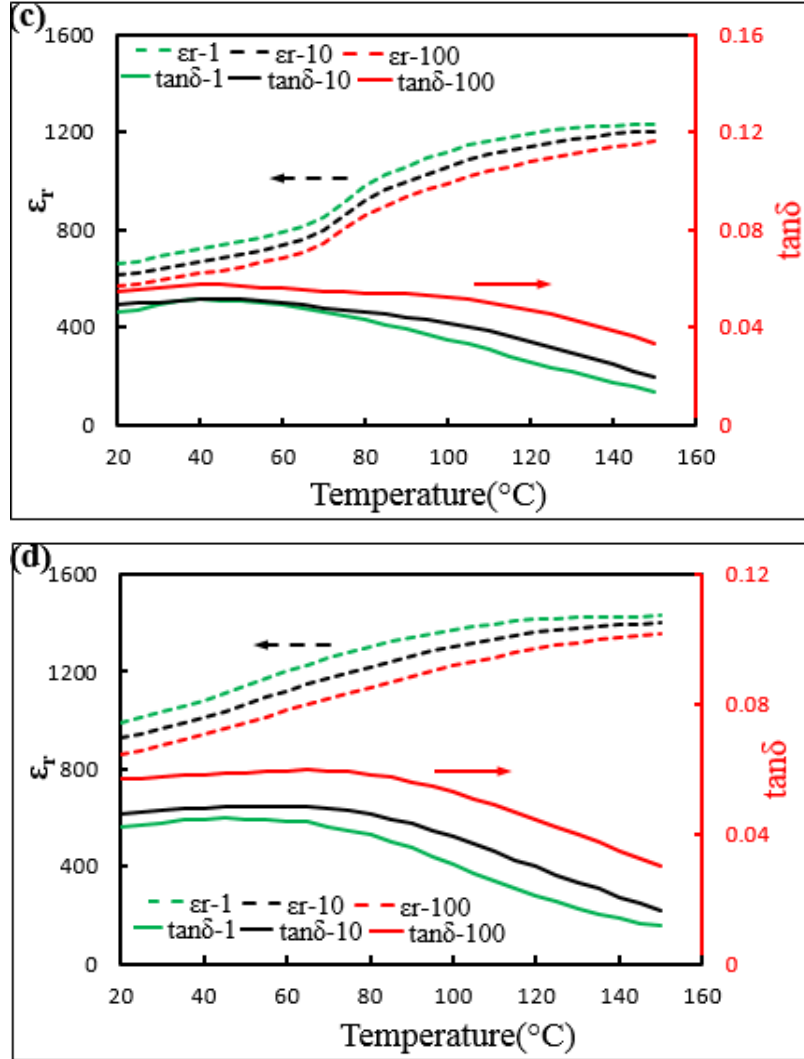


Figure 8-3: Relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) vs temperature for (a) NBT-0.06BT, (b) 0.002La-NBT-0.06BT-0.002Ta, (c) 0.005La-NBT-0.06BT-0.002Ta and (d) 0.01La-NBT-0.06BT-0.002Ta at three different frequencies 1, 10, and 100 (kHz).

Table 8-2: Relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) values at room and depolarization temperatures.

Sample name, xLa-NBT-0.06BT-yTa	At room temperature		At depolarization temperature		
	ϵ_r	$\tan\delta$	ϵ_r	$\tan\delta$	T_d (°C)
A, NBT-0.06BT	396.16	0.0436	582.33	0.051	115
B, 0.002La-NBT-0.06BT- 0.002Ta	1073.85	0.0616	1208.76	0.066	45
C, 0.005La-NBT-0.06BT- 0.002Ta	671.22	0.0472	721.15	0.052	40
D, 0.01La-NBT-0.06BT- 0.002Ta	1008.88	0.0429	1112.04	0.045	45

8.1.2.4 Effects of La and Ta on pyroelectric properties

The figure of merits (*FOMs*) represent a standard and an efficient way to evaluate pyroelectric material performance [2,38], and have been characterized as key parameters in the pyroelectric applications [23].

The calculation of the *FOMs* is based on the values of pyroelectric coefficient, relative dielectric permittivity, the dielectric loss tangent and the specific heat [39]. There are several types of *FOMs* which are more appropriate to certain pyroelectric materials applications and are derived from these application requirements [23,38,40].

In this study, the pyroelectric coefficient (p) of xLa-NBT-0.06BT-yTa was measured from 20 to 90 °C for all samples.

The measurements of the p and FOMs were carried out using the Equations 1-11 and 1-15 to 1-19 in chapter 1 [19,26,40,41].

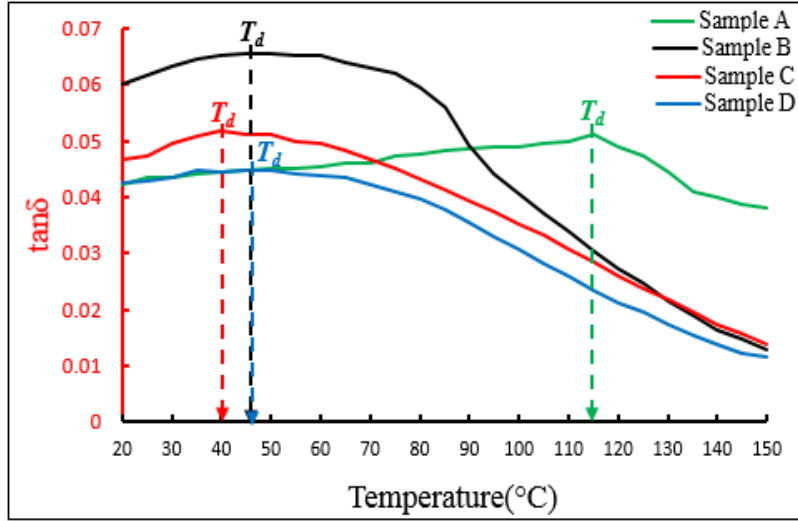


Figure 8-4: The identification of the T_d values of all samples by dielectric method (loss tangent ($\tan \delta$) against temperature ($^{\circ}\text{C}$)) for all samples at 1 kHz.

Fig. 8-5(b) shows the variation in pyroelectric coefficient (p) as a function of temperature for $x\text{La-NBT-}0.06\text{BT-}y\text{Ta}$ from 20 to 90°C . Samples B and C show very similar profiles differentiated only by their own relative T_d values which coincide with the maximum observed p values for the Samples. The T_d value for Sample A clearly lies outside the measurement window as previously mentioned so it is difficult to comment on its likely profile. Although all sample compositions are believed to be at the MPB according to the XRD results, Sample D shows significantly different responses to B and C. There is a clear evidence of a broad p maximum for Sample D, which indicates a relaxor phase transition, and the peak value of $5.4 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$ at T_d , although it is small compared to Samples B and C, it still represents a better value than PZT. The higher concentration of La^{3+} dopant can give lower pyroelectric coefficient for NBT-0.06BT at T_d because it shifts the composition outside MPB [23] and also the A-site vacancies created by doping La^{3+} and Ta^{5+} may locate outside the grain boundary, which

suppresses the movement of grain boundaries, and therefore reduces the polarisation as a result, it significantly decreases the pyroelectric coefficient for Sample D.

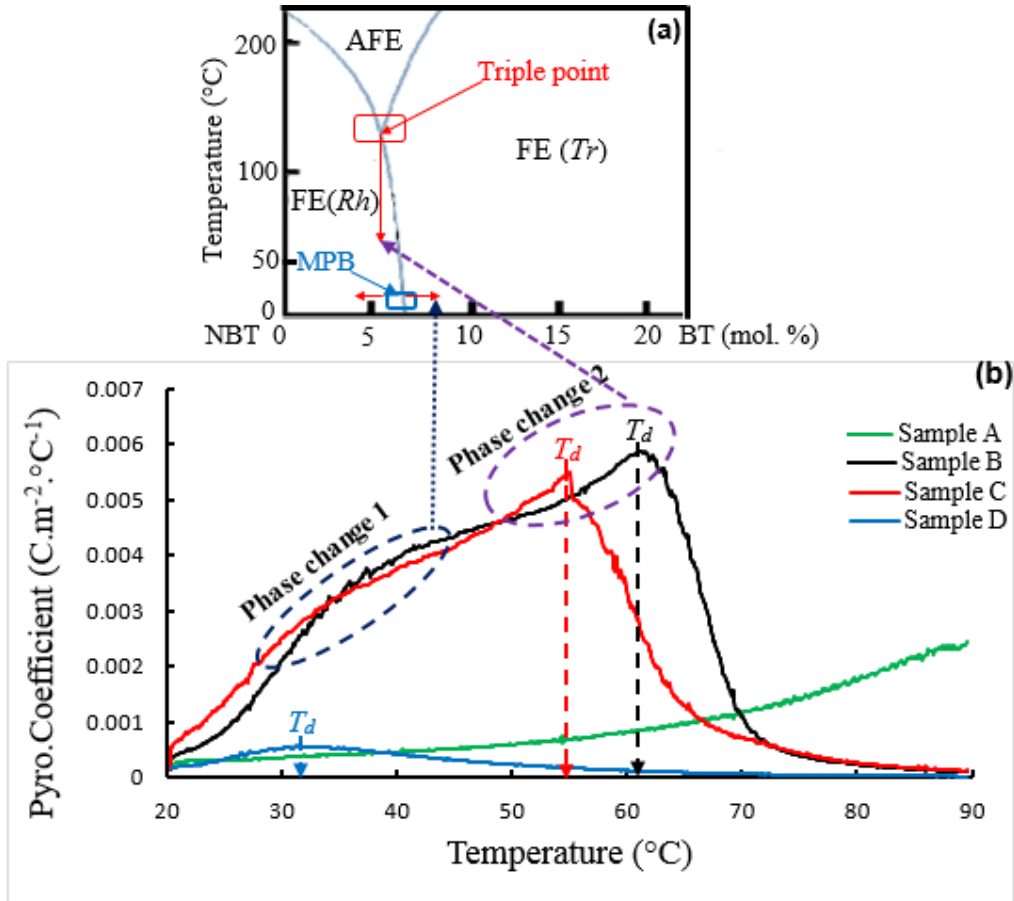


Figure 8-5: (a) Part of the (1-x)NBT-xBT phase diagram; (b) pyroelectric coefficient (*p*) vs temperature for all samples and the identification of the depolarization temperature (*T_d*). The two phase changes in Samples B and C that correspond to the change of FE (*Rh* + *Tr*) to FE (*Tr*) (phase change 1) and the change of FE (*Tr*) to AFE (phase change 2) were pointed out in the (1-x)NBT-xBT phase diagram (a).

The pyroelectric results seem strongly affected by the La³⁺ and Ta⁵⁺ concentrations as well as the depolarization temperature.

The shape of the profiles for samples B and C may be indicative of two phase changes, ((1 and 2) in Fig. 8-5 (b)) taking place within the temperature window. According to the (1-x)NBT-xBT phase diagram (Fig 8-5 (a)) [42], by La^{3+} and Ta^{5+} co-doping, the triple point was lowered, which means the phase transition from FE to AFE occurs at lower temperature and at the same time, MPB was shifted either to BT-poor end (in case La replaces Na and/or Bi and Ta replaces Ti) or BT-rich end (in case La replaces Ba and Ta replaces Ti). Thus, the two-phase changes are from ferroelectric MPB ($Rh + Tr$) to ferroelectric (Tr), (Fig. 8-5 (b), phase change 1) and then from ferroelectric (Tr) to antiferroelectric (Fig. 8-5 (b), phase-change 2).

At RT, the p values show an increase for Samples A to C. This trend can possibly be linked to the microstructure change of these samples. The trend in the values of c/a ratio in Table 8-1 matches the trend in p values. Sample C has the largest value which means that it has a more tetragonal unit cell which contributes to a greater pyroelectric response.

The huge increase in the pyroelectric value at T_d is clearly linked to the effect of the phase transition as confirmed in literature [1,27,29,39,46,43–45]. At RT, the pyroelectric coefficient values for Samples B and C are higher than those of PZT and other lead-free ceramic compositions (Tables 8-3 and 8-4) [30,38,39,46].

At RT, the F_i and F_v values show an increase from Samples A to C then decrease and at T_d , they show an even larger increase Samples B and C show the optimum values at RT and T_d respectively, which is due to the large p values and lower ϵ_r of these two samples achieved at RT and T_d . These values are higher than those of PZT and other lead-free ceramic compositions at RT (Tables 3 and 4).

F_D values of all samples at RT and 90°C or T_d show lower values; however, F_D values for doped samples are much less than for undoped sample. These values for Sample B, C, and D may be linked to the higher values of the relative permittivity and the dielectric loss than the undoped sample though the pyroelectric coefficient values of Samples B and C are quite higher than its value in Sample A.

The F_C values of xLa-NBT-0.06BT-yTa at RT and at three of frequencies from 33 to 1000 (Hz) were calculated and listed in Table 5. In general, the materials suitable for infrared detectors should have the F_C threshold value at $\sim 3 \pm 1 \times 10^{-9} \text{ C.cm}^{-2} \cdot ^\circ\text{C}^{-1}$ [3]. The composition of 0.002La-NBT-0.06BT-0.002Ta (Sample B) presents F_C values which are suitable for infrared detectors at RT and this frequency range (Table 8-4).

However, Samples A, C, and D show F_C values which are either less than the threshold value (Samples A and D) or higher than its value (Samples C) (Table 8-5). Rodríguez-Ruiz *et al.*, [3] calculated the F_C of $0.935\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.065BaTiO_3 ceramics which equals to $1.44 \times 10^{-9} \text{ C.cm}^{-2} \cdot ^\circ\text{C}^{-1}$, this value lower than the threshold value. The high F_C values for Sample B are due to the high p and the low relative permittivity.

The stability of pyroelectric materials with frequency and temperature represents one of the important parameters in pyroelectric applications [47]. Figs. 8-6 (a, b, and c) and 7 (a and b) present the FOMs (F_V , F_D , and F_C) dependence of xLa-NBT-0.06BT-yTa ceramics on frequency and temperature. The F_V , F_D , and F_C show an excellent frequency stability at the whole measurement window. However, Sample C (Fig. 8-6 (b)) presents a fluctuation in F_D at frequency ranging from 33 to 200 Hz, which shows the highest value $\sim 20.33 (\mu\text{Pa}^{-1/2})$ at 33 Hz and then decreases to $14.85 (\mu\text{Pa}^{-1/2})$ at 80 Hz. After that, F_D increases again to $16.04 (\mu\text{Pa}^{-1/2})$ at 200 Hz (Fig. 8-6 (b)).

F_V and F_D show two different temperature dependences in the measurement window. In Fig 8-7, Samples A and D show reasonably stable profiles, while Samples B and C show an increasing dependence at the same measurement window. The unstable profile of F_V and F_D for Samples B and C follows the similar trend in pyroelectric coefficient that highly increases with rising temperature (Fig. 8-5).

Table 8-3: Pyroelectric coefficient (p) and FOMs (F_i , F_v , and F_D) results at RT of NBT-0.06BT and xLa-NBT-0.06BT-yTa in the present study and literature.

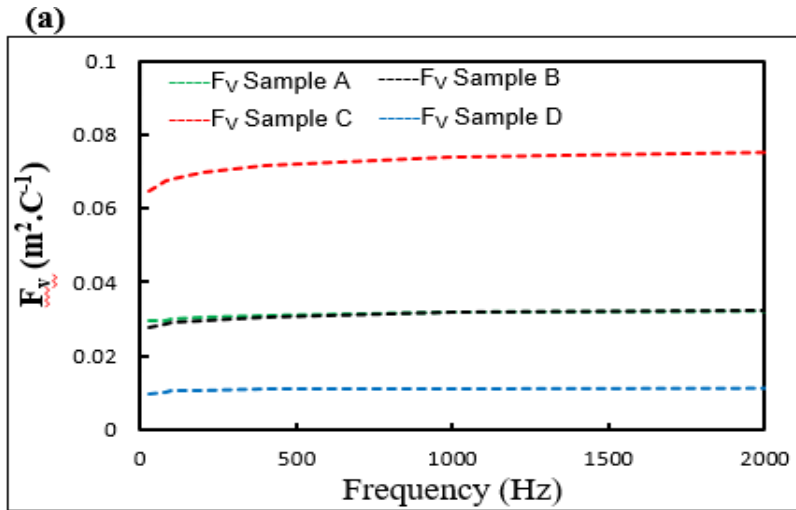
Composition	$p \times 10^{-4}$ (C.m⁻².°C⁻¹) at RT	$F_i \times 10^{-10}$ (m.V⁻¹) at RT	F_v (m².C⁻¹) at 1kHz at RT	$F_D \times 10^{-6}$ (Pa^{-1/2}) at 1kHz at RT
NBT-0.06BT	3.15	1.12	0.021	9.08
0.002La-NBT-0.06BT-0.002Ta	8.43	3.01	0.032	1.24
0.005La-NBT-0.06BT-0.002Ta	12.92	4.61	0.078	2.76
0.01La-NBT-0.06BT-0.002Ta	2.87	1.03	0.012	0.05
PZT	4.14	1.42	0.008	9.01
NBT-0.07BZT	5.71	2.03	0.022	10.50
NBT-0.06BT-0.002Mn	3.52	-	-	-
BNKBT	3.25	1.95	0.026	13.43
KNLNTS	1.90	0.93	0.007	11.51
NKLBT-0.05BT	3.63	1.27	0.017	-

Table 8-4: Pyroelectric coefficient (p) and FOMs (F_i , F_v , and F_D) results at 90 °C or T_d of NBT-0.06BT and xLa-NBT-0.06BT-yTa in the present study and literature.

Composition	$p \times 10^{-4} (\text{C.m}^{-2}.\text{°C}^{-1})$ at 90 °C or T_d	$F_i \times 10^{-10} (\text{m.V}^{-1})$ at 90 °C or T_d	$F_v (\text{m}^2.\text{C}^{-1})$ at 1kHz at 90 °C or T_d	$F_D \times 10^{-6} (\text{Pa}^{-1/2})$ at 1kHz at 90 °C or T_d
NBT-0.06BT	23.94 at 90 °C	8.55 at 90 °C	0.19 at 90 °C	65.5 at 90 °C
0.002La-NBT-0.06BT-0.002Ta	58.62 at 61.3 °C	20.94 at 61.3 °C	0.18 at 61.3 °C	7.60 at 61.3 °C
0.005La-NBT-0.06BT-0.002Ta	54.00 at 54.9 °C	19.28 at 54.9 °C	0.28 at 54.9 °C	10.46 at 54.9 °C
0.01La-NBT-0.06BT-0.002Ta	5.39 at 33.27 °C	1.93 at 33.27 °C	0.02 at 33.27 °C	7.19 at 33.27 °C
NBT-0.07BZT	20.00 at 50 °C	7.31 at 50 °C	0.07 at 50 °C	33.6 at 50 °C
NBT-0.07BZT	2.21 at 87 °C	-	-	-

Table 8-5: The figure of merit FC results at room temperature and wide frequency range from 33 to 1000 (Hz) of NBT-0.06BT and xLa-NBT-0.06BT-yTa ceramics in present study and literature.

Sample names, xLa-NBT-0.06BT-yTa	FOM, F_c ($\times 10^{-9}$ C. cm^{-2} $^{\circ}\text{C}^{-1}$) at RT		
	33Hz	0.1Hz	1kHz
A, NBT-0.06BT	-	1.53	1.58
B, 0.002La-NBT-0.06BT-0.002Ta	2.40	2.46	2.57
C, 0.005La-NBT-0.06BT-0.002Ta	4.55	4.67	4.99
D, 0.01La-NBT-0.06BT-0.002Ta	0.84	0.86	0.90



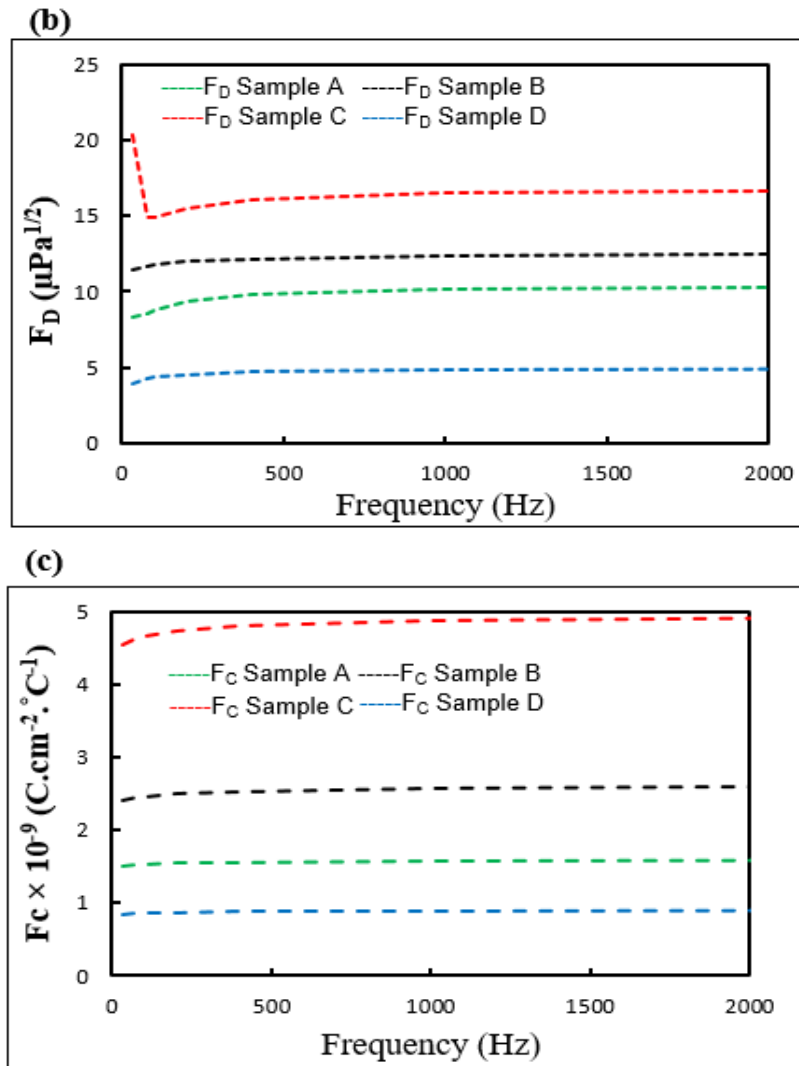


Figure 8-6: FOMs (F_v , F_D , and F_C) vs. frequency ranging from 33 to 2000 HZ. (a) F_v vs. f ; (b) F_D vs. f , and (c) F_C vs.

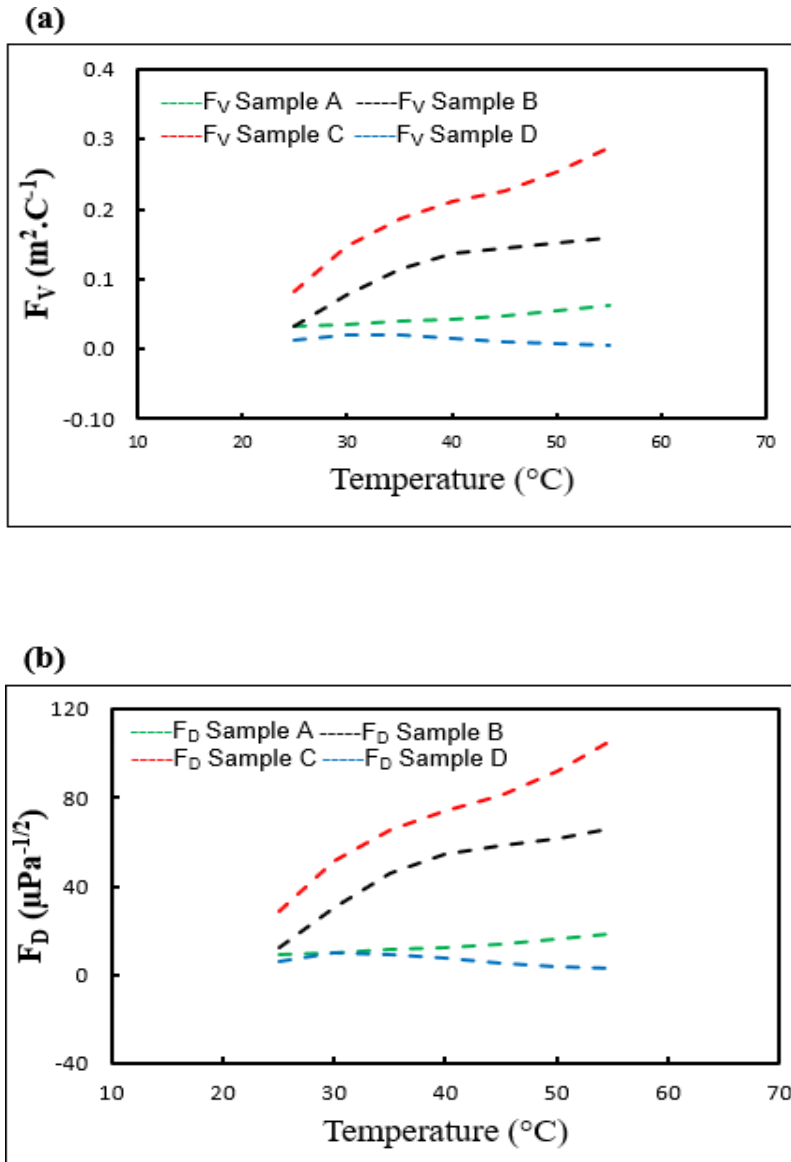


Figure 8-7: FOMs (F_V and F_D) vs. temperature ranging from 25 to 55 °C. (a) F_V vs. T and (b) F_D vs. T.

8.1.3 Conclusion

La^{3+} and Ta^{5+} co-doping in NBT-0.06BT ceramics does not significantly change the crystal lattices and the doped samples remain in MPB region. Depolarization temperature (T_d) was significantly reduced and pyroelectric coefficient of NBT-0.06BT ceramics greatly increases both at room temperature and T_d upon doping

La^{3+} (0.2 - 0.5%) and Ta^{5+} (0.2%). FOMs, F_i , F_v and F_c , are increased with the dopants with F_c value suitable for infrared detector application at RT. The pyroelectric coefficient of La^{3+} and Ta^{5+} co-doped NBT-0.06BT shows one order of magnitude higher than those observed in PZT materials and other lead-free compositions, and also the FOMs are comparable with or even better than those shown in PZT and other lead-free ceramics, demonstrating that xLa-NBT-0.06-yTa ceramics, particularly at $0.2 \leq x \leq 0.5$ (%) and $y = 0.2\%$, are promising materials for infrared detectors and other pyroelectric applications in a wide temperature range.

8.1.4 References

1. Anem S., Rao KS., Rao KH. Investigation of lanthanum substitution in lead-free BNBT ceramics for transducer applications. *Ceramics International*. Elsevier; 2016; Available at: DOI:10.1016/j.ceramint.2016.06.173
2. Xu Q., Huang DP., Chen M., Chen W., Liu HX., Kim BH. Effect of bismuth excess on ferroelectric and piezoelectric properties of a $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{-BaTiO}_3$ composition near the morphotropic phase boundary. *Journal of Alloys and Compounds*. 2009; 471(1–2): 310–316. Available at: DOI:10.1016/j.jallcom.2008.03.078
3. Guo F., Yang B., Zhang S., Wu F., Liu D., Hu P., et al. Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-xBa}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition. *Applied Physics Letters*. 2013; 103(18): 182906. Available at: DOI:10.1063/1.4828675
4. Chen M., Xu Q., Kim BH., Ahn BK., Ko JH., Kang WJ., et al. Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ piezoelectric ceramics. *Journal of the European Ceramic Society*. 2008; 28: 843–849. Available at: DOI:10.1016/j.jeurceramsoc.2007.08.007
5. Li Q., Wang J., Ma L., Fan H., Li Z. Large electrocaloric effect in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ferroelectric ceramics by La_2O_3 addition. *Materials Research Bulletin*. Elsevier Ltd; 2016; 74: 57–61.

- Available at: DOI:10.1016/j.materresbull.2015.10.010
6. Hiruma Y., Nagata H., Takenaka T. Formation of Morphotropic Phase Boundary and Electrical Properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--Ba}(\text{Al}_{1/2}\text{Nb}_{1/2})\text{O}_3$ Solid Solution Ceramics. *Japanese Journal of Applied Physics*. 2009; 48(9): 09KC08. Available at: DOI:10.1143/JJAP.48.09KC08
 7. Le Goupil F., Bennett J., Axelsson AK., Valant M., Berenov A., Bell AJ., et al. Electrocaloric enhancement near the morphotropic phase boundary in lead-free NBT-KBT ceramics. *Applied Physics Letters*. 2015; 107(17): 103–107. Available at: DOI:10.1063/1.4934759
 8. Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Crystallographica Section A*. 1976; 32(5): 751–767. Available at: DOI:10.1107/S0567739476001551
 9. Razak KA., Yip CJ., Sreekantan S. Synthesis of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) and Pr doped BNT using the soft combustion technique and its properties. *Journal of Alloys and Compounds*. Elsevier B.V.; 2011; 509(6): 2936–2941. Available at: DOI:10.1016/j.jallcom.2010.11.163
 10. Liu LY., Zhu MK., Hou YD., Yan H., Liu RP. Abnormal piezoelectric and dielectric behavior of $0.92\text{Na}(0.5)\text{Bi}(0.5)\text{TiO}_3\text{--}0.08\text{BaTiO}_3$ induced by La doping. *Journal of Materials Research*. 2007; 22(5): 1188–1192. Available at: DOI:10.1557/Jmr.2007.0173
 11. McQuade RR., Dolgos MR. A review of the structure-property relationships in lead-free piezoelectric $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{--}(x)\text{BaTiO}_3$. *Journal of Solid State Chemistry*. Elsevier; 2015; 3: 1–8. Available at: DOI:10.1016/j.jssc.2016.01.008
 12. Ma C., Tan X. Phase diagram of unpoled lead-free – ceramics. *Solid State Communications*. 2010; 150(33–34): 1497–1500. Available at: DOI:10.1016/j.ssc.2010.06.006
 13. Do NB., Lee HB., Yoon CH., Kang JK., Lee JS., Kim IW. Effect of Ta-Substitution on the Ferroelectric and Piezoelectric Properties of $\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{TiO}_3$ Ceramics. *Transactions on Electrical and Electronic Materials*. 2011; 12(2): 64–67. Available at:

DOI:10.4313/TEEM.2011.12.2.64

14. Petnoi N., Bomlai P., Jiansirisomboon S., Watcharapasorn A. Effects of Nb-doping on the micro-structure and dielectric properties of (Bi_{0.5}Na_{0.5})TiO₃ ceramics. *Ceramics International*. Elsevier; 2013; 39(SUPPL.1): S113–S117. Available at: DOI:10.1016/j.ceramint.2012.10.045
15. Kumari R., Ahlawat N., Agarwal A., Sanghi S., Sindhu M. Structural transformation and investigation of dielectric properties of Ca substituted (Na_{0.5}Bi_{0.5})_{0.95-x}Ba_{0.05}CaxTiO₃ ceramics. *Journal of Alloys and Compounds*. Elsevier Ltd; 2016; Available at: DOI:10.1016/j.jallcom.2016.11.200
16. Cho J-H., Jeong Y-H., Nam J-H., Yun J-S., Park Y-J. Phase transition and piezoelectric properties of lead-free (Bi_{1/2}Na_{1/2})TiO₃–BaTiO₃ ceramics. *Ceramics International*. 2014; 40: 8419–8425. Available at: DOI:10.1016/j.ceramint.2014.01.051
17. Fu P., Xu Z., Chu R., Li W., Zang G., Hao J. Piezoelectric, ferroelectric and dielectric properties of La₂O₃-doped (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ lead-free ceramics. *Materials & Design*. Elsevier Ltd; 2010; 31(2): 796–801. Available at: DOI:10.1016/j.matdes.2009.07.056
18. Balakt AM., Shaw CP., Zhang Q. Enhancement of pyroelectric properties of lead-free 0.94Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃ ceramics by La doping. *Journal of the European Ceramic Society*. 2016; : 6–13. Available at: DOI:10.1016/j.jeurceramsoc.2016.12.021
19. Martínez FL., Hinojosa J., Doménech G., Fernández-luque FJ., Zapata J., Ruiz R., et al. Dielectric Constant Tunability at Microwave Frequencies and Pyroelectric Behavior. *IEEE transactions on ultrasonics, ferroelectrics, and frequency control*. 2013; 60(8): 1595–1602. Available at: DOI:10.1109/TUFFC.2013.2740.
20. Balakt AM., Shaw CP., Zhang Q. The decrease of depolarization temperature and the improvement of pyroelectric properties by doping Ta in lead-free 0.94Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃ ceramics. *Ceramics International*. December 2016; Available at: DOI:10.1016/j.ceramint.2016.12.004
21. Guggilla P., Batra AK., Currie JR., Aggarwal MD., Alim MA., Lal RB.

- Pyroelectric ceramics for infrared detection applications. *Materials Letters*. 2006; 60(16): 1937–1942. Available at: DOI:10.1016/j.matlet.2005.05.086
22. Islam MR., Galib RH., Sharif A., Hasan M., Zubair MA., Islam MF. Correlation of charge defects and morphology with magnetic and electrical properties of Sr and Ta codoped BiFeO₃. *Journal of Alloys and Compounds*. Elsevier Ltd; 2016; 688: 1186–1194. Available at: DOI:10.1016/j.jallcom.2016.07.134
 23. Anton EM., Jo W., Damjanovic D., Rdel J. Determination of depolarization temperature of (Bi_{1/2}Na_{1/2})TiO₃-based lead-free piezoceramics. *Journal of Applied Physics*. 2011; 110(9): 1–14. Available at: DOI:10.1063/1.3660253
 24. Guo Y., Gu M., Luo H. Antiferroelectric phase and pyroelectric response in (NayBi_z)Ti_{1-x}O₃(1-x)-xBaTi₃ ceramics. *Journal of the American Ceramic Society*. 2011; 94(5): 1350–1353. Available at: DOI:10.1111/j.1551-2916.2011.04509.x
 25. Jo W., Daniels J., Damjanovic D., Kleemann W., Rodel J. Two-stage processes of electrically induced-ferroelectric to relaxor transition in 0.94(Bi_{1/2}Na_{1/2})TiO₃-0.06BaTiO₃. *Applied Physics Letters*. 2013; 102(19): 0–4. Available at: DOI:10.1063/1.4805360
 26. Balakt AM., Shaw CP., Zhang Q. The effects of Ba²⁺ content on depolarization temperature and pyroelectric properties of lead-free 0.94Na_{0.5}Bi_{0.5}TiO₃ - 0.06Ba_{1+x}TiO₃ ceramics. *Journal of Materials Science: Materials in Electronics*. 2016; 27: 12947–12954. Available at: DOI:10.1007/s10854-016-5433-1
 27. Kang W-S., Lee S-K., Koh J-H. AC conductivity and dielectric properties of (Bi,Na)TiO₃-BaTiO₃ lead free ceramics. *Ceramics International*. 2015; 41(5): 6925–6932. Available at: DOI:10.1016/j.ceramint.2015.01.147
 28. Wang X., Tang X., Chan H. Electromechanical and ferroelectric properties of (Bi_{1/2}Na_{1/2})TiO₃-(Bi_{1/2}K_{1/2})TiO₃-BaTiO₃ lead-free piezoelectric ceramics. *Applied physics letters*. 2004; 85(1): 91. Available at: DOI:10.1063/1.1767592
 29. Yao Z., Chu R., Xu Z., Hao J., Li W., Li G. Processing and enhanced electrical properties of Sr_{1-x}(K_{0.5}Bi_{0.5})xBi₂Nb₂O₉ lead-free piezoelectric ceramics. *Ceramics International*. Elsevier; 2016; 42(9): 10619–10623. Available at:

DOI:10.1016/j.ceramint.2016.03.156

30. Hiruma Y., Yoshii K., Nagata H., Takenaka T. Investigation of Phase Transition Temperatures on $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 Lead-free Piezoelectric Ceramics by Electrical Measurements. *Ferroelectrics*. 2007; 346(773557621): 114–119. Available at: DOI:10.1080/00150190601180471
31. Rödel J., Jo W., Seifert K.T.P., Anton E.M., Granzow T., Damjanovic D. Perspective on the development of lead-free piezoceramics. *Journal of the American Ceramic Society*. 2009; 92(6): 1153–1177. Available at: DOI:10.1111/j.1551-2916.2009.03061.x
32. Sung Y.S., Kim M.H. Effects of B-site Donor and Acceptor Doping in Pb-free $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ Ceramics. *Ferroelectrics*. 2010; (March 2017): 217. Available at: DOI:10.5772/13903
33. Balakt A.M., Shaw C.P., Zhang Q. The decrease of depolarization temperature and the improvement of pyroelectric properties by doping Ta in lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 ceramics. *Ceramics International*. December 2017; 43: 3726–3733. Available at: DOI:10.1016/j.ceramint.2016.12.004
34. Shi T., Li G., Zhu J. Compositional design strategy for high performance ferroelectric oxides with perovskite structure. *Ceramics International*. Elsevier; 2016; Available at: DOI:10.1016/j.ceramint.2016.11.085
35. Jo W., Daniels J.E., Jones J.L., Tan X., Thomas P a., Damjanovic D., et al. Evolving morphotropic phase boundary in lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 piezoceramics. *Journal of Applied Physics*. 2011; 109(1): 14110. Available at: DOI:10.1063/1.3530737
36. Ranjan R., Dwiwedi A. Structure and dielectric properties of $(\text{Na}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$: $0 \leq x \leq 0.10$. *Solid State Communications*. 2005; 135: 394–399. Available at: DOI:10.1016/j.ssc.2005.03.053
37. Cao W., Li W., Zhang T., Sheng J., Hou Y., Feng Y., et al. High-Energy Storage Density and Efficiency of $(1-x)[0.94\text{NBT}-0.06\text{BT}]-x\text{ST}$ Lead-Free Ceramics. *Energy Technology*. 2015; 3(12): 1198–1204. Available at: DOI:10.1002/ente.201500173

38. Lau ST., Cheng CH., Choy SH., Lin DM., Kwok KW., Chan HLW. Lead-free ceramics for pyroelectric applications. *Journal of Applied Physics*. 2008; 103(10): 10–13. Available at: DOI:10.1063/1.2927252
39. Yoon MS., Khansur NH., Ur SC. The effect of pre-milling/pre-synthesis process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized $0.94[(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3]-0.06[\text{Ba}(1+x)\text{TiO}_3]$. *Ceramics International*. Elsevier Ltd and Techna Group S.r.l.; 2010; 36(4): 1265–1275. Available at: DOI:10.1016/j.ceramint.2010.01.011
40. Abo, Jiro Kobune M., Nishimura T., Yazaw T., Nakai Y. Effects of manganese addition on pyroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)_{0.94}(\text{BaTiO}_3)_{0.06}$ ceramics. *Integrated Ferroelectrics*. 2006; 80(1): 87–95. Available at: DOI:10.1080/10584580600656502
41. Kanuru SR., Baskar K., Dhanasekaran R. Synthesis, structural, morphological and electrical properties of NBT–BT ceramics for piezoelectric applications. *Ceramics International*. Elsevier; 2016; 42(5): 6054–6064. Available at: DOI:10.1016/j.ceramint.2015.12.162
42. Search H., Journals C., Contact A., Iopscience M. $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 System for Lead-Free Piezoelectric Ceramics. *Jpn. J. Appl. Phys.* 1991; 2236(20/07/1991): 2236–2239.
43. Patel S., Chauhan A., Kundu S., Madhar NA., Llahi B., Vaish R., et al. Tuning of dielectric, pyroelectric and ferroelectric properties of $0.715\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3-0.065\text{BaTiO}_3-0.22\text{SrTiO}_3$ ceramic by internal clamping. *AIP Advances*. 2015; 5(8): 87145. Available at: DOI:10.1063/1.4929328
44. Lee SG., Kim C Il., Kim BC. Dielectric properties of screen-printed $(\text{Ba},\text{Sr},\text{Ca})\text{TiO}_3$ thick films modified with Al_2O_3 for microwave device applications. *Journal of the European Ceramic Society*. 2004; 24(1): 157–162. Available at: DOI:10.1016/S0955-2219(03)00252-8
45. Li XJ., Xi ZZ., Long W., Fang PY. Synthesis of antiferroelectric $(\text{Bi}_{0.534}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ ceramics with high phase transition temperature and broad temperature range by a solid-state reaction method. *Chinese Science Bulletin*. 2013; 58(23): 2893–2897. Available at:

DOI:10.1007/s11434-013-5972-2

46. Xu C., Lin D., Kwok KW. Structure, electrical properties and depolarization temperature of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{--BaTiO}_3$ lead-free piezoelectric ceramics. *Solid State Sciences*. 2008; 10(7): 934–940. Available at: DOI:10.1016/j.solidstatesciences.2007.11.003
47. Liu C., Qian K., Lu F., Chen Z., Fang B., Ding J., et al. Enhancing pyroelectric property of $\text{Pb}(\text{Fe}_{1/4}\text{Sc}_{1/4}\text{Nb}_{1/2})\text{O}_3$ ceramics. *Journal of Alloys and Compounds*. Elsevier B.V.; 2014; 596: 164–166. Available at: DOI:10.1016/j.jallcom.2014.01.104

8.2 (B) Co-doping A&B sites of $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 with lanthanum oxide ($x\text{La}_2\text{O}_3$) is $x=0.5$ and different concentrations of tantalum oxide ($y\text{Ta}_2\text{O}_3$), $0.0 \leq y \leq 1.0$.

This part of chapter 8 is based on a paper, which is currently under review in the Journal of material science.

8.2.1 Experimental

La^{3+} and Ta^{5+} co-doped 0.94NBT - 0.06BT (NBT - 0.06BT) ceramics were prepared by a solid-state synthesis technique. The raw materials were as same as in chapter 8-1

The amounts of powders were calculated according to the chemical formula $x\text{La}_2\text{O}_3$ - $0.94(\text{Na Bi})_{0.5}\text{TiO}_3$ - 0.06BaTiO_3 - $y\text{Ta}_2\text{O}_3$, where $x = y = 0.0\%$ (Sample A); $x = 0.5\%$, $y = 0.2\%$ (Sample B); $x = y = 0.5\%$ (Sample C); and $x = 0.5\%$, $y = 1.0\%$ (Sample D).

8.2.2 Results and discussion

8.2.2.1 Effects of La and Ta on Microstructure

Fig. 8-8 (a) shows XRD spectra of co-doped NBT - 0.06BT ceramics powders calcined at 850°C for 3 hr. All samples (A-D) present a pure perovskite (ABO_3) phase structure with no evidence of any secondary phase indicating that both dopants (La^{3+} and Ta^{5+}) diffused into NBT - 0.06BT main lattice and formed new $x\text{La}$ - NBT - 0.06BT - $y\text{Ta}$ polycrystalline solid solution. The different contents of the dopants did not cause a significant change in the phase structure of NBT - 0.06BT .

Fig. 8-8 (b) shows splitting of the peak $[111]$ into $[003]$ and $[021]$ at 39.0° to 41.0° for all the samples indicating the existence of rhombohedral (Rh) phase. This splitting matches that previously reported for undoped NBT XRD patterns [1,2]. Further splitting was noticed in the $[200]$ peak into $[200]$ and $[002]$ at 45.5° - 47.5° , for samples A, B, and C which indicates the existence of tetragonal (Tr) phase in the NBT lattice (Fig. 1(c)), while the phase structure of sample D shows a single $[200]$ peak, (Fig. 1(c)). The co-existence of both Rh and Tr phases in $x\text{La}$ - NBT -

0.06BT-yTa at the doping content up to $x = y = 0.5\%$ verifies that samples A, B, and C are at a MPB region. In undoped NBT-xBT the co-existence of *Rh* and *Tr* at $x = 0.06$ was widely reported in the literature [3-6]. Therefore, the phase structures of samples A, B, and C remain in the MPB area and are consistent with that reported in literature [3-9]. However, the composition of sample D slightly shifts away from the MPB region possibly due to the high concentration of the dopants.

According to the ionic matching relationship [10], the ionic radius of all elements in NBT-0.06BT are Na^+ (1.39 Å, CN 12) (CN=coordination number), Bi^{3+} (1.31 Å, CN 12), Ba^{2+} (1.61 Å, CN12) [4,7] and Ti^{4+} (0.61 Å, CN 6). The comparison of these values with La^{3+} (1.36 Å, CN12) and Ta^{5+} (0.64 Å, CN6) reveals that the La^{3+} can substitute A-site ions and the Ta^{5+} ions [11,12] can substitute B-site Ti^{4+} ion in NBT-0.06BT due to the radius similarity.

The Goldschmidt tolerance factor (*t*) relation could be calculated by using Equation 1-12 in Chapter 1 [15,16] to determine the perovskite structure stability:

The tolerance factor value of stable perovskite structure is in the range of 0.77-0.99 [15,16]. The calculated average *t* value for all compositions in this study is ~ 0.976 , which means that all compositions possess a stable structure.

Table 8-6 illustrates the lattice parameters (Å), *c/a* ratio, and the average grain size of all the samples.

Table 8-6 shows that the lattice parameters (“*a=b*” and “*c*”) are affected by doped La^{3+} and Ta^{5+} , as shown by the *c* parameters for samples B to D (Table 1). The calculation of the *c/a* ratio reveals that the Samples B, C, and D have a bigger ratio of *c/a* than Sample A indicating that doped samples have bigger tetragonal cells in their structure than the undoped sample A.

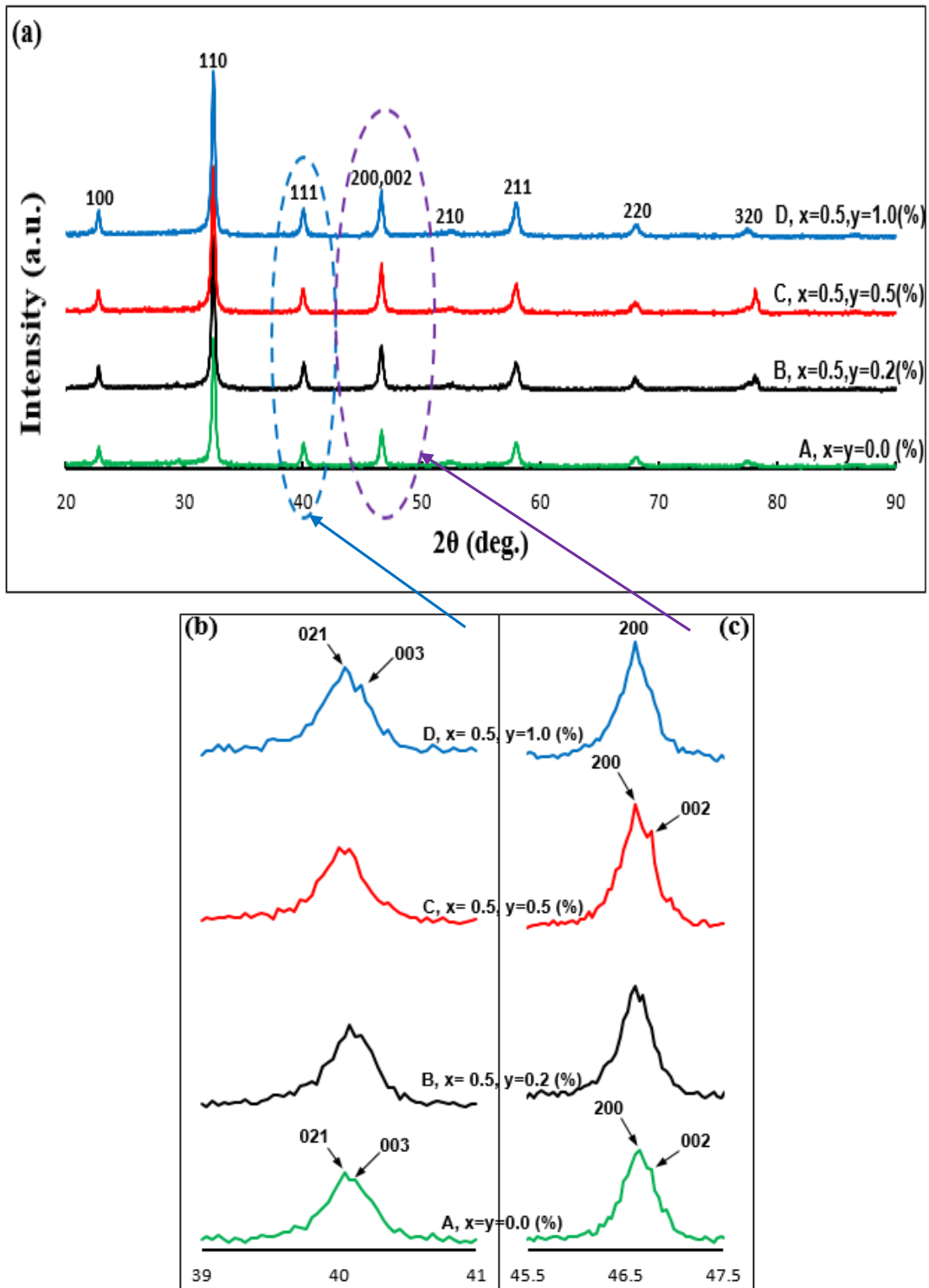


Figure 8-8: (a) XRD patterns of NBT-0.06BT and xLa-NBT-0.06BT-yTa; (b) enlargement of [111] peak split into [003] and [021] at 39.0° to 41.0° ; (c) enlargement of [200] peak split into [200] and [002] at 45.5° to 47.5° .

Table 8-6: Lattice parameters (Å), c/a ratio, and the average grain size of NBT-0.06BT and xLa-NBT-0.06BT-yTa ceramics.

Sample name, xLa-NBT-0.06BT-yTa	Lattice parameter (Å)		c/a ratio	Average grain size (μm)
	a	c		
A, NBT-0.06BT	5.5113	13.4744	2.4449	1.78
B, 0.005La-NBT-0.06BT-0.002Ta	5.4935	13.5048	2.4584	2.05
C, 0.005La-NBT-0.06BT-0.005Ta	5.5118	13.4955	2.4485	1.70
D, 0.005La-NBT-0.06BT-0.01Ta	5.5113	13.4876	2.4488	1.59

Fig. 8-9 exhibits the morphology of all xLa-NBT-0.06BT-yTa samples by SEM. Generally, all samples show quite dense structures, but some missing grain porosity can be seen for Sample A, which is not apparent with doping. Sample A presents distinguishable granular and rod-shaped grains. In the co-doped samples, the granular morphology starts to dominate as the surface layer tends to merge with the underlying morphology.

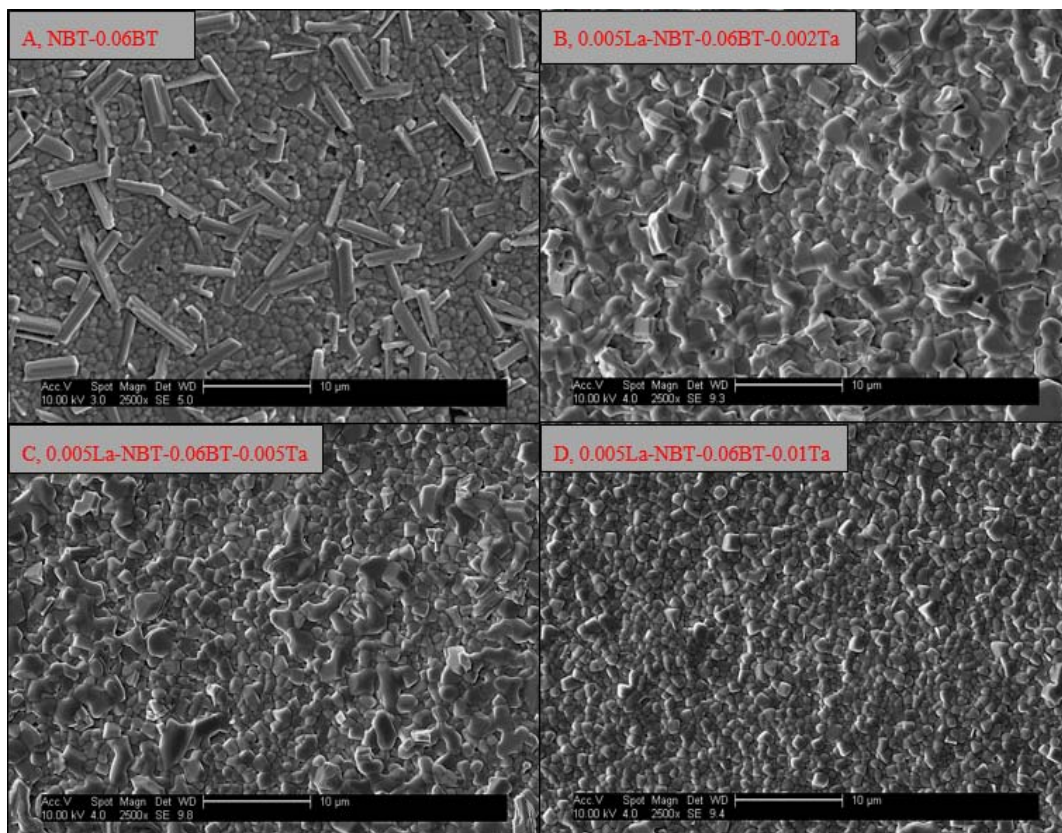


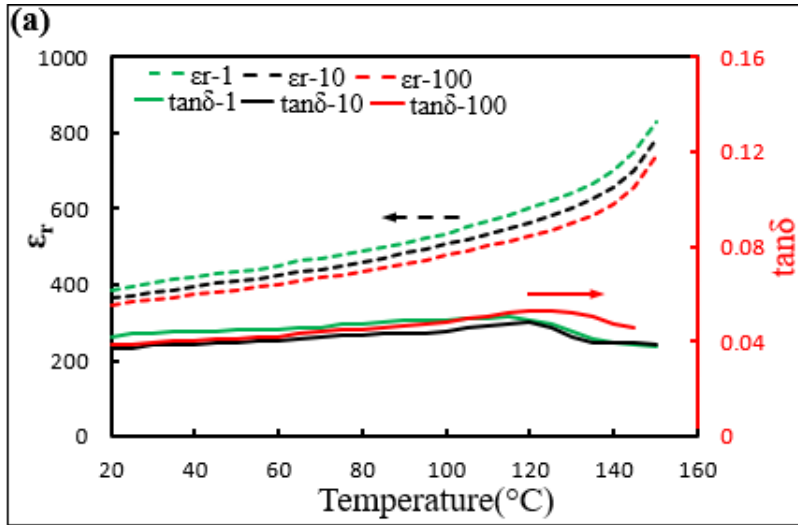
Figure 8-9: SEM morphology of NBT-0.06BT and xLa-NBT-0.06BT-yTa ceramics.

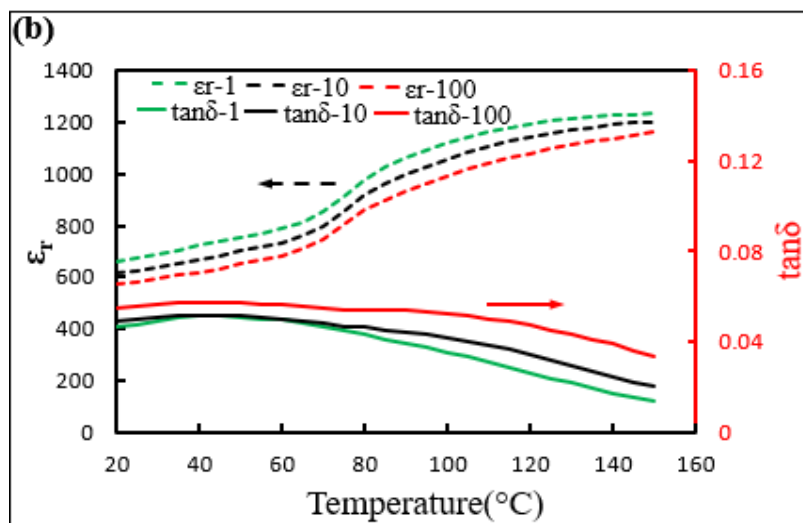
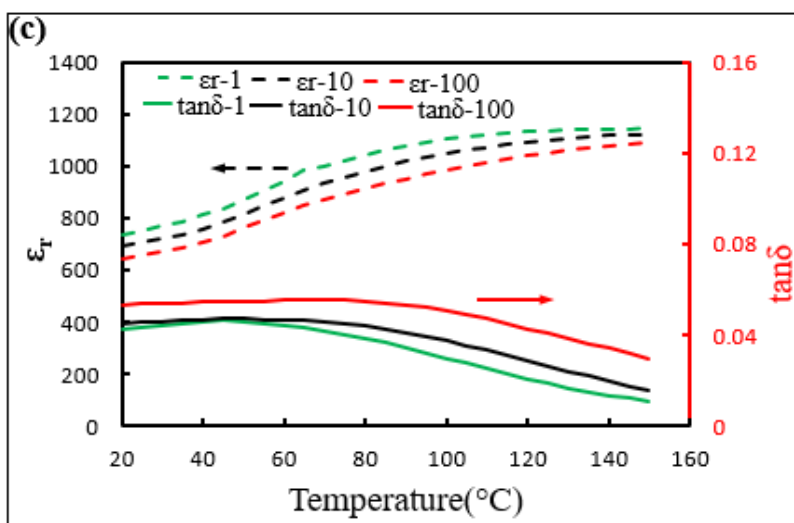
The grains in Samples B, C, and D present a uniform distribution (Fig 8-9). The average grain size varies with La^{3+} and Ta^{5+} concentrations and appears to increase from Sample A to B but then reduces for C and D. La^{3+} enhances the growth of the grains in NBT-0.06BT when it substitutes Na^+ resulting in A-site vacancies in order to keep charge balance [1,17,18]. Generally speaking, creation of the A-site vacancies is quite beneficial for the mass transportation [18,19]. This mass transport might be responsible for increasing the grain growth in the NBT-0.06BT with increasing La^{3+} content [18,19]. On the contrary, Ta^{5+} as a donor element may behave as an inhibitor to the grain growth in the NBT-0.06BT system, in which Ta^{5+} will replace Ti^{4+} according to the radius analogy [11,12,14,20,21]. As a result, the average grain size is increased (Sample B) with the addition of unequal concentrations of La^{3+} (0.5%) and Ta^{5+} (0.2%), so the effects of La^{3+} on the grain size are more pronounced than Ta^{5+} . Secondly, when

the doped amounts of La^{3+} and Ta^{5+} are equal ($x=y=0.5\%$), the average grain size shows a reduction. This is possibly due to competing dopants cancelling effect. Finally, with more Ta^{5+} content (Sample D), the average grain size shows further reduction (Table 8-6).

8.2.2.2 Effects of La and Ta on dielectric properties

Fig. 8-10 (a-d) shows the change of the dielectric properties of poled undoped and co-doped NBT-0.06BT as a function of temperature from 20 to 150 °C at three different frequencies from 1 to 100 (kHz).





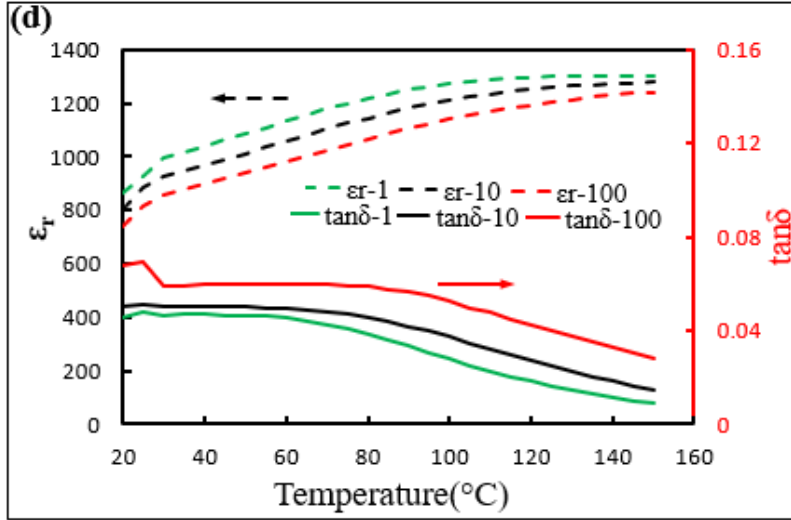


Figure 8-10: Relative permittivity (ϵ_r) and loss tangent ($\tan\delta$) vs temperature for (a) NBT-0.06BT, (b) 0.005La-NBT-0.06BT-0.002Ta, (c) 0.005La-NBT-0.06BT-0.005Ta, and (d) 0.005La-NBT-0.06BT-0.01Ta at three frequencies 1, 10, and 100 .

Sample A shows a relative permittivity (ϵ_r) of ~ 396 at RT and 1 kHz (Fig. 8-10 (a)). However, Samples B, C, and D (Fig. 8-10 (b to d)) present considerably higher ϵ_r values, which are around 671, 754, and 925, respectively. The ϵ_r of all samples increases with temperature below T_c or T_M , which is a typical behavior of ferroelectric materials [21]. The co-doped Samples B, C, and D show a pronounced inflexion in ϵ_r with temperature which is not observed for Sample A (Fig. 8-10(a-d)), although there is evidence showing that the inflexion may occur outside the temperature measurement window.

In oxide ferroelectric ceramics, relative permittivity normally increases due to inverse correlation with average grain size [22,23]. In this work, Sample D has the smallest average grain size and shows the highest ϵ_r , but the dominating factor effecting ϵ_r more likely relates to the dopant effects.

The dielectric loss ($\tan\delta$) of the undoped sample is around 0.044 at RT and 1 kHz and after co-doping, becomes ~ 0.047 , ~ 0.044 , ~ 0.048 , for samples B, C and D respectively. From literature, $\tan\delta$ shows a maximum value at the depolarization

temperature (T_d) [24-26]. In this work the estimation of this maximum has been more difficult due to the subtle variations in $\tan\delta$, across the temperature range. The estimate of T_d for sample A appears at $\sim 115^\circ\text{C}$ whilst similar estimates for samples B, C and D are proposed at around 40, 45, and $<40^\circ\text{C}$, respectively. The dielectric loss at T_d is around 0.051, 0.052, 0.047 and 0.048 for samples A, B, C and D, respectively (Fig. 8-11). The relative permittivity at T_d is around 582, 721, 837, and 925 for Samples A, B, C and D, respectively. The dielectric results at ϵ_r clearly show that the La^{3+} and Ta^{5+} co-doping has a significant effect on the ϵ_r values, and the large increase in ϵ_r observed near T_d is in agreement with that generally seen for ferroelectric ceramics in literature.

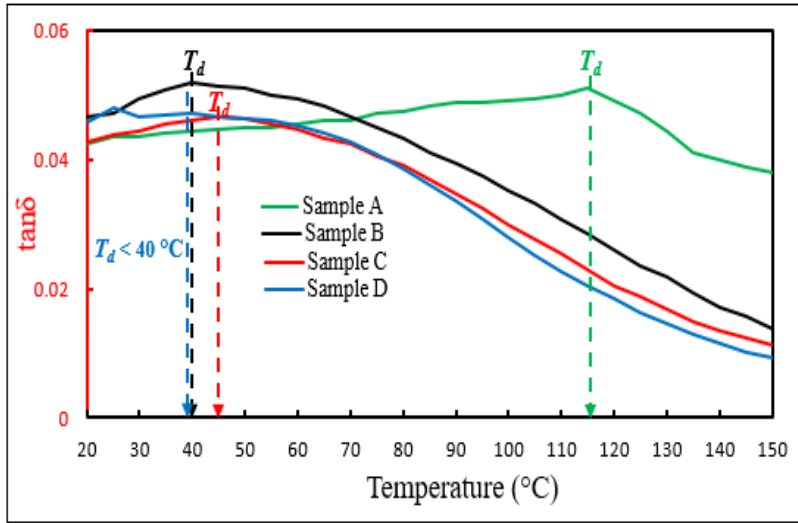


Figure 8-11: The identification of the T_d values of all samples by dielectric method (loss tangent ($\tan\delta$) against temperature ($^\circ\text{C}$)) for all samples at 1 kHz.

8.2.2.3 Effects of La and Ta on depolarization temperature

In this study, there is an attempt to subjectively identify T_d by two methods: (1) Dielectric method (dielectric loss vs temperature plots in Fig. 8-11) [24,26-28]; (2) Pyroelectric method, (pyroelectric coefficient (p) vs temperature plots in Fig. 8-12).

Although the dielectric loss method has been reported in literature [24,26-28] as a viable approach, figure 8-11 shows that we can only tentatively predict T_d in this work primarily based on the temperature range limitations of the equipment and the flat nature of figure 8-11 in the region of interest. However, by looking at figure 4 we can propose that the T_d values for samples A to D are 115°, 40°, 45° and <40 °C respectively.

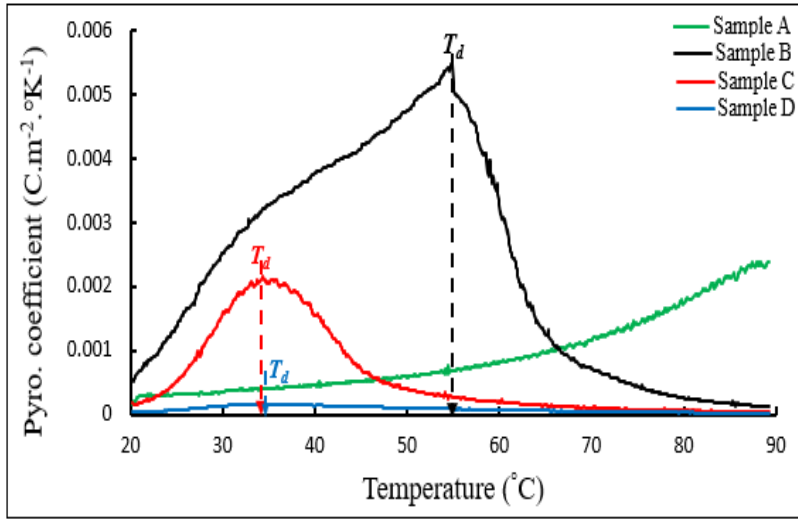


Figure 8-12: Pyroelectric coefficient (p) vs. temperature for all samples and identification of the depolarization temperature (T_d).

The second method to find the T_d is by observing the temperature, at which the maximum pyroelectric coefficient value is obtained. It is widely known that the maximum p value can be obtained at the phase transition temperatures [1,29-31]. In this study, the first phase transition (from Ferroelectric phase (FR) to intermediate phase) temperature in NBT-0.06BT [24,31-33] is utilised to identify the T_d as shown in figure 8-12. As expected from above, the exact T_d could not be identified for sample A by this method due to the upper temperature limit of the equipment being only 90 °C. For the co-doped materials, the peak maxima are more clearly defined and values of ~55°, 35° and 35-37 °C for samples B, C, and D, respectively, can be initially extracted from them. In the case of sample B

however, the shape of the plot suggests there may be two phase boundaries in close proximity due to the pronounced “shouldering” which appears in a similar location to the peak maxima of samples C and D.

The reason behind the observed decrease in the T_d might be attributed to two factors. Firstly, the replacement of La^{3+} to Na^+ generates A-site vacancies [1,17,18]. The ferroelectric domain stability is affected by the coupling between A-site cations and ferroelectric (TiO_6). This stability decreases with the increases of A-site dopant content [5,17,34]. Secondly, the degree of freedom for B-site ion movement in the TiO_6 octahedra due to doping with Ta^{5+} (0.64 Å) that has a bigger ionic radius than Ti^{4+} (0.605 Å) [11,12,20,35] is reduced. The Ta^{5+} will occupy a larger space in oxygen octahedral than the Ti^{4+} . As a consequence of this, the ferroelectric properties become weakened [20,26,36], which results in the phase transition from ferroelectric (*FE*) to relaxor anti-ferroelectric (*relaxor AFE*) to be at lower temperature [4,17,20,31,37,38]. From figure 8-12 it is interesting to observe what is apparently happening in terms of phase boundary changes, particularly in terms of the Ta^{5+} effects on the shape of the plot of sample B compared with C and D. Possibly because of the close proximity of the morphotropic phase boundary and triple point for these NBT-BT compositions, the subsequent depression of the triple point temperature could mean that there is a particular critical composition (Sample B) where on heating you can pass from rhombohedral to tetragonal to antiferroelectric, but with a slight compositional change sideways (Sample C) you find only the rhombohedral to antiferroelectric transition.

8.2.2.4 Effects of La and Ta on pyroelectric properties

As mentioned above the pyroelectric coefficient (p) is considered as an important parameter in the selection of materials for pyroelectric applications [24,27]. The efficient way to evaluate pyroelectric performance of a material is by calculating the figure of merits (*FOMs*) [2,24,39]. The calculation of the *FOMs* is based on the values of pyroelectric coefficient, relative dielectric permittivity, the dielectric loss tangent and the specific heat [3,39-41], there are several types of *FOMs* depending on the applications [3,24,39-42].

In this study, the pyroelectric coefficients (p) of xLa-NBT-0.06BT-yTa were measured from 20 to 90 °C for undoped sample A or 20 to T_d for doped samples (B, C, and D).

The measurements of the p and calculation of FOMs were carried out using the Equations 1-11 and 1-15 to 1-18 in chapter 1 [3,6,24,39-44].

Fig. 8-12 shows the pyroelectric coefficient (p) as a function of temperature for xLa-NBT-0.06BT-yTa from 20 to 90 °C. Samples B and C show well defined profiles differentiated only by the T_d values, which coincide with the maximum observed p values. Sample B shows a considerably higher p value than sample C, which can probably be related to the close proximity of the two-phase transitions proposed above in section 8.2.3.3. The T_d value for sample A clearly lies outside the measurement window as previously mentioned so it is difficult to discuss its likely profile. Sample D shows a significantly different response relative to B and C. It shows the lowest p value of all the samples. The low p value can be linked to the sample structure that has slightly shifted from the MPB area, as supported by the XRD study (Fig. 8-8, (c)). The pyroelectric results seem strongly affected by the La^{3+} and Ta^{5+} concentrations as well as the depolarization temperature.

Pyroelectric coefficient(p) and FOMs F_i , F_v , and F_D values for all the samples at RT are listed in Table 8-7 whereas Table 8-8 presents these values at 90 °C or T_d . At RT, the p values show an increase for the doped B and C samples compared to the undoped sample A. The trend in the values of c/a ratio in Table 8-6 agrees with the trend in p values. Sample B has the largest c/a value, which means that Sample B has more tetragonality than the other co-doped Samples and that contributes to a greater pyroelectric response. The difference in magnitude of the maximum p values between Samples B and C can also be linked to the difference in transition taking place, ie. tetragonal to antiferroelectric compared with rhombohedral to antiferroelectric.

The huge increase in p at T_d is clearly linked to the shift in the phase transition as confirmed in literature [1,27,29,31,33,45-47]. At RT, p values for Samples B

and C are higher than those of PZT and other lead-free ceramic compositions (Tables 8-7 and 8-8) [27,28,33,39].

At RT, the F_i and F_v values for samples B and C are greater than the undoped sample but for sample D are worse. At T_d , the co-doped materials show a decrease in F_i and F_v for samples B to D with only Sample B being higher than the undoped material. The optimum values at RT for Samples B and C, and for Sample B has at T_d , are due to the larger p values and lower ϵ_r that these two samples possess. Promisingly, these FOMs are higher than those of PZT and other lead-free ceramic compositions at RT (Table 8-7).

F_D values of all samples at RT and 90°C or T_d , show lower values than F_D for PZT and some other lead-free compositions [3,39]. However, the F_D values of the doped samples are much less than that of the undoped sample due to their larger relative permittivity and dielectric loss even though their p values, particularly for Samples B and C, are much higher than that in Sample A.

Table 8-7: Pyroelectric coefficient (p) and FOMs (F_i , F_v , and F_D) results at room temperature (RT) of NBT-0.06BT and xLa-NBT-0.06BT-yTa in the present study and literature.

Composition	$p \times 10^{-4}$ (C.m⁻².°C⁻¹) at RT	$F_i \times 10^{-10}$ (m.V⁻¹) at RT	F_v (m².C⁻¹) at 1kHz at RT	$F_D \times 10^{-6}$ (Pa^{-1/2}) at 1kHz at RT
NBT-0.06BT	3.15	1.12	0.021	9.08
0.005La-NBT-0.06BT-0.002Ta	12.92	4.61	0.078	2.84
0.005La-NBT-0.06BT-0.005Ta	5.12	1.83	0.027	1.13
0.005La-NBT-0.06BT-0.01Ta	0.64	0.23	0.003	0.11
PZT	4.14	1.42	0.008	9.01
NBT-0.07BZT	5.71	2.03	0.022	10.50
NBT-0.06BT-0.002Mn	3.52	-	-	-
BNKBT	3.25	1.95	0.026	13.43
KNLNTS	1.90	0.93	0.007	11.51
NKLBT-0.05BT	3.63	1.27	0.017	-

Table 8-8: Pyroelectric coefficient (p) and FOMs (F_i , F_v , and F_D) results at 90 °C or T_d of NBT-0.06BT and xLa-NBT-0.06BT-yTa in the present study and literature.

Composition	$p \times 10^{-4} (\text{C.m}^{-2}.\text{°C}^{-1})$ at 90 °C or T_d	$F_i \times 10^{-10} (\text{m.V}^{-1})$ at 90 °C or T_d	$F_v (\text{m}^2.\text{C}^{-1})$ at 1kHz at 90 °C or T_d	$F_D \times 10^{-6} (\text{Pa}^{-1/2})$ at 1kHz at 90 °C or T_d
NBT-0.06BT	23.9 at 90 °C	8.6 at 90 °C	0.19 at 90 °C	65.5 at 90 °C
0.005La-NBT-0.06BT-0.002Ta	54.0 at 54.9 °C	19.3 at 54.9 °C	0.28 at 54.9 °C	10.5 at 54.9 °C
0.005La-NBT-0.06BT-0.005Ta	20.6 at 35.1 °C	7.4 at 35.1 °C	0.11 at 35.1 °C	4.2 at 35.1 °C
0.005La-NBT-0.06BT-0.01Ta	1.6 at 35.5 °C	0.6 at 35.5 °C	0.01 at 35.5 °C	0.3 at 35.5 °C
NBT-0.07BZT	20.0 at 50 °C	7.33 at 50 °C	0.07 at 50 °C	33.6 at 50 °C
NBT-0.07BZT	22.1 at 87 °C	-	-	-

8.2.3 Conclusion

The compositions of co-doped lead-free NBT-0.06BT ceramics with different contents of La^{3+} and Ta^{5+} up to $x = y = 0.5\%$ remain in the MPB region and no significant structural change was detected. The depolarization temperature (T_d), observed by two methods, was significantly reduced and the pyroelectric coefficient of NBT-0.06BT ceramics was greatly increased both at room and depolarization temperatures. FOMs, F_i , and F_v increased with the increase of the dopant contents at RT up to $x = y = 0.5\%$ and up to $x=0.5\%$ and $y = 0.2\%$ at T_d . The pyroelectric coefficient of La^{3+} and Ta^{5+} co-doped NBT-0.06BT shows a one order of magnitude increase than that observed in PZT materials and other lead-free compositions. Likewise, the FOMs, F_i , and F_v are comparable with or even better than those observed in PZT materials and other lead-free compositions, demonstrating that $x\text{La-NBT-0.06-yTa}$ ceramics, particularly at $x = 0.5\%$ and $0.2 \leq y \leq 0.5$ (%), are promising materials for infrared detectors and other pyroelectric applications in a wide temperature range.

8.2.4 References

1. S. Anem, K.S. Rao, and K.H. Rao, "Investigation of lanthanum substitution in lead-free BNBT ceramics for transducer applications," *Ceram. Int.*, (2016).
2. Q. Xu, D.P. Huang, M. Chen, W. Chen, H.X. Liu, and B.H. Kim, "Effect of bismuth excess on ferroelectric and piezoelectric properties of a $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{-BaTiO}_3$ composition near the morphotropic phase boundary," *J. Alloys Compd.*, **471** [1–2] 310–316 (2009).
3. F. Guo, B. Yang, S. Zhang, F. Wu, D. Liu, P. Hu, Y. Sun, D. Wang, *et al.*, "Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-xBa}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition," *Appl. Phys. Lett.*, **103** [18] 182906 (2013).
4. M. Chen, Q. Xu, B.H. Kim, B.K. Ahn, J.H. Ko, W.J. Kang, and O.J. Nam, "Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ piezoelectric ceramics," *J. Eur. Ceram. Soc.*, **28** 843–849 (2008).

5. Q. Li, J. Wang, L. Ma, H. Fan, and Z. Li, "Large electrocaloric effect in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ferroelectric ceramics by La_2O_3 addition," *Mater. Res. Bull.*, **74** 57–61 (2016).
6. A.M. Balakt, C.P. Shaw, and Q. Zhang, "The effects of Ba^{2+} content on depolarization temperature and pyroelectric properties of lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - 0.06\text{Ba}_{1+x}\text{TiO}_3$ ceramics," *J. Mater. Sci. Mater. Electron.*, **27** 12947–12954 (2016).
7. R. McQuade and M.R. Dolgos, "A review of the structure-property relationships in lead-free piezoelectric $(1-x)\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-(x)\text{BaTiO}_3$," *J. Solid State Chem.*, 0–19 (2016).
8. A.M. Balakt, C.P. Shaw, and Q. Zhang, "The decrease of depolarization temperature and the improvement of pyroelectric properties by doping Ta in lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.06\text{BaTiO}_3$ ceramics," *Ceram. Int.*, **43** 3726–3733 (2017).
9. A.M. Balakt, C.P. Shaw, and Q. Zhang, "Enhancement of pyroelectric properties of lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3-0.06\text{BaTiO}_3$ ceramics by La doping," *J. Eur. Ceram. Soc.*, **37** [4] 1459–1466 (2017).
10. R.D. Shannon, "Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides," *Acta Crystallogr. Sect. A*, **32** [5] 751–767 (1976).
11. N.B. Do, H.B. Lee, C.H. Yoon, J.K. Kang, J.S. Lee, and I.W. Kim, "Effect of Ta-Substitution on the Ferroelectric and Piezoelectric Properties of $\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{TiO}_3$ Ceramics," *Trans. Electr. Electron. Mater.*, **12** [2] 64–67 (2011).
12. N. Petnoi, P. Bomlai, S. Jiansirisomboon, and A. Watcharapasorn, "Effects of Nb-doping on the micro-structure and dielectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramics," *Ceram. Int.*, **39** [SUPPL.1] S113–S117 (2013).
13. T.H. Dinh, H.-Y. Lee, C.-H. Yoon, R.A. Malik, Y.-M. Kong, J.-S. Lee, and V.D.N. Tran, "Effect of lanthanum doping on the structural, ferroelectric, and strain properties of $\text{Bi}_{1/2}(\text{Na}_{0.82}\text{K}_{0.18})_{1/2}\text{TiO}_3$ lead-free ceramics," *J. Korean Phys. Soc.*, **62** [7] 1004–1008 (2013).
14. M.R. Islam, R.H. Galib, A. Sharif, M. Hasan, M.A. Zubair, and M.F. Islam,

- “Correlation of charge defects and morphology with magnetic and electrical properties of Sr and Ta codoped BiFeO₃,” *J. Alloys Compd.*, **688** 1186–1194 (2016).
15. Z. Li, M. Yang, J.S. Park, S.H. Wei, J.J. Berry, and K. Zhu, “Stabilizing Perovskite Structures by Tuning Tolerance Factor: Formation of Formamidinium and Cesium Lead Iodide Solid-State Alloys,” *Chem. Mater.*, **28** [1] 284–292 (2016).
 16. J.-H. Cho, Y.-H. Jeong, J.-H. Nam, J.-S. Yun, and Y.-J. Park, “Phase transition and piezoelectric properties of lead-free (Bi_{1/2}Na_{1/2})TiO₃–BaTiO₃ ceramics,” *Ceram. Int.*, **40** 8419–8425 (2014).
 17. A.M. Balakt, C.P. Shaw, and Q. Zhang, “Enhancement of pyroelectric properties of lead-free 0.94Na_{0.5}Bi_{0.5}TiO₃–0.06BaTiO₃ ceramics by La doping,” *J. Eur. Ceram. Soc.*, 6–13 (2016).
 18. P. Fu, Z. Xu, R. Chu, W. Li, G. Zang, and J. Hao, “Piezoelectric, ferroelectric and dielectric properties of La₂O₃-doped (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ lead-free ceramics,” *Mater. Des.*, **31** [2] 796–801 (2010).
 19. C. Zhou, X. Liu, W. Li, and C. Yuan, “Structure and piezoelectric properties of Bi_{0.5}Na_{0.5}TiO₃–Bi_{0.5}K_{0.5}TiO₃–BiFeO₃ lead-free piezoelectric ceramics,” *Mater. Chem. Phys.*, **114** [2–3] 832–836 (2009).
 20. A.M. Balakt, C.P. Shaw, and Q. Zhang, “The decrease of depolarization temperature and the improvement of pyroelectric properties by doping Ta in lead-free 0.94Na_{0.5}Bi_{0.5}TiO₃–0.06BaTiO₃ ceramics,” (2016).
 21. P. Guggilla, A.K. Batra, J.R. Currie, M.D. Aggarwal, M.A. Alim, and R.B. Lal, “Pyroelectric ceramics for infrared detection applications,” *Mater. Lett.*, **60** [16] 1937–1942 (2006).
 22. Y. Tan, J. Zhang, Y. Wu, C. Wang, V. Koval, B. Shi, H. Ye, R. McKinnon, *et al.*, “Unfolding grain size effects in barium titanate ferroelectric ceramics,” *Sci. Rep.*, **5** [1] 9953 (2015).
 23. D. Shihua, S. Tianxiu, Y. Xiaojing, and L. Guanghua, “Effect of Grain Size of BaTiO₃ Ceramics on Dielectric Properties,” *Ferroelectrics*, **402** [1] 55–59 (2010).
 24. E.M. Anton, W. Jo, D. Damjanovic, and J. Rdel, “Determination of

- depolarization temperature of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based lead-free piezoceramics," *J. Appl. Phys.*, **110** [9] 1–14 (2011).
25. Y. Guo, M. Gu, and H. Luo, "Antiferroelectric phase and pyroelectric response in $(\text{Na}_{1-x}\text{Bi}_x)\text{TiO}_3$ - $x\text{BaTiO}_3$ ceramics," *J. Am. Ceram. Soc.*, **94** [5] 1350–1353 (2011).
 26. W. Jo, J. Daniels, D. Damjanovic, W. Kleemann, and J. Rödel, "Two-stage processes of electrically induced-ferroelectric to relaxor transition in $0.94(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - 0.06BaTiO_3 ," *Appl. Phys. Lett.*, **102** [19] 0–4 (2013).
 27. M.S. Yoon, N.H. Khansur, and S.C. Ur, "The effect of pre-milling/pre-synthesis process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized $0.94[(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3]$ - $0.06[\text{Ba}(1+x)\text{TiO}_3]$," *Ceram. Int.*, **36** [4] 1265–1275 (2010).
 28. C. Xu, D. Lin, and K.W. Kwok, "Structure, electrical properties and depolarization temperature of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - BaTiO_3 lead-free piezoelectric ceramics," *Solid State Sci.*, **10** [7] 934–940 (2008).
 29. W.-S. Kang, S.-K. Lee, and J.-H. Koh, "AC conductivity and dielectric properties of $(\text{Bi},\text{Na})\text{TiO}_3$ - BaTiO_3 lead free ceramics," *Ceram. Int.*, **41** [5] 6925–6932 (2015).
 30. X. Wang, X. Tang, and H. Chan, "Electromechanical and ferroelectric properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -($\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ - BaTiO_3 lead-free piezoelectric ceramics," *Appl. Phys. Lett.*, **85** [1] 91 (2004).
 31. Z. Yao, R. Chu, Z. Xu, J. Hao, W. Li, and G. Li, "Processing and enhanced electrical properties of $\text{Sr}_{1-x}(\text{K}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_2\text{Nb}_2\text{O}_9$ lead-free piezoelectric ceramics," *Ceram. Int.*, **42** [9] 10619–10623 (2016).
 32. J. Rödel, W. Jo, K.T.P. Seifert, E.M. Anton, T. Granzow, and D. Damjanovic, "Perspective on the development of lead-free piezoceramics," *J. Am. Ceram. Soc.*, **92** [6] 1153–1177 (2009).
 33. Y. Hiruma, K. Yoshii, H. Nagata, and T. Takenaka, "Investigation of Phase Transition Temperatures on $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -($\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 Lead-free Piezoelectric Ceramics by Electrical Measurements," *Ferroelectrics*, **346** [773557621] 114–119 (2007).
 34. L.Y. Liu, M.K. Zhu, Y.D. Hou, H. Yan, and R.P. Liu, "Abnormal piezoelectric

- and dielectric behavior of $0.92\text{Na}(0.5)\text{Bi}(0.5)\text{TiO}_3\text{-}0.08\text{BaTiO}_3$ induced by La doping,” *J. Mater. Res.*, **22** [5] 1188–1192 (2007).
35. T. Shi, G. Li, and J. Zhu, “Compositional design strategy for high performance ferroelectric oxides with perovskite structure,” *Ceram. Int.*, (2016).
 36. Y. Hiruma, H. Nagata, and T. Takenaka, “Formation of Morphotropic Phase Boundary and Electrical Properties of $(\text{Bi } 1/2 \text{ Na } 1/2)\text{TiO}_3\text{-Ba}(\text{Al } 1/2 \text{ Nb } 1/2)\text{O}_3$ Solid Solution Ceramics,” *Jpn. J. Appl. Phys.*, **48** [9] 09KC08 (2009).
 37. R. Ranjan and A. Dwiwedi, “Structure and dielectric properties of $(\text{Na}_{0.50}\text{Bi}_{0.50})_{1-x}\text{Ba}_x\text{TiO}_3$: $0 \leq x \leq 0.10$,” *Solid State Commun.*, **135** 394–399 (2005).
 38. W. Cao, W. Li, T. Zhang, J. Sheng, Y. Hou, Y. Feng, Y. Yu, and W. Fei, “High-Energy Storage Density and Efficiency of $(1-x)[0.94\text{NBT-}0.06\text{BT}]\text{-}x\text{ST}$ Lead-Free Ceramics,” *Energy Technol.*, **3** [12] 1198–1204 (2015).
 39. S.T. Lau, C.H. Cheng, S.H. Choy, D.M. Lin, K.W. Kwok, and H.L.W. Chan, “Lead-free ceramics for pyroelectric applications,” *J. Appl. Phys.*, **103** [10] 10–13 (2008).
 40. C. Liu, K. Qian, F. Lu, Z. Chen, B. Fang, J. Ding, Y. Shan, and H. Imoto, “Enhancing pyroelectric property of $\text{Pb}(\text{Fe}_{1/4}\text{Sc}_{1/4}\text{Nb}_{1/2})\text{O}_3$ ceramics,” *J. Alloys Compd.*, **596** 164–166 (2014).
 41. R. Rodríguez-Ruiz, R. González-Ballesteros, a. Flores-Cuautle, and E. Suaste-Gómez, “Determination of the Pyroelectric Coefficient for $(\text{Bi } 0.5 \text{ Na } 0.5) 0.935 \text{ Ba } 0.065 \text{ TiO}_3$ Piezoelectric Ceramics,” *Ferroelectrics*, **368** [1] 216–223 (2008).
 42. M. Abo, Jiro Kobune, T. Nishimura, T. Yazaw, and Y. Nakai, “Effects of manganese addition on pyroelectric properties of $(\text{Bi } 0.5 \text{ Na } 0.5 \text{ TiO}_3) 0.94 (\text{BaTiO}_3) 0.06$ ceramics,” *Integr. Ferroelectr.*, **80** [1] 87–95 (2006).
 43. F.L. Martínez, J. Hinojosa, G. Doménech, F.J. Fernández-luque, J. Zapata, R. Ruiz, and L. Pardo, “Dielectric Constant Tunability at Microwave Frequencies and Pyroelectric Behavior,” *IEEE Trans. Ultrason. Ferroelectr. Freq. Control*, **60** [8] 1595–1602 (2013).
 44. S.R. Kanuru, K. Baskar, and R. Dhanasekaran, “Synthesis, structural, morphological and electrical properties of NBT–BT ceramics for piezoelectric

- applications,” *Ceram. Int.*, **42** [5] 6054–6064 (2016).
45. S. Patel, A. Chauhan, S. Kundu, N.A. Madhar, B. Llahi, R. Vaish, and K.B.R. Varma, “Tuning of dielectric, pyroelectric and ferroelectric properties of $0.715\text{Bi}0.5\text{Na}0.5\text{TiO}_3\text{-}0.065\text{BaTiO}_3\text{-}0.22\text{SrTiO}_3$ ceramic by internal clamping,” *AIP Adv.*, **5** [8] 87145 (2015).
46. S.G. Lee, C. Il Kim, and B.C. Kim, “Dielectric properties of screen-printed $(\text{Ba,Sr,Ca})\text{TiO}_3$ thick films modified with Al_2O_3 for microwave device applications,” *J. Eur. Ceram. Soc.*, **24** [1] 157–162 (2004).
47. X.J. Li, Z.Z. Xi, W. Long, and P.Y. Fang, “Synthesis of antiferroelectric $(\text{Bi}0.534\text{Na}0.5)0.94\text{Ba}0.06\text{TiO}_3$ ceramics with high phase transition temperature and broad temperature range by a solid-state reaction method,” *Chinese Sci. Bull.*, **58** [23] 2893–2897 (2013).

9 Synthesis and Characterisation of the Composite Pyroelectric Ceramic Material (CCPCM) by merging two A-site ((0.2 and 0.5) %La) doped NBT-0.06BT compositions

A composite material has basically been defined as the combination of two or more materials that results in better properties than those of the individual components used alone [1]. Generally, a composite is considered to be any multiphase material that exhibits a significant proportion of the properties of both constituent phases such that a better combination of properties is realized [2]. Therefore, composite materials have been proven as a way for improve the materials properties in compare with its original components. In this scope, this chapter it has been merged two A-site doped pyroelectric ceramic compositions aiming to enlarge and extend the pyroelectric working temperature of the lead-free NBT-0.06BT ceramic material.

9.1.1 Experimental

The raw materials used in this study were powders, lithium oxide (Li_2O), 99.5%, bismuth oxide (Bi_2O_3), 99.999%, sodium carbonate (Na_2CO_3), 99.5%, barium carbonate (BaCO_3), 99.98%, and Titanium dioxide (TiO_2), > 99.8% (all Sigma-Aldrich).

In this study, two synthesis routes were utilized. A solid-state synthesis route was selected to prepare Composition A, 0.002La-doped 0.94NBT-0.06BT and Composition B, 0.005La-doped 0.94NBT-0.06BT. The full details about the synthesis way was reported in chapter 2 (Fig. 2-2). While the synthesis procedure of Composition M was prepared by mixing equal weight amount of two compositions 0.002La-0.94NBT-0.06BT and 0.005La-doped 0.94NBT-0.06BT and then sintered by SPS, for full details of the preparation method please, see Figure 2-3 in chapter 2.

The SPS equipment utilized to sinter Composition M is (HPD 25/1 FCT (Germany)), and sintering temperature was 1000 °C under pressure 50 MPa for 5 min with heating and cooling rates of 100 °C /min.

The pellets obtained by SPS were polished on both sides using different silicon carbide papers. Then the pellets were annealed at 850 °C in a furnace for 20 hrs., at a heating ramp and cooling rate of 10 °C per min. in a furnace to remove the carbon from the pellets and also to release the residual stress after sintering by SPS.

Compositions A, B, and M have been characterized in the same way that followed in the samples in the previous chapters please, see chapter 2.

9.1.2 Results and discussion

9.1.2.1 Microstructure

Fig. 9-5 (a, b, and c) shows X-ray diffraction patterns of Compositions M (C_M from now afterwards), A (C_A) and B (C_B). C_M presents a single perovskite phase without any detectable secondary phase, which is well agreed with the XRD patterns of C_A and C_B .

Fig. 9-5 (b) presents the split in peak [111] into [003] and [021] at 39.0° to 41.0° for all compositions, indicating the existence of rhombohedral (*Rh*) phase. This split agrees with the phase structure of undoped NBT [3,4]. Another split has been spotted in the peak [200] into [200] and [002], which indicates the existence of tetragonal (*Tr*) phase in NBT lattice [5-11] (Fig. 9-5 (c)). The coexistence of both *Rh* and *Tr* phases in C_M , C_A , and C_B , verifies that all compositions are at the morphotropic phase boundary (*MPB*) region [12]. In undoped NBT-xBT the coexistence of *Rh* + *Tr* at $x = 0.06-0.07$ was reported in literature [7,13,14]. Despite the synthesis route of C_M is completely different from that of C_A and C_B the phase structure of C_M remains in the *MPB* region and its phase structure is consistent with that reported in literature [7,13-16].

Table 9-5 lists the lattice parameters, c/a ratio, cell volume, the average grain size and the density of all the compositions. The lattice parameters “ $a = b$ ” and “ c ” of C_M are slightly affected by composition combination and the sintering technique, where “ c ” shows higher value than C_A , but it’s slightly lower than C_B value (Table 9-1). C_M shows higher tetragonality ($c/a \sim 2.4806$) than both C_A ($c/a \sim 2.4386$) and C_B ($c/a \sim 2.4535$) (Table 9-1).

However, C_M shows the lowest cell volume $\sim 252.405 \text{ \AA}^3$ among three compositions (Table 9-1). The average grain size of C_M also shows a considerable decrease compared with C_A and C_B , (Table 9-1). The changes in average grain size in C_M can be attributed to the fact that the SPS sintering technique largely suppresses the grain growth due to a very short sintering time [17-22].

Fig. 9-6 (a-c) illustrates the SEM morphology of all compositions. C_M shows a completely different feature than C_A and C_B . It presents a structure with many pores (Fig. 9-5 (a)). No obvious pores can be observed in C_A and C_B (Fig. 9-2 (b and c)). C_A and C_B exhibit rod shape grains in a wide range of sizes. However, C_M did not show clear grain shapes under current magnification.

C_M shows a density around $5.852 \text{ (gm.cm}^{-3}\text{)}$ which is higher than C_A and C_B (Table 9-5), in spite of the existence of many noticeable pores.

This result is in agreement with literature [12,18-23]. The higher density in C_M can be understood that SPS helps enhance the densification of C_M [12,18-23].

9.1.2.2 Dielectric properties

Fig. 9-7 (a-b) illustrates the change of the dielectric properties of poled ceramic C_M , C_A , and C_B , as a function of temperature from 20°C up to 150°C at 1 kHz. C_M shows dielectric permittivity (ϵ_r) of ~ 344 at room temperature (RT) and 1 kHz (Fig. 9-7 (a)), whereas C_A and C_B show much higher ϵ_r values which are around 600 – 700 (Fig. 9-3 (a)) [10]. The ϵ_r for all compositions increases with rising temperature, which behaves like a typical ferroelectric material [24,25].

The relative permittivity vs. temperature plot demonstrates an obvious declining after a certain temperature in C_A and C_B (Fig. 9-7 (a)). This declining in ϵ_r starts at temperature $\sim 70^\circ\text{C}$ and 69°C for C_A and C_B , respectively. However, it could not be identified in C_M (Fig. 9-7 (a)).

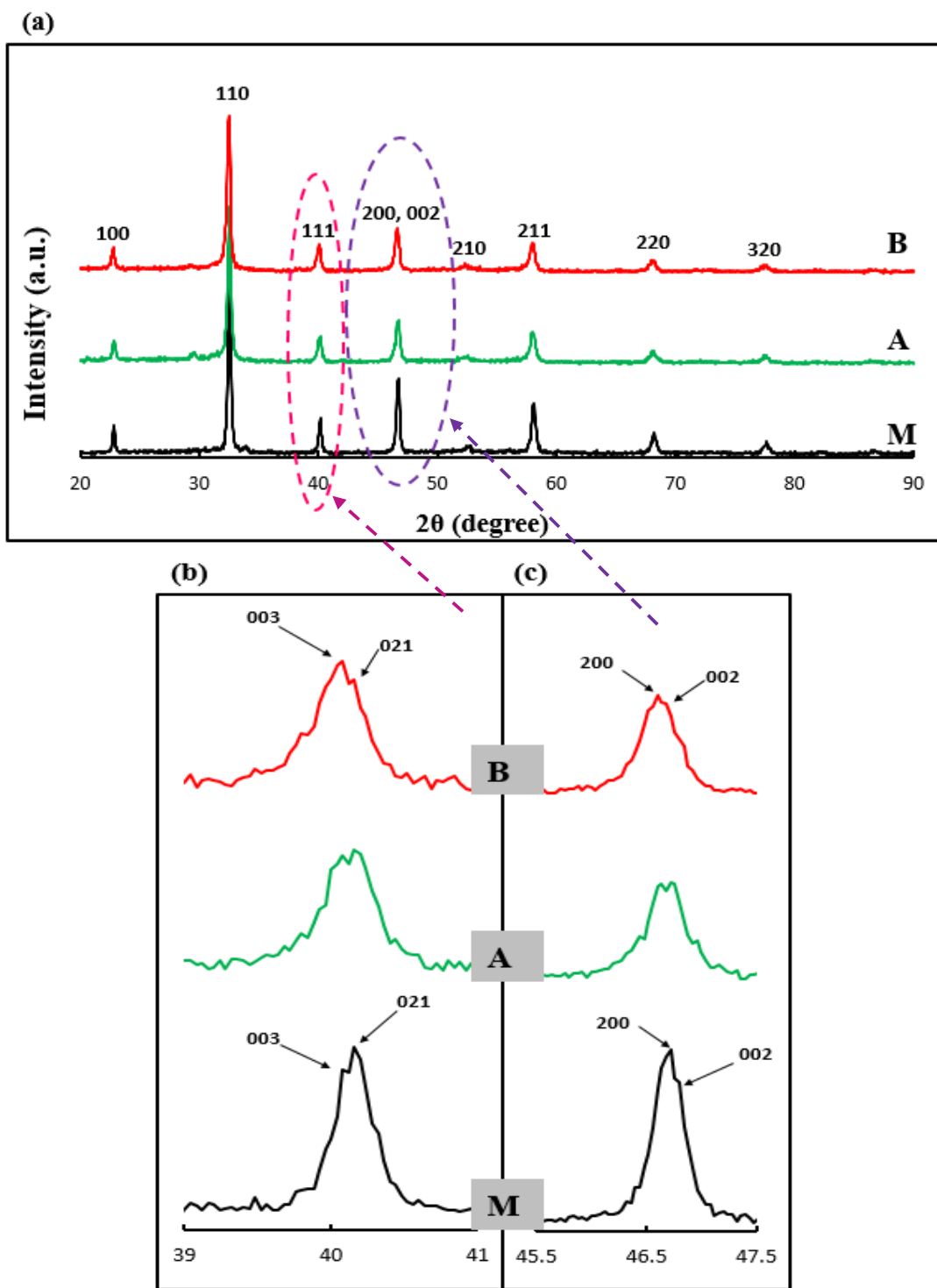
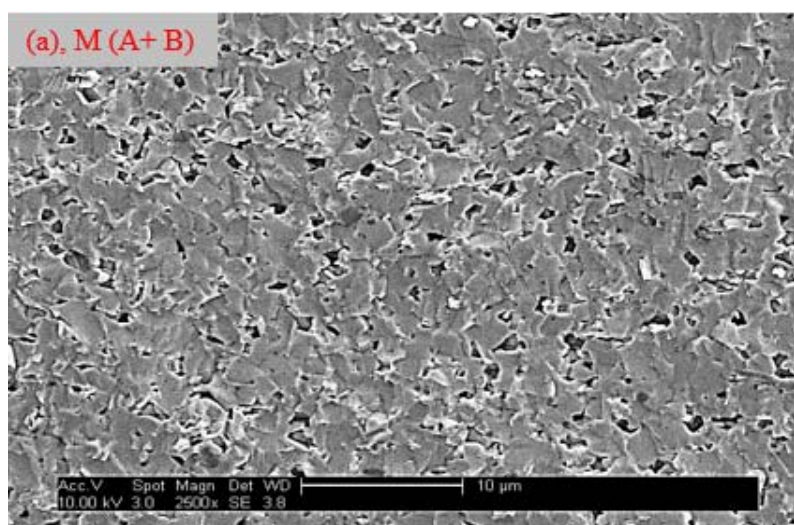


Figure 9-1: (a) XRD patterns of compositions M, A (0.002La-NBT0.06BT), and B (0.005La-NBT0.06BT); (b) enlargement of [111] peak split into [003] and [021] at 39.0° to 41.0°; (c) enlargement of [200] peak split into [200] and [002] at 45.5° to 47.5°.

Table 9-1: The lattice parameters ($\text{\AA}$), c/a ratio, cell volume ($\text{\AA}^3$), average grain size (μm), and density (gm. cm^{-3}) of Composition M, A, and B.

Composition name, xLa-NBT-0.06BT	Lattice parameter ($\text{\AA}$)		c/a ratio	Cell volume ($\text{\AA}^3$)	Average grain size (μm)	Density (gm.cm^{-3})
	a=b	c				
M, (A+B)	5.489	13.505	2.481	252.405	0.917	5.852
A, 0.002La-NBT- 0.0BT	5.518	13.456	2.439	354.786	2.85	5.841
B, 0.005La-NBT- 0.0BT	5.505	13.506	2.454	354.447	2.71	5.785



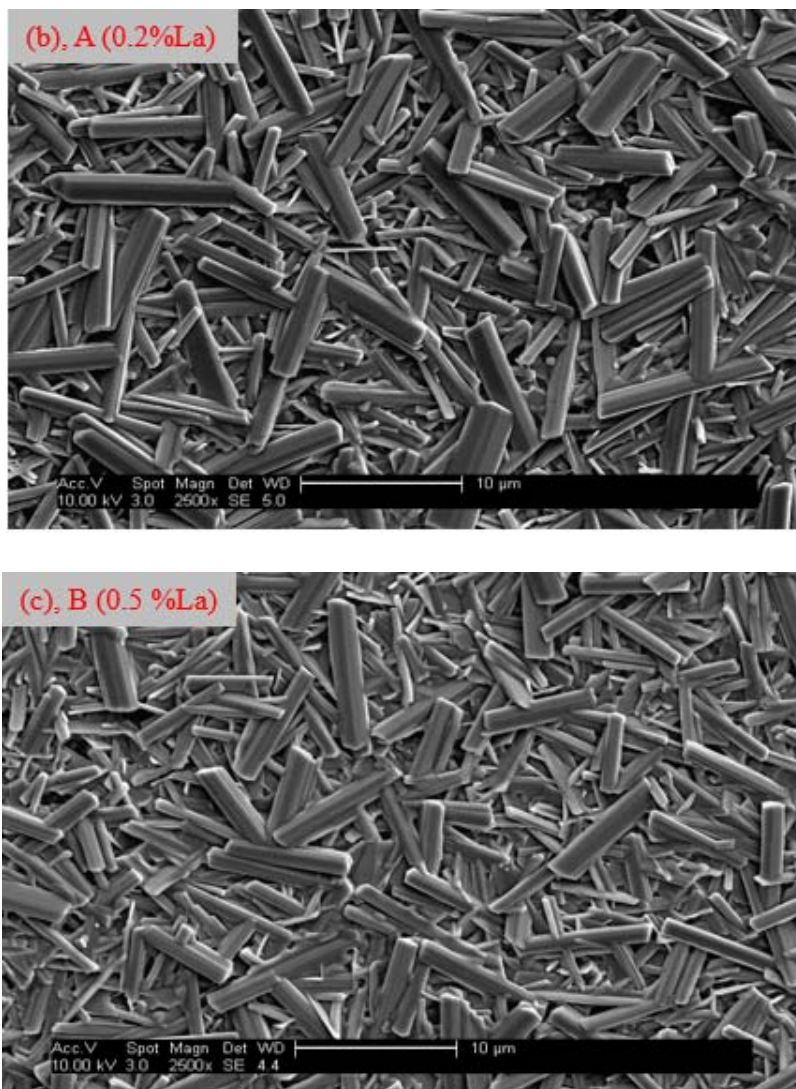


Figure 9-2: The SEM morphology of Compositions M (a), A (b), and B (c).

The dielectric loss ($\tan\delta$) of C_M is much lower (~ 0.027) than those of C_A and C_B , which are around 0.057 and 0.061, respectively at RT and 1 kHz, (Fig. 9-7 (b)). With the increase of temperature, dielectric losses of C_A and C_B increase to the maximum value at the temperature that is widely known as the depolarization temperature (T_d) [26-29] and then decreases. The T_d of C_A and C_B are around 75 °C and 70 °C, respectively [12] (Fig. 9-7 (b)).

C_M , however, exhibits an unusual $\tan\delta$ profile, which shows a continuously increasing within the temperature window. Despite that the graph of dielectric loss vs. temperature of C_M did not show the depolarization temperature within the temperature window, it might appear at the lower end outside the measurement window [12].

Obviously, C_A and C_B show higher $\tan\delta$ than C_M up to 90 °C (Fig. 9-7 (b)) then C_M shows a higher $\tan\delta$ than C_A and C_B . The $\tan\delta$ of C_M presents low and reasonably stable dielectric profile below 90 °C with modest increases in ϵ_r with increasing temperature in the measurement window. While C_A and C_B show quite different dielectric profiles with a sharp increase in both ϵ_r and $\tan\delta$ ($\tan\delta$ up to T_d) in the same measuring window. This lower and reasonably stable temperature profile in the ϵ_r and $\tan\delta$ of C_M is quite beneficial for pyroelectric applications.

9.1.2.3 Depolarization temperature

Apart from dielectric method, T_d could also be identified by pyroelectric method (Fig. 9-8) (a and b)) [30]. In this study, the temperature at which pyroelectric coefficient shows a peak at $FE - AFE$ phase transition was utilized as a second method to identify the T_d for C_M , C_A and C_B , (Fig. 9-8 (a, and b)).

The T_d identified by this method are 40, 68 and 74 °C for C_M , C_A and C_B , respectively, (Fig. 9-8 (a, and b)).

It is widely known that the performance of the ferroelectric materials is strongly related to their microstructure and to average grain size [19,31-34]. C_M with the smaller grain size than C_A and C_B shows a lower phase transition temperature [17,29,30] and therefore more grain boundary [22]. The grain boundary is not ferroelectric phase, thus the volume fraction of the grain boundary in C_M increases with the decrease of grain size. As a result, the ferroelectric properties will be weakened and thus the phase transition shifts to low temperature [22].

Comparing the T_d results for C_A and C_B which have been obtained by two methods, dielectric and pyroelectric, the latter method shows T_d values lower than the former method, which agrees with the results reported by Anton *et al.* [26].

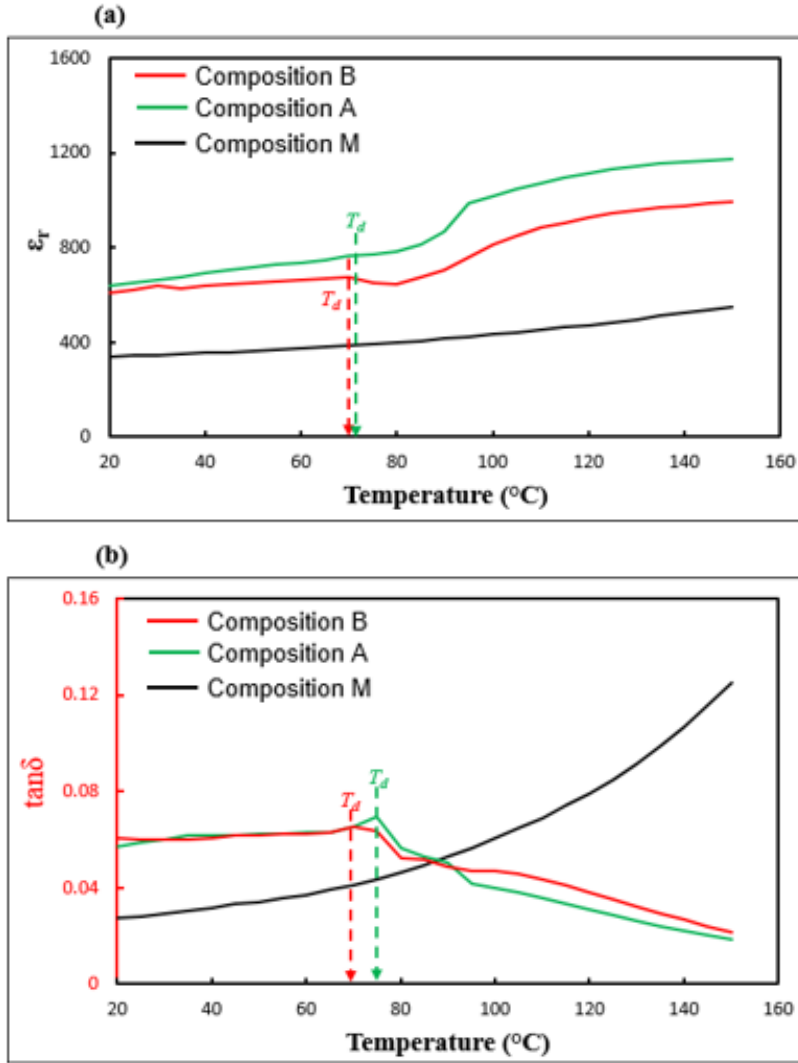


Figure 9-3: (a-c) the temperature dependence of the dielectric permittivity (ϵ_r) and dielectric loss ($\tan\delta$) respectively of Compositions M to B, in wide temperature range and at 1 kHz and identify of the depolarization temperature (T_d).

9.1.2.4 Pyroelectric properties

Pyroelectric coefficient (p) of a material is one of important parameters to be considered for the pyroelectric applications [26,35] and defined as the change of spontaneous polarization (P) produced by a fluctuation of temperature and defined as [36,37]:

$$p = \frac{\Delta P}{\Delta T} \quad (9-1)$$

Figure of merits (*FOMs*) is another important parameter to be considered as well as represents a standard and efficient method to evaluate the performance of a pyroelectric material [4,26,38].

The calculation of the *FOMs* is based on the values of pyroelectric coefficient, relative dielectric permittivity, dielectric loss tangent and specific heat [28,36-40]. There are several types of *FOMs* depending on the special pyroelectric applications such as infrared or thermal imaging [30,38-42].

In the current study, the pyroelectric coefficients (p) of all the samples were measured from 20 °C to 90 °C. The calculations of pyroelectric coefficient(p) and *FOM* have been done using Equations 1-11 and 1-17 in chapter 1 at room and depolarization temperature [13,30,38-40,42].

Fig. 9-8 (a and b) shows the dependence of p as a function of temperature for all compositions from 20 to 90 °C. A broad p profile without a distinguishable sharp peak was shown in C_M in Fig. 9-8 (a). However, single sharp pyroelectric coefficient peak was observed at T_d in C_A and C_B . These pyroelectric responses coincide with the phase transition from *FE* to *AFE* or relaxor-*AFE* phases at T_d (Fig. 9-8 (a)).

While C_M shows this phase change at a lower and broader temperature range between 30 °C to 55 °C (Fig. 9-8 (b)). In addition, p value of C_M exhibits fluctuations at an average value of $6.72 \times 10^{-4} \text{ C.m}^{-2}.\text{°C}^{-1}$ with the maximum p appearing at $7.10 \times 10^{-4} \text{ C.m}^{-2}.\text{°C}^{-1}$ between 30 – 55 °C, a 9 % variation (Fig.9-8 (b)).

The pyroelectric response of C_M may be attributed to its structure. C_M is composed of many tiny compositions that are compacted in different percentage of C_A and C_B (Fig. 9-8 (b)).

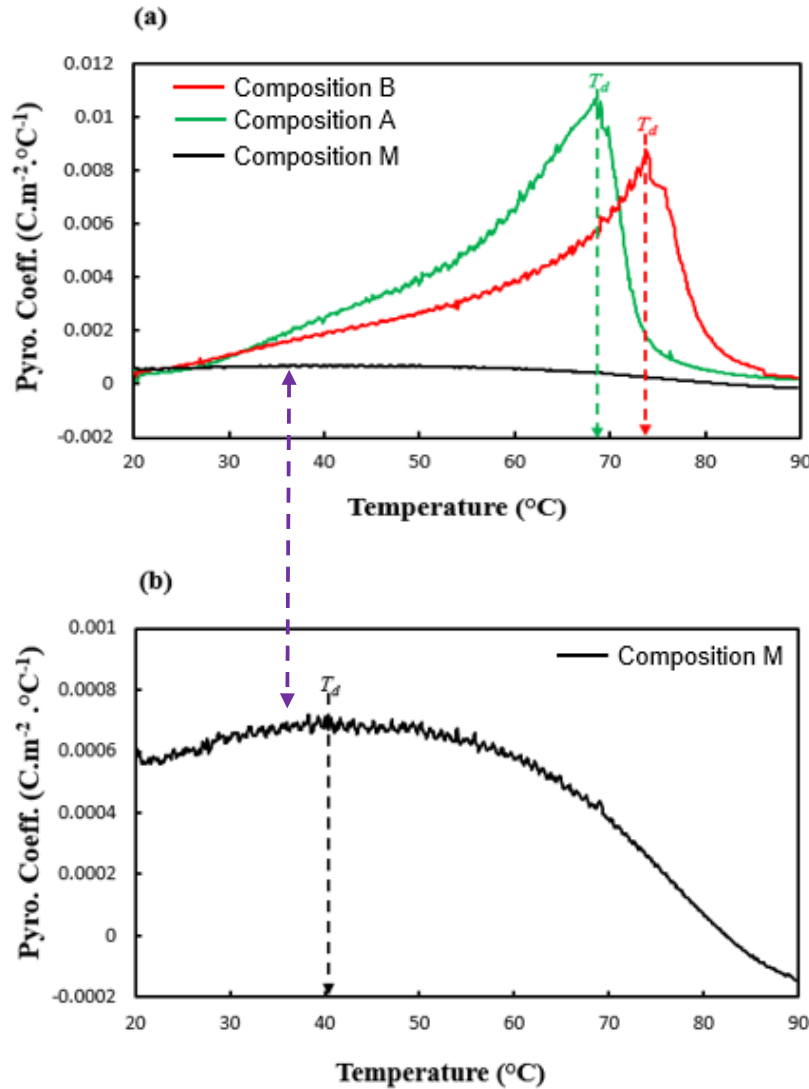


Figure 9-4: (a) the pyroelectric coefficient (p) vs temperature (°C) for Compositions M, A, and B, at temperature from 20 °C to 90 °C , and identify of the T_d for Compositions A, and B. (b) enlargement of the pyroelectric coefficient curve of Composition M with identify of the T_d for the same Compositions.

Those tiny dissimilar compositions would show slightly different pyroelectric response. As a result, the pyroelectric response is smeared to a wide temperature range (30 - 55 °C), (Fig. 9-8 (b)). The wide temperature response in pyroelectric coefficient over a range of $\sim 25 \text{°C}$ that has been achieved in C_M may give rise to a potential breakthrough in pyroelectric device applications.

Pyroelectric coefficient(p) and FOM F_D for C_M , C_A and C_B at RT and T_d are listed in Table 9-2. C_M shows a p value between C_A and C_B at RT, but higher than PZT and other lead-free compositions (Tables 9-2) [14,29,38,43]. In contrast, at T_d C_M presents lower p value than C_A and C_B , PZT, and other lead-free compositions (Tables 9-2). C_B presents the highest p at RT, while C_A at T_d .

At T_d , the lower p value can possibly link to a lower depolarization temperature of C_M . It is widely known that the phase transition from FE to AFE or relaxer AFR happened at T_d [44-48], which means that the ferroelectric material might lose most of its ferroelectric long rang order at this temperature. C_M shows T_d at around 40 °C, which is far lower than T_d of C_A and C_B . However, at T_d , the huge increases of p in C_A and C_B can be interpreted due to the positive correlation between p and pyroelectric current (I_p), which reaches the maximum at T_d [49]. It has been reported that the peak p value of (1-x)NBT-xBT can be achieved at phase transition temperatures [44-48]. Therefore, the large p values obtained at T_d are most likely related to a phase transition.

C_M shows a much higher F_D than C_A and C_B at both room and depolarization temperatures (Tables 9-2), though C_A and C_B have higher p values at T_d . In addition, C_M also shows a higher F_D than PZT and all other lead-free compositions at RT (Tables 9-2), which is due to the higher p (at RT) and the lower dielectric properties (ϵ_r and $\tan\delta$) of this composition.

Table 9-2: The pyroelectric coefficient (p) and the figure of merit F_D at room (RT) and depolarization temperature (T_d).

Composition name, xLa-NBT-0.06BT	$p \times 10^{-4}$ (C.m ⁻² .°C ⁻¹) at RT	$p \times 10^{-4}$ (C.m ⁻² .°C ⁻¹) at T_d	F_D (μPa ^{-1/2}) at 1kHz at RT	F_D (μPa ^{-1/2}) at 1kHz at T_d
M (A+B)	5.93	7.10 at 40 °C	23.0	25.3 at 40 °C
A 0.002La-NBT-0.06BT	5.15	105.4 at 68 °C	1.0	18.2 at 68 °C
B 0.005La-NBT-0.06BT	7.42	86.1 at 74 °C	1.4	15.8 at 74 °C
PZT	4.14	-	9.01	-
NBT-0.07BZT	5.7	20.0 at 50 °C	10.5	33.6 at 50 °C
NBT-0.06BT-0.002Mn	3.5	-	-	-
BNKBT	3.25	-	13.43	-
KNLNTS	1.9	-	11.5	-
NKLBT-0.05BT	3.6	-	-	-

9.1.3 Conclusion

A compositionally graded pyroelectric composition (*CGPC*) of NBT-0.06BT was synthesized by merging two different compositions using SPS technique.

The *CGPC* remains in MPB area. However, the grain size of the *CGPC* significantly reduces in comparison with those in C_A and C_B . The pyroelectric coefficient of *CGPC* stays stable in a broad temperature range (25 °C). Between 30 °C to 55 °C the p of *CGPC* shows an average value (6.72×10^{-4} C. m⁻².°C⁻¹) of C_A and C_B with a variation of $\sim \pm 9$ %. At RT , the p value of *CGPC* shows ~ 5.93

$\times 10^{-4} \text{ C.m}^{-2}.\text{ }^{\circ}\text{C}^{-1}$ that is close to the average pyroelectric coefficient value ($6.29 \times 10^{-4} \text{ C.m}^{-2}.\text{ }^{\circ}\text{C}^{-1}$) of C_A and C_M . Figure of merit (F_D) of the CGPC presents higher values of 23 and 25 $\mu\text{Pa}^{-1/2}$ at both room and depolarization temperatures, respectively. Both pyroelectric coefficient and figure-of-merit of CGPC exceed PZT and other lead-free materials at both RT and T_d . The new compositionally graded pyroelectric ceramic composition might be a very promising material for pyroelectric applications that require to be operated in a wide temperature range.

9.1.4 References

1. F.C.Cambell. Structural Composite Materials. Book. 2010; : 630. Available at: DOI:10.4032/9789814364287
2. William D Callister JDGR. Materials science. Book. 2015;
3. Anem S., Rao KS., Rao KH. Investigation of lanthanum substitution in lead-free BNBT ceramics for transducer applications. Ceramics International. Elsevier; 2016; Available at: DOI:10.1016/j.ceramint.2016.06.173
4. Xu Q., Huang DP., Chen M., Chen W., Liu HX., Kim BH. Effect of bismuth excess on ferroelectric and piezoelectric properties of a $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3$ - BaTiO_3 composition near the morphotropic phase boundary. Journal of Alloys and Compounds. 2009; 471(1–2): 310–316. Available at: DOI:10.1016/j.jallcom.2008.03.078
5. Balakt AM., Shaw CP., Zhang Q. The effects of Ba^{2+} content on depolarization temperature and pyroelectric properties of lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - 0.06\text{Ba}_{1+x}\text{TiO}_3$ ceramics. Journal of Materials Science: Materials in Electronics. 2016; 27: 12947–12954. Available at: DOI:10.1007/s10854-016-5433-1
6. Cho J-H., Jeong Y-H., Nam J-H., Yun J-S., Park Y-J. Phase transition and piezoelectric properties of lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 ceramics. Ceramics International. 2014; 40: 8419–8425. Available at: DOI:10.1016/j.ceramint.2014.01.051
7. Chen M., Xu Q., Kim BH., Ahn BK., Ko JH., Kang WJ., et al. Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ piezoelectric ceramics.

- Journal of the European Ceramic Society. 2008; 28: 843–849. Available at: DOI:10.1016/j.jeurceramsoc.2007.08.007
8. Cheng SY., Shieh J., Lu HY., Shen CY., Tang YC., Ho NJ. Structure analysis of bismuth sodium titanate-based A-site relaxor ferroelectrics by electron diffraction. Journal of the European Ceramic Society. Elsevier Ltd; 2013; 33(11): 2141–2153. Available at: DOI:10.1016/j.jeurceramsoc.2013.03.020
 9. Kanuru SR., Baskar K., Dhanasekaran R. Synthesis, structural, morphological and electrical properties of NBT–BT ceramics for piezoelectric applications. Ceramics International. Elsevier; 2016; 42(5): 6054–6064. Available at: DOI:10.1016/j.ceramint.2015.12.162
 10. Kumari R., Ahlawat N., Agarwal A., Sanghi S., Sindhu M., Ahlawat N. Phase transformation and impedance spectroscopic study of Ba substituted Na_{0.5}Bi_{0.5}TiO₃ ceramics. Journal of Alloys and Compounds. Elsevier B.V; 2016; 676: 452–460. Available at: DOI:10.1016/j.jallcom.2016.03.088
 11. Levanyuk AP. Phase transitions and domain structures in thin ferroelectric films. Phase Transitions. Taylor & Francis; 2015; 88(7): 682–691. Available at: DOI:10.1080/01411594.2014.986732
 12. Balakt AM., Shaw CP., Zhang Q. Enhancement of pyroelectric properties of lead-free 0.94Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃ ceramics by La doping. Journal of the European Ceramic Society. 2017; 37(4): 1459–1466. Available at: DOI:10.1016/j.jeurceramsoc.2016.12.021
 13. Guo F., Yang B., Zhang S., Wu F., Liu D., Hu P., et al. Enhanced pyroelectric property in (1-x)(Bi_{0.5}Na_{0.5})TiO₃-xBa(Zr_{0.055}Ti_{0.945})O₃: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition. Applied Physics Letters. 2013; 103(18): 182906. Available at: DOI:10.1063/1.4828675
 14. Li Q., Wang J., Ma L., Fan H., Li Z. Large electrocaloric effect in (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ lead-free ferroelectric ceramics by La₂O₃ addition. Materials Research Bulletin. Elsevier Ltd; 2016; 74: 57–61. Available at: DOI:10.1016/j.materresbull.2015.10.010
 15. Hiruma Y., Nagata H., Takenaka T. Formation of Morphotropic Phase Boundary and Electrical Properties of (Bi_{1/2}Na_{1/2})TiO₃–Ba(Al_{1/2}Nb_{1/2})TiO₃

-)O 3 Solid Solution Ceramics. Japanese Journal of Applied Physics. 2009; 48(9): 09KC08. Available at: DOI:10.1143/JJAP.48.09KC08
16. Le Goupil F., Bennett J., Axelsson AK., Valant M., Berenov A., Bell AJ., et al. Electrocaloric enhancement near the morphotropic phase boundary in lead-free NBT-KBT ceramics. Applied Physics Letters. 2015; 107(17): 103–107. Available at: DOI:10.1063/1.4934759
 17. Shen Z., Johnsson M., Zhao Z., Nygren M. Spark Plasma Sintering of Alumina. Journal of the American Ceramic Society. 2002; 85(8): 1921–1927. Available at: DOI:10.1111/j.1151-2916.2002.tb00381.x
 18. Munir ZA., Anselmi-Tamburini U., Ohyanagi M. The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method. Journal of Materials Science. 2006; 41(3): 763–777. Available at: DOI:10.1007/s10853-006-6555-2
 19. Hungria T., Galy J., Castro A. Spark plasma sintering as a useful technique to the nanostructuration of piezo-ferroelectric materials. Advanced Engineering Materials. 2009. pp. 615–631. Available at: DOI:10.1002/adem.200900052
 20. Jamaludin SNS., Mustapha F., Nuruzzman DM., Shah Nor Basri. A review on the fabrication techniques of functionally graded ceramic-metallic materials in advanced composites. Scientific Research and Essays. 2013; 8(21): 828–840. Available at: DOI:10.5897/SRE2012.0743
 21. Buscaglia MT., Viviani M., Zhao Z., Buscaglia V., Nanni P. Synthesis of BaTiO₃ core-shell particles and fabrication of dielectric ceramics with local graded structure. Chemistry of Materials. 2006; 18(17): 4002–4010. Available at: DOI:10.1021/cm060403j
 22. Mudinepalli VR., Lin W-C., Song S-H., Murty BS. Spark Plasma Sintering Temperature Effect on Structural, Dielectric and Ferroelectric Properties of Ba_{0.9}Sr_{0.1}TiO₃ Nanocrystalline Ceramics. Journal of Electronic Materials. 2015; 44(11): 4308–4315. Available at: DOI:10.1007/s11664-015-4005-0
 23. Shen Z., Johnsson M., Zhao Z., Nygren M. Spark Plasma Sintering of Alumina. Journal of the American Ceramic Society. 2002; 85(8): 1921–1927. Available at: DOI:10.1111/j.1151-2916.2002.tb00381.x

24. Islam MR., Galib RH., Sharif A., Hasan M., Zubair MA., Islam MF. Correlation of charge defects and morphology with magnetic and electrical properties of Sr and Ta codoped BiFeO₃. *Journal of Alloys and Compounds*. Elsevier Ltd; 2016; 688: 1186–1194. Available at: DOI:10.1016/j.jallcom.2016.07.134
25. Guggilla P., Batra AK., Currie JR., Aggarwal MD., Alim MA., Lal RB. Pyroelectric ceramics for infrared detection applications. *Materials Letters*. 2006; 60(16): 1937–1942. Available at: DOI:10.1016/j.matlet.2005.05.086
26. Anton EM., Jo W., Damjanovic D., Rdel J. Determination of depolarization temperature of (Bi_{1/2}Na_{1/2})TiO₃-based lead-free piezoceramics. *Journal of Applied Physics*. 2011; 110(9): 1–14. Available at: DOI:10.1063/1.3660253
27. Guo Y., Gu M., Luo H. Antiferroelectric phase and pyroelectric response in (NayBi z)Ti_{1-x}O₃(1-x)-xBaTi₃ ceramics. *Journal of the American Ceramic Society*. 2011; 94(5): 1350–1353. Available at: DOI:10.1111/j.1551-2916.2011.04509.x
28. Jo W., Daniels J., Damjanovic D., Kleemann W., Rodel J. Two-stage processes of electrically induced-ferroelectric to relaxor transition in 0.94(Bi_{1/2}Na_{1/2})TiO₃-0.06BaTiO₃. *Applied Physics Letters*. 2013; 102(19): 0–4. Available at: DOI:10.1063/1.4805360
29. Hiruma Y., Nagata H., Takenaka T., Member S. Phase-Transition Temperatures and Piezoelectric Properties of (Bi 1 / 2 Na 1 / 2) TiO 3 -. 2007; 54(12): 2493–2499.
30. ABE J., KOBUNE M., NISHIMURA T., YAZAW T., NAKAI Y. Effects of manganese addition on pyroelectric properties of (Bi_{0.5}Na_{0.5}TiO₃)_{0.94}(BaTiO₃)_{0.06} ceramics. *Integrated Ferroelectrics*. 2006; 80(1): 87–95. Available at: DOI:10.1080/10584580600656502
31. Dudina D V., Mukherjee AK. Reactive spark plasma sintering: Successes and challenges of nanomaterial synthesis. *Journal of Nanomaterials*. 2013; 2013. Available at: DOI:10.1155/2013/625218
32. Mudinepalli VR., Leng F., Reddy MP., Lin WC., Murty BS. Structural, dielectric and ferroelectric properties of lead-free Na_{0.5}Bi_{0.5}TiO₃ ceramics prepared by spark plasma sintering technique. *Indian Journal of Physics*. Springer India; 2015; 90(October): 0–7. Available at: DOI:10.1007/s12648-

33. Fu P., Xu Z., Chu R., Li W., Zang G., Hao J. Piezoelectric, ferroelectric and dielectric properties of La₂O₃-doped (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ lead-free ceramics. *Materials & Design*. Elsevier Ltd; 2010; 31(2): 796–801. Available at: DOI:10.1016/j.matdes.2009.07.056
34. Zhou C., Liu X., Li W., Yuan C. Structure and piezoelectric properties of Bi_{0.5}Na_{0.5}TiO₃-Bi_{0.5}K_{0.5}TiO₃-BiFeO₃ lead-free piezoelectric ceramics. *Materials Chemistry and Physics*. 2009; 114(2–3): 832–836. Available at: DOI:10.1016/j.matchemphys.2008.10.063
35. Yoon MS., Khansur NH., Ur SC. The effect of pre-milling/pre-synthesis process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized 0.94[(Bi_{0.5}Na_{0.5})TiO₃]-0.06[Ba(1+x)TiO₃]. *Ceramics International*. Elsevier Ltd and Techna Group S.r.l.; 2010; 36(4): 1265–1275. Available at: DOI:10.1016/j.ceramint.2010.01.011
36. Abo, Jiro Kobune M., Nishimura T., Yazaw T., Nakai Y. Effects of manganese addition on pyroelectric properties of (Bi_{0.5}Na_{0.5}TiO₃)_{0.94}(BaTiO₃)_{0.06} ceramics. *Integrated Ferroelectrics*. 2006; 80(1): 87–95. Available at: DOI:10.1080/10584580600656502
37. Hosseini M., Moosavi SJ. The effect of microstructure on the pyroelectric properties of PZT ceramics. *Ceramics International*. 2000; 26: 541–544.
38. Lau ST., Cheng CH., Choy SH., Lin DM., Kwok KW., Chan HLW. Lead-free ceramics for pyroelectric applications. *Journal of Applied Physics*. 2008; 103(10): 10–13. Available at: DOI:10.1063/1.2927252
39. Martínez FL., Hinojosa J., Doménech G., Fernández-luque FJ., Zapata J., Ruiz R., et al. Dielectric Constant Tunability at Microwave Frequencies and Pyroelectric Behavior. *IEEE transactions on ultrasonics, ferroelectrics, and frequency control*. 2013; 60(8): 1595–1602. Available at: DOI:10.1109/TUFFC.2013.2740.
40. Rodríguez-Ruiz R., González-Ballesteros R., Flores-Cuautle a., Suaste-Gómez E. Determination of the Pyroelectric Coefficient for (Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}TiO₃ Piezoelectric Ceramics. *Ferroelectrics*. 2008; 368(1): 216–223. Available at: DOI:10.1080/00150190802368537

41. Patel S., Chauhan A., Kundu S., Madhar NA., Llahi B., Vaish R., et al. Tuning of dielectric, pyroelectric and ferroelectric properties of $0.715\text{Bi}0.5\text{Na}0.5\text{TiO}_3\text{-}0.065\text{BaTiO}_3\text{-}0.22\text{SrTiO}_3$ ceramic by internal clamping. *AIP Advances*. 2015; 5(8): 87145. Available at: DOI:10.1063/1.4929328
42. Liu C., Qian K., Lu F., Chen Z., Fang B., Ding J., et al. Enhancing pyroelectric property of $\text{Pb}(\text{Fe}_{1/4}\text{Sc}_{1/4}\text{Nb}_{1/2})\text{O}_3$ ceramics. *Journal of Alloys and Compounds*. Elsevier B.V.; 2014; 596: 164–166. Available at: DOI:10.1016/j.jallcom.2014.01.104
43. Li XJ., Xi ZZ., Long W., Fang PY. Synthesis of antiferroelectric $(\text{Bi}_{0.534}\text{Na}_{0.5})0.94\text{Ba}0.06\text{TiO}_3$ ceramics with high phase transition temperature and broad temperature range by a solid-state reaction method. *Chinese Science Bulletin*. 2013; 58(23): 2893–2897. Available at: DOI:10.1007/s11434-013-5972-2
44. Xu C., Lin D., Kwok KW. Structure, electrical properties and depolarization temperature of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{-BaTiO}_3$ lead-free piezoelectric ceramics. *Solid State Sciences*. 2008; 10(7): 934–940. Available at: DOI:10.1016/j.solidstatesciences.2007.11.003
45. Rawat M., Yadav KL., Kumar A., Patel PK., Adhlakha N., Rani J. Structural, dielectric and conductivity properties of Ba^{2+} doped $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramic. *Advanced Materials Letters*. 2012; 3(4): 286–292. Available at: DOI:10.5185/amlett.2012.2322
46. Hiruma Y., Yoshii K., Nagata H., Takenaka T. Investigation of Phase Transition Temperatures on $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-(Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ Lead-free Piezoelectric Ceramics by Electrical Measurements. *Ferroelectrics*. 2007; 346(773557621): 114–119. Available at: DOI:10.1080/00150190601180471
47. Search H., Journals C., Contact A., Iopscience M. $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{-BaTiO}_3$ System for Lead-Free Piezoelectric Ceramics. *Jpn. J. Appl. Phys.* 1991; 2236(20/07/1991): 2236–2239.
48. Yao Z., Chu R., Xu Z., Hao J., Li W., Li G. Processing and enhanced electrical properties of $\text{Sr}_{1-x}(\text{K}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_2\text{Nb}_2\text{O}_9$ lead-free piezoelectric ceramics.

- Ceramics International. Elsevier; 2016; 42(9): 10619–10623. Available at: DOI:10.1016/j.ceramint.2016.03.156
49. Lee SG., Kim C Il., Kim BC. Dielectric properties of screen-printed (Ba,Sr,Ca)TiO₃ thick films modified with Al₂O₃ for microwave device applications. Journal of the European Ceramic Society. 2004; 24(1): 157–162. Available at: DOI:10.1016/S0955-2219(03)00252-8

10 Project Overall Discussion

This study aimed, firstly, to enhance the pyroelectric properties of the lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ ceramics over a broad temperature range, and secondly, to control and decrease the depolarization temperature (T_d) to near room temperature (RT) using three different methods, which included modifying the initial material composition, doping ions into A- or/and B-sites in the initial material composition, and synthesising composite pyroelectric ceramic material (*CPCM*).

Those three main points were discussed in detail in the individual chapters and this Chapter aims to link the main points to provide an overall understanding to this work.

10.1 Microstructure

The microstructure of NBT-0.06BT was significantly affected by the three primary mechanisms that were followed to improve the pyroelectric properties of this composition. In addition, these mechanisms moved T_d near RT . The microstructural changes of the NBT-0.06BT are listed:

1. Stoichiometric variation of NBT-0.06BT original compositions by changing one or two or all the A-site (Na, Bi, and Ba) element contents.

The NBT-0.06BT microstructure was affected by the variation of the A-site element concentrations. Increasing the Ba^{2+} concentration solely from $x=0.00$ to 0.03 changed the structure of NBT-0.06BT. The lattice parameters ($a=b$) show a slight increase with increasing Ba^{2+} content. However, the stoichiometric and nonstoichiometric compositions showed little variation in the “c” parameter except for the NBT-0.06B_{1.01}T composition, which showed a decrease. The density of nonstoichiometric compositions varied with altering the barium content, and NBT-0.06B_{1.02}T showed the highest density among all compositions. The average grain size decreased with increasing the barium content and reached a minimum at $x=0.02$. Barium performs as an inhibitor of the grains growth in NBT system. In PZT and PLZT (La-containing PZT), the comparable effect was noticed when Pb^{2+} was substituted with Ba^{2+} [1-3].

Furthermore, the alteration of the A-site ($\text{Na}_{(x)}$, $\text{Bi}_{(y)}$, and $\text{Ba}_{(z)}$) element content caused significant changes in the microstructure of the $\text{N}_x\text{B}_y\text{T}-0.06\text{B}_z\text{T}$ material. The lattice parameters profoundly increased with adding more x, y, and z content. Conversely, the average grain size and the density presented noticeable reduction with the change of the stoichiometry compared to the initial composition and the addition of Na, Bi, and Ba concentrations.

All these $\text{Na}_{(x)}\text{Bi}_{(y)}\text{TiO}_3-0.06\text{Ba}_{(z)}\text{TiO}_3$ structural changes may be interpreted in terms of the compositional changes that occurred throughout the heat treatments (calcining and sintering) at high temperature. The loss of sodium is likely more significant than that of bismuth due to the higher volatility of Na. Hence, the composition may shift to a Bi^{3+} -nonstoichiometry state after calcining and sintering. Usually, the Bi^{3+} behaves as an inhibitor of grain growth in NBT microstructures. Consequently, the excess in bismuth content can reduce the grain size [4]. Besides the effect of Bi^{3+} , the increase of the Ba^{2+} content also reduces the grains size, enhancing the prevention the grain growth [1–3,5]. In PZT ceramics it was noticed that the same reduction effect in the grain size of due to substitution of lead with barium as mention before [1-3,5]. The density of nonstoichiometric compositions reduced due to the above reasons.

2. Doping A-or/and B-sites of NBT-0.06BT with other elements (La and/or Ta).

Doping A-site of the material with lanthanum (up to 1.00 (mol %)) largely increases the lattice parameters, average grains size, and the density of the doped compositions.

La^{3+} may enhance the growth of $\text{NBT}-0.06\text{BT}-x\text{La}$ grains when La^{3+} substituted Na^+ . As a result, A-site vacancies will be created to keep charge balance. Creation of the A-site vacancies is quite beneficial for the mass transportation. This mass transport may be responsible for boosting the grain growth in $\text{NBT}-0.06\text{BT}-x\text{La}$ with increasing La^{3+} concentration [6,7].

Doping B-site of $\text{NBT}-0.06\text{BT}$ with $x\text{Ta}^{5+}$ (up to 1.00 (mol %)) also affected the material microstructure. Both the lattice parameters and the density of the doped compositions increased even though the average size of grains reduced.

The reduction of grain size and the increases in the density of doped compositions are due to the creation of cation vacancies in A-site. Ta^{5+} replaces Ti^{4+} due to the radius analogy [2,8-11], but there is a valence difference between them. Thus, Ta^{5+} behaves as a donor, and to maintain the charge balance in the system, A-site vacancies form. These A-site vacancies may locate at the grain boundaries due to the thermodynamic stability of the system. These A-site vacancies restrict the grain growth. Thus, the Ta^{5+} can act as an inhibitor. As a result, doping NBT-BT system with donor elements prevents the growth of the grains [12,13] and as mentioned previously the creation of A-site vacancies helps to increase the density of the dopant compositions due to mass transport [6,7].

Doping both sites of the NBT-0.06BT with xLa and yTa in two different ranges of concentrations ($0.0 \leq x \leq 1.00$; $y=0.002$) and ($x=0.005$; $0.0 \leq y \leq 1.00$) affects the microstructure of the NBT-0.06BT material.

The xLa-NBT-0.06BT-yTa ($0.0 \leq x \leq 1.00$; $y=0.002$), shows an increase in the lattice parameters, average grain size, and the density of the doped compositions. The growth of grains in size can be assigned to dopants effect. La^{3+} enhances the grains' growth in NBT-0.06BT system when it substitutes either Na^{+} and/or Ba^{2+} because of the creation of vacancies in A-site to keep charge balance [6, 9,14]. Tantalum affects the compositions in a contrary way to lanthanum. The Ta^{5+} performs as an inhibitor to the grain growth in NBT-0.06BT due to the valence difference between Ta^{5+} and Ti^{4+} [11,15,16]. As a result, A-site vacancies will be created, as mentioned before [12,13,15].

However, doping A (xLa)- and B (yTa)-sites with, ($x=0.005$ and $0.0 \leq y \leq 1.00$) demonstrates considerable changes in NBT-0.06BT microstructure. NBT-0.06BT shifts outside MPB area by increasing Ta^{5+} content to 1.00 (mol %). Also, the lattice parameters and the density of the co-doped compositions increased with increasing A- and B-site dopant contents, but the average grain size decreased.

The average of grain size increased by increasing of lanthanum and tantalum concentration at $x=0.005$ and $y=0.002$, while it has decreased when further La and Ta concentration is raised up to $x=0.005$ and $y=0.01$. Lanthanum enhances the growth of grains in NBT-0.06BT when it substitutes sodium resulting in A-site

vacancies due to charge unbalance [6,10,14,17]. So, the grains will grow in NBT-0.06BT with the increase of La^{3+} content [10,17]. On the contrary, tantalum as a donor element may behave as an inhibitor to the grain growth in NBT-0.06BT, in which Ta^{5+} will replace Ti^{4+} according to the radius analogy [11-13,15,16]. As a result, the average grain size increased with the addition of different concentrations of La^{3+} (0.005) and Ta^{5+} (0.002), so the effects of La^{3+} on the grain size are more pronounced than Ta^{5+} . Secondly, when the doped amounts of La^{3+} and Ta^{5+} are equal ($x=y=0.005$), the average grain size shows a reduction. The grain reduction is possibly due to competing dopants cancelling the effect. Finally, with more Ta^{5+} content ($x=0.005$; $y=0.01$), the average grain size shows further reduction.

3. Effects of forming CPCMs on the NBT-0.06BT microstructure.

A CPCM was formed by merging two doped $x\text{La-NBT-0.06BT}$, ($x=0.2$ and 0.5 (%)) compositions. The lattice parameters and density demonstrated an obvious increase.

The CPCMs have been manufactured from the $0.002\text{Ta-NBT-0.06BT} + 0.005\text{Ta-NBT-0.06BT}$ compositions which demonstrated considerable reduction in lattice parameters and density.

The average grain size was substantially reduced in the CPCMs.

The reason for the reduction in the average grain size and the density of the CPCMs can be attributed to two factors: firstly, the spark plasma sintering (SPS) technique, which represents the primary factor significantly suppresses the grain growth due to short sintering time [12,13,18-23]; secondly, the effect of doping A-site by increasing La^{3+} concentrations.

Therefore, this study reveals that the microstructure of the NBT-0.06BT was significantly affected by the composition stoichiometry, doping A-site and forming CPCMs.

10.2 Dielectric properties

The dielectric properties were also significantly affected by modifying the compositions by varying the initial concentration of one or two or all the A-site elements and forming A- or B-site doped NBT-0.06BT CPCM. s.

The dielectric properties (dielectric permittivity (ϵ_r) and loss tangents ($\tan\delta$)) were studied as a function of two variables, frequency and temperature.

At RT, ϵ_r and $\tan\delta$ in all the compositions decrease with increasing frequency, which is characteristic of dielectric and ferroelectric materials. This behaviour is because the dipoles in these materials which are following the field at low frequency and contribute to the permittivity value. This contribution decreases as frequency increases and the dipoles start to struggle to follow the changing field [2,4,24,25].

Likewise, after poling most of the compositions showed a reduction for both ϵ_r and $\tan\delta$ at RT, which can be understood because the poling field induces long-range ferroelectric order in these samples [2,26]. Similar behaviour was observed in poled PLZT and PMN materials [2,12,26].

The dielectric properties of the poled compositions demonstrated a significant correlation with increasing temperature. In this study, ϵ_r for all the compositions increases with increasing temperature from 20 °C up to 150 °C. This behaviour is typical for ferroelectric materials [2,26,27].

The dielectric loss of most compositions also increased with the increasing temperature up to a certain point before decreasing. This temperature at which dielectric loss exhibits a maximum value has been commonly referred to as the depolarization temperature (T_d) [23,28,29].

Another variable affecting both the ϵ_r and the $\tan\delta$ was modifying the material compositions and the dielectric permittivity and loss show different values as a response to those parameters.

10.3 Depolarization temperature

In this study, the depolarization temperature (T_d) was successfully identified for most of the compositions by two methods: firstly, by observing the peak on dielectric permittivity or dielectric loss vs temperature plot. Secondly, by observing peaks on pyroelectric coefficient (p) vs temperature plot.

The T_d showed a decrease with the experimental compositional changes and the possible reasons for the lowering of T_d are:

1- Modifying NBT-0.06B_{1+x}T by increasing barium content from $x=0.00$ to 0.03 decreases T_d . Ba²⁺ replaced A-site ions rather than B-site [3,32] due to radius similarity as previously stated, resulting in the generation of A-site vacancies when Ba²⁺ replaces Na⁺. These vacancies reduce long-range ferroelectric ordering and weaken the coupling between A-site ions and TiO₆ octahedron, as a result inducing the phase change at lower temperature [3,32]. These results agree with the literature [33-35].

However, the decrease of T_d in N_xB_yT-0.06B_zT was due to the excess amount of bismuth and/or deficiency of sodium and also due to an excess of barium concentration in the case of Na_{0.5}Bi_{0.534}T-0.06Ba_{1.02}T. According to Yoon *et al.*, Guo *et al.*, and Li *et al.*, [3,28,34] the T_d coincides with phase transition from ferroelectric to a so-called “intermediate” phase. This change showed a shift of T_d toward lower temperature in the compositions with excess Bi³⁺ and/or deficit of Na⁺. Excess Bi³⁺ concentrations in nonstoichiometric compositions are to replace the A-site ions, Na⁺, Bi³⁺ and Ba²⁺ rather than B-site Ti⁴⁺ [3,34] as discussed before, which results in the generation of A-site vacancies when Bi³⁺ replaces Na⁺. These A-site vacancies reduce long-range ferroelectric ordering and weaken the coupling between A-site ions and TiO₆ octahedron, as a result, inducing the phase change at lower temperature [3,34]. These results are in agreements with the literature but also reveal that the T_d can be reduced and shifted towards lower temperature not only by changing the Bi³⁺ / Na⁺ ratio but also by modifying all the A-site ions (Na⁺, Bi³⁺, and Ba²⁺) contents [5,27,28].

2- Doping A-site of NBT-0.06BT with different lanthanum concentrations also lowers the depolarization temperature. This shift in T_d may be because La^{3+} (1.36 Å) has larger ionic radii than Bi^{3+} (1.31 Å). NBT-0.06BT doped with larger elements have been shown to shift T_d toward low temperature [4,10,33,34,36,37], whereas doping NBT-0.06BT with elements that have a small radius such as shift T_d to high temperature [37-40].

Likewise, doping various concentrations of Ta^{5+} in NBT-0.06BT caused the same effect. Doping elements which have a bigger ionic radius than Ti^{4+} may be responsible for the decrease of T_d to lower temperature. These elements consumed a larger space in the oxygen octahedron than the elements with smaller ionic radii. Therefore, it may reduce the degree of freedom for B-site ion moving in the TiO_6 octahedra. As a result, it weakens the ferroelectric properties [41] of NBT-0.06BT, and shifted the phase transition from ferroelectric (*FE*) to antiferroelectric (*AFE*) [10,16,26,28,42,43] or intermediate phase [2,23,32] at lower temperature. Thus, undoped NBT-0.06BT [44] shows T_d at higher temperature than B-site doped with bigger radii elements such as NBT-0.06BT-Nd [35]; NBT-0.06Ba(ZrTi)O₃ [45]; NBT-0.06Ba(MnTi)O₃ [46].

Also, similar reasons can be used to interpret the shifting of the depolarization temperature to lower temperature in La^{3+} and Ta^{5+} co-doped compositions.

3- The pyroelectric composite material prepared in this work contained smaller grain size than the solid-state synthesised compositions and showed a lower T_d , which can be linked to both the average grain size and the grain boundaries [47,49]. The compositions with smaller grain size have more grain boundaries than those with bigger grain size [22], and these grain boundaries are not a ferroelectric phase [22]. Thus, the volume fraction of the grain boundaries in CPCM increases with the decrease of the grain size. As a result, the ferroelectric properties will be weakened and hence the phase transition shifts to low temperature [22].

10.4 Pyroelectric properties

The pyroelectric properties (pyroelectric coefficient (p) and the figure of merits F_i , F_v , F_D , and F_C) of all compositions in the current study were obtained. The pyroelectric properties of the NBT-0.06BT ceramic were enhanced through three mechanisms discussed before. The reasons behind this enhancement in pyroelectric properties can be summarised:

1- Changing the initial concentrations of one or two or all the A-site elemental content:

NBT-0.06B_{1.02}T showed the highest p and FOMs (F_i , F_v , and F_D), among all other compositions. These enhancements can be due to the fact that increasing Ba²⁺ contents from $x=1.00$ to $x = 1.02$ reduced the distortion in perovskite structure because the replacement of Na⁺ (1.39 Å) by Ba²⁺ (1.61 Å) improved the tetragonality in NBT-0.06B_{1.02}T [46,50,51]. In addition, the huge p value at T_d may relate to the effect.

Likewise, the composition Na_{0.52}Bi_{0.52}T-0.06BT with an excess of Na⁺ and Bi³⁺ concentrations by (2%) demonstrated having the highest p and FOMs (F_i , F_v , and F_D), at RT and T_d . These results can be related to the microstructural change in this composition. Na_{0.52}Bi_{0.52}T-0.06BT has a bigger c/a ratio (tetragonality) than all other compositions [29,32,44,52,53].

2- Doping A- or /and B-sites of the NBT-0.06BT with different La³⁺ or/and Ta⁵⁺ concentrations.

For A-site doped NBT-0.06B, the 0.005La-NBT-0.06BT composition showed the highest p value at RT whereas 0.002La-NBT-0.06BT showed the largest pyroelectric coefficient at T_d . These results are probably linked to the change in the structure of those compositions. The calculation of c/a ratio revealed that 0.005La-NBT-0.06BT has a higher c/a ratio, which means that 0.005La-NBT-0.06BT composition possesses more tetragonality in its structure than 0.002La-NBT-0.06BT at RT. The huge increase in p at T_d is attributed to the correlation between p and pyroelectric current (I_p), which reached to the maximum at T_d [52]. The large p values obtained at T_d are most likely related to the effect of the phase transition. The T_d coincides with the phase transition

temperature [3,6,46,56]. Also, both compositions 0.002La-NBT-0.06BT and 0.002La-NBT-0.06BT presented higher FOMs (F_i , F_v , and F_c) than the undoped and doped compositions. The higher FOMs are due to the high pyroelectric coefficient of those compositions and the lower ϵ_r and $\tan\delta$ values.

For B-site ($x\text{Ta}$, $x=0.00$, 0.002 , 0.005 , and 0.01) doped compositions, NBT-0.06BT-0.002Ta showed the highest pyroelectric coefficient and FOMs (F_i , F_v , and F_c) among all other undoped and also doped compositions at room and depolarization temperatures. The reason for these proportion can be linked to two factors: *firstly*, the microstructural changes in this composition. The measurement of c/a ratio revealed that NBT-0.06BT-0.002Ta has a bigger ratio (~ 2.4578) than NBT-0.06BT-0.005Ta (~ 2.4536), which means that NBT-0.06BT-0.002Ta shows more tetragonality in its structure than NBT-0.06BT-0.005Ta. *Secondly*, the position of the MPB for these compositions. The tolerance factor calculation revealed that the x_{MPB} value was 0.0604 which means that the composition of NBT-0.06BT-0.002Ta is in the MPB. The huge improvements in p at T_d can be attributed to the improved pyroelectric current (I_p), which reached the maximum at T_d as previously state. In pyroelectric materials, the increase in temperature will alter the lattice spacing of the nonsymmetrical ions location, which changes the spontaneous polarization of pyroelectric materials. The variation of the spontaneous polarization generates the I_p [52] so, the optimum current (I_p) and pyro coefficient (p) appear at T_d because the maximum change of the spacing appears at T_d [52].

Similarly, the significant increase in p at T_d for NBT-0.06BT-0.002Ta is related to the NBT-0.06BT-0.002Ta composition being located at the MPB, which makes the reorientation of ferroelectric domains easier resulting in a sharp change in polarization [8]. It has been reported that the optimum pyroelectric coefficient value of $(1-x)\text{NBT}-x\text{BT}$ materials can be achieved at the phase transition temperature [29,32,44,53]. Hence, the ultimate p values obtained at T_d in this study relates to the phase transition [1,23,54,55].

3- In CPCM, p and FOMs were found to be increased compared to the two original compositions and the potential operational temperature range has also been extended from 1-2 °C to a range of 10 – 25 °C.

For the CPCM synthesised by merging two doped compositions 0.002La-NBT-0.06BT and 0.005La-NBT-0.06BT this material seems to exhibit the highest and the widest pyroelectric coefficient temperature responses compared to the other CGPCs. The high p value at RT can be directly linked to the microstructure of the CPCM which showed the highest tetragonality ratio ($c/a \sim 2.4806$) than both the component 0.002La-NBT-0.06BT ($c/a \sim 2.4386$) and 0.005La-NBT-0.06BT ($c/a \sim 2.4535$) compositions and the other CGPCs.

As a conclusion, these microstructural changes in these materials due to its compositional variation such as lattice parameters, tetragonality ratio and average grain sizes have been shown to enhance the pyroelectric properties.

10.5 References

1. Chen M., Xu Q., Kim B.H., Ahn B.K., Ko J.H., Kang W.J., et al. Structure and electrical properties of $(\text{Na}_{0.5}\text{Bi}_{0.5})_{1-x}\text{Ba}_x\text{TiO}_3$ piezoelectric ceramics. Journal of the European Ceramic Society. 2008; 28: 843–849. Available at: DOI:10.1016/j.jeurceramsoc.2007.08.007
2. Hiruma Y., Yoshii K., Nagata H., Takenaka T. Investigation of Phase Transition Temperatures on $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ - BaTiO_3 Lead-free Piezoelectric Ceramics by Electrical Measurements. Ferroelectrics. 2007; 346(773557621): 114–119. Available at: DOI:10.1080/00150190601180471
3. Xu C., Lin D., Kwok K.W. Structure, electrical properties and depolarization temperature of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ - BaTiO_3 lead-free piezoelectric ceramics. Solid State Sciences. 2008; 10(7): 934–940. Available at: DOI:10.1016/j.solidstatesciences.2007.11.003
4. Yoon M.S., Khansur N.H., Ur S.C. The effect of pre-milling/pre-synthesis

- process and excess Ba on the microstructure and dielectric/piezoelectric properties of nano-sized $0.94[(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3]-0.06[\text{Ba}(1+x)\text{TiO}_3]$. *Ceramics International*. Elsevier Ltd and Techna Group S.r.l.; 2010; 36(4): 1265–1275. Available at: DOI:10.1016/j.ceramint.2010.01.011
5. Balakt AM., Shaw CP., Zhang Q. The effects of Ba^{2+} content on depolarization temperature and pyroelectric properties of lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3 - 0.06\text{Ba}_{1+x}\text{TiO}_3$ ceramics. *Journal of Materials Science: Materials in Electronics*. 2016; 27: 12947–12954. Available at: DOI:10.1007/s10854-016-5433-1
 6. Anem S., Rao KS., Rao KH. Investigation of lanthanum substitution in lead-free BNBT ceramics for transducer applications. *Ceramics International*. Elsevier; 2016; Available at: DOI:10.1016/j.ceramint.2016.06.173
 7. Martínez FL., Hinojosa J., Doménech G., Fernández-luque FJ., Zapata J., Ruiz R., et al. Dielectric Constant Tunability at Microwave Frequencies and Pyroelectric Behavior. *IEEE transactions on ultrasonics, ferroelectrics, and frequency control*. 2013; 60(8): 1595–1602. Available at: DOI:10.1109/TUFFC.2013.2740.
 8. Razak KA., Yip CJ., Sreekantan S. Synthesis of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ (BNT) and Pr doped BNT using the soft combustion technique and its properties. *Journal of Alloys and Compounds*. Elsevier B.V.; 2011; 509(6): 2936–2941. Available at: DOI:10.1016/j.jallcom.2010.11.163
 9. Fu P., Xu Z., Chu R., Li W., Zang G., Hao J. Piezoelectric, ferroelectric and dielectric properties of La_2O_3 -doped $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ceramics. *Materials & Design*. Elsevier Ltd; 2010; 31(2): 796–801. Available at: DOI:10.1016/j.matdes.2009.07.056
 10. Xu Q., Huang DP., Chen M., Chen W., Liu HX., Kim BH. Effect of bismuth excess on ferroelectric and piezoelectric properties of a $(\text{Na}_{0.5}\text{Bi}_{0.5})\text{TiO}_3\text{-BaTiO}_3$ composition near the morphotropic phase boundary. *Journal of Alloys and Compounds*. 2009; 471(1–2): 310–316. Available at: DOI:10.1016/j.jallcom.2008.03.078

11. Petnoi N., Bomlai P., Jiansirisomboon S., Watcharapasorn A. Effects of Nb-doping on the micro-structure and dielectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3$ ceramics. *Ceramics International*. Elsevier; 2013; 39(SUPPL.1): S113–S117. Available at: DOI:10.1016/j.ceramint.2012.10.045
12. Guggilla P., Batra AK., Currie JR., Aggarwal MD., Alim MA., Lal RB. Pyroelectric ceramics for infrared detection applications. *Materials Letters*. 2006; 60(16): 1937–1942. Available at: DOI:10.1016/j.matlet.2005.05.086
13. Islam MR., Galib RH., Sharif A., Hasan M., Zubair MA., Islam MF. Correlation of charge defects and morphology with magnetic and electrical properties of Sr and Ta codoped BiFeO_3 . *Journal of Alloys and Compounds*. Elsevier Ltd; 2016; 688: 1186–1194. Available at: DOI:10.1016/j.jallcom.2016.07.134
14. Balakt AM., Shaw CP., Zhang Q. Enhancement of pyroelectric properties of lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ ceramics by La doping. *Journal of the European Ceramic Society*. 2016; : 6–13. Available at: DOI:10.1016/j.jeurceramsoc.2016.12.021
15. Balakt AM., Shaw CP., Zhang Q. The decrease of depolarization temperature and the improvement of pyroelectric properties by doping Ta in lead-free $0.94\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ ceramics. *Ceramics International*. December 2016; Available at: DOI:10.1016/j.ceramint.2016.12.004
16. Do NB., Lee HB., Yoon CH., Kang JK., Lee JS., Kim IW. Effect of Ta-Substitution on the Ferroelectric and Piezoelectric Properties of $\text{Bi}_{0.5}(\text{Na}_{0.82}\text{K}_{0.18})_{0.5}\text{TiO}_3$ Ceramics. *Transactions on Electrical and Electronic Materials*. 2011; 12(2): 64–67. Available at: DOI:10.4313/TEEM.2011.12.2.64
17. Zhou C., Liu X., Li W., Yuan C. Structure and piezoelectric properties of $\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3\text{-BiFeO}_3$ lead-free piezoelectric ceramics. *Materials Chemistry and Physics*. 2009; 114(2–3): 832–836. Available at: DOI:10.1016/j.matchemphys.2008.10.063

18. Balakt AM., Shaw CP., Zhang Q. The decrease of depolarization temperature and the improvement of pyroelectric properties by doping Ta in lead-free $0.94\text{Na}0.5\text{Bi}0.5\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ ceramics. 2016; Available at: DOI:10.1016/j.ceramint.2016.12.004
19. Shen Z., Johnsson M., Zhao Z., Nygren M. Spark Plasma Sintering of Alumina. *Journal of the American Ceramic Society*. 2002; 85(8): 1921–1927. Available at: DOI:10.1111/j.1151-2916.2002.tb00381.x
20. Munir ZA., Anselmi-Tamburini U., Ohyanagi M. The effect of electric field and pressure on the synthesis and consolidation of materials: A review of the spark plasma sintering method. *Journal of Materials Science*. 2006; 41(3): 763–777. Available at: DOI:10.1007/s10853-006-6555-2
21. Jamaludin SNS., Mustapha F., Nuruzzman DM., Shah Nor Basri. A review on the fabrication techniques of functionally graded ceramic-metallic materials in advanced composites. *Scientific Research and Essays*. 2013; 8(21): 828–840. Available at: DOI:10.5897/SRE2012.0743
22. Buscaglia MT., Viviani M., Zhao Z., Buscaglia V., Nanni P. Synthesis of BaTiO_3 core-shell particles and fabrication of dielectric ceramics with local graded structure. *Chemistry of Materials*. 2006; 18(17): 4002–4010. Available at: DOI:10.1021/cm060403j
23. Mudinepalli VR., Lin W-C., Song S-H., Murty BS. Spark Plasma Sintering Temperature Effect on Structural, Dielectric and Ferroelectric Properties of $\text{Ba}_{0.9}\text{Sr}_{0.1}\text{TiO}_3$ Nanocrystalline Ceramics. *Journal of Electronic Materials*. 2015; 44(11): 4308–4315. Available at: DOI:10.1007/s11664-015-4005-0
24. Anton EM., Jo W., Damjanovic D., Rdel J. Determination of depolarization temperature of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -based lead-free piezoceramics. *Journal of Applied Physics*. 2011; 110(9): 1–14. Available at: DOI:10.1063/1.3660253
25. Hiruma Y., Nagata H., Takenaka T., Member S. Phase-Transition Temperatures and Piezoelectric Properties of $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ -.

2007; 54(12): 2493–2499.

26. Kang W-S., Lee S-K., Koh J-H. AC conductivity and dielectric properties of (Bi,Na)TiO₃–BaTiO₃ lead free ceramics. *Ceramics International*. 2015; 41(5): 6925–6932. Available at: DOI:10.1016/j.ceramint.2015.01.147
27. Sapper E., Schaab S., Jo W., Granzow T., Rödel J. Influence of electric fields on the depolarization temperature of Mn-doped (1-x)Bi_{1/2}Na_{1/2}TiO₃-xBaTiO₃. *Journal of Applied Physics*. 2012; 111(1): 14105. Available at: DOI:10.1063/1.3674275
28. Li M., Zhang H., Cook SN., Li L., Kilner JA., Reaney IM., et al. Dramatic influence of A-site nonstoichiometry on the electrical conductivity and conduction mechanisms in the perovskite oxide Na_{0.5}Bi_{0.5}TiO₃. *Chemistry of Materials*. 2015; 27(2): 629–634. Available at: DOI:10.1021/cm504475k
29. Guo Y., Gu M., Luo H. Antiferroelectric phase and pyroelectric response in (NayBi z)Ti_{1-x}O₃(1-x)-xBaTi₃ ceramics. *Journal of the American Ceramic Society*. 2011; 94(5): 1350–1353. Available at: DOI:10.1111/j.1551-2916.2011.04509.x
30. Jo W., Daniels J., Damjanovic D., Kleemann W., Rodel J. Two-stage processes of electrically induced-ferroelectric to relaxor transition in 0.94(Bi_{1/2}Na_{1/2})TiO₃-0.06BaTiO₃. *Applied Physics Letters*. 2013; 102(19): 0–4. Available at: DOI:10.1063/1.4805360
31. Balakt AM., Shaw CP., Zhang Q. Large pyroelectric properties at reduced depolarization temperature in A-site nonstoichiometry composition of lead-free 0.94Na_xBi_yTiO₃–0.06Ba_zTiO₃ ceramics. *Journal of Materials Science*. 2017; 52(12): 7382–7393. Available at: DOI:10.1007/s10853-017-0973-1
32. Balakt AM., Shaw CP., Zhang Q. The decrease of depolarization temperature and the improvement of pyroelectric properties by doping Ta in lead-free 0.94Na_{0.5}Bi_{0.5}TiO₃-0.06BaTiO₃ ceramics. *Ceramics*

- International. December 2017; 43: 3726–3733. Available at: DOI:10.1016/j.ceramint.2016.12.004
33. Balakt AM., Shaw CP., Zhang Q. Enhancement of pyroelectric properties of lead-free $0.94\text{Na}0.5\text{Bi}0.5\text{TiO}3\text{-}0.06\text{BaTiO}3$ ceramics by La doping. *Journal of the European Ceramic Society*. 2017; 37(4): 1459–1466. Available at: DOI:10.1016/j.jeurceramsoc.2016.12.021
 34. Balakt AM., Shaw CP., Zhang Q. Giant pyroelectric properties in La and Ta co-doped lead-free $0.94\text{Na}0.5\text{Bi}0.5\text{TiO}3\text{-}0.06\text{BaTiO}3$ ceramics. *Journal of Alloys and Compounds*. 2017; 709: 82–91. Available at: DOI:10.1016/j.jallcom.2017.03.143
 35. Li XJ., Xi ZZ., Long W., Fang PY. Synthesis of antiferroelectric $(\text{Bi}0.534\text{Na}0.5)0.94\text{Ba}0.06\text{TiO}3$ ceramics with high phase transition temperature and broad temperature range by a solid-state reaction method. *Chinese Science Bulletin*. 2013; 58(23): 2893–2897. Available at: DOI:10.1007/s11434-013-5972-2
 36. Rawat M., Yadav KL., Kumar A., Patel PK., Adhlakha N., Rani J. Structural, dielectric and conductivity properties of Ba^{2+} doped $(\text{Bi}0.5\text{Na}0.5)\text{TiO}3$ ceramic. *Advanced Materials Letters*. 2012; 3(4): 286–292. Available at: DOI:10.5185/amlett.2012.2322
 37. Cao W., Li W., Zhang T., Sheng J., Hou Y., Feng Y., et al. High-Energy Storage Density and Efficiency of $(1-x)[0.94\text{NBT-}0.06\text{BT}]\text{-}x\text{ST}$ Lead-Free Ceramics. *Energy Technology*. 2015; 3(12): 1198–1204. Available at: DOI:10.1002/ente.201500173
 38. Li Q., Wang H., Fan H., Long C., Liu X. Ferroelectric, electromechanical, and dielectric properties of $(\text{Na}0.5\text{Bi}0.5)0.94\text{Ba}0.06\text{TiO}3$ co-doped MnO_2 and La_2O_3 lead-free ceramics. *Journal of Materials Science*. 2013; 49(1): 211–217. Available at: DOI:10.1007/s10853-013-7694-x
 39. Shi J., Yang W. Piezoelectric and dielectric properties of Dy_2O_3 -doped $(\text{Bi}0.5\text{Na}0.5)0.94\text{Ba}0.06\text{TiO}3$ lead-free ceramics. *Journal of Alloys and*

- Compounds. Elsevier B.V.; 2009; 472(1–2): 267–270. Available at: DOI:10.1016/j.jallcom.2008.04.038
40. Wang X., Chan HLW., Choy CL. Piezoelectric and dielectric properties of CeO₂-added (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ lead-free ceramics. Solid State Communications. 2003; 125(7–8): 395–399. Available at: DOI:10.1016/S0038-1098(02)00816-5
 41. Peng Fu, Zhijun Xu, Ruiqing Chu, Wei Li, Qian Xie, Yanjie Zhang QC. Effect of Dy₂O₃ on the structure and electrical properties of (Bi_{0.5}Na_{0.5})_{0.94}Ba_{0.06}TiO₃ lead-free piezoelectric ceramics. Journal of Alloys and Compounds. Elsevier B.V.; 2010; 508: 546–553. Available at: DOI:10.1016/j.jallcom.2010.08.117
 42. Dai YJ., Zhang S., Shrout TR., Zhang XW. Piezoelectric and ferroelectric properties of Li-doped (Bi_{0.5}Na_{0.5})TiO₃–(Bi_{0.5}K_{0.5})TiO₃–BaTiO₃ lead-free piezoelectric ceramics. Journal of the American Ceramic Society. 2010; 93(4): 1108–1113. Available at: DOI:10.1111/j.1551-2916.2009.03535.x
 43. Jo W., Daniels JE., Jones JL., Tan X., Thomas P a., Damjanovic D., et al. Evolving morphotropic phase boundary in lead-free (Bi_{1/2}Na_{1/2})TiO₃–BaTiO₃ piezoceramics. Journal of Applied Physics. 2011; 109(1): 14110. Available at: DOI:10.1063/1.3530737
 44. Ranjan R., Dwiwedi A. Structure and dielectric properties of (Na_{0.50}Bi_{0.50})_{1–x}Ba_xTiO₃: 0≤x≤0.10. Solid State Communications. 2005; 135: 394–399. Available at: DOI:10.1016/j.ssc.2005.03.053
 45. Zhang S., Kouna AB., Aulbach E., Jo W., Granzow T., Ehrenberg H., et al. Lead-free piezoceramics with giant strain in the system Bi_{0.5}Na_{0.5}TiO₃–BaTiO₃–K_{0.5}Na_{0.5}NbO₃. II. Temperature dependent properties. Journal of Applied Physics. 2008; 103(3): 34108. Available at: DOI:10.1063/1.2838476
 46. Yao Z., Chu R., Xu Z., Hao J., Li W., Li G. Processing and enhanced

- electrical properties of $\text{Sr}_{1-x}(\text{K}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_2\text{Nb}_2\text{O}_9$ lead-free piezoelectric ceramics. *Ceramics International*. Elsevier; 2016; 42(9): 10619–10623. Available at: DOI:10.1016/j.ceramint.2016.03.156
47. Li Q., Wang J., Ma L., Fan H., Li Z. Large electrocaloric effect in $(\text{Bi}_{0.5}\text{Na}_{0.5})_{0.94}\text{Ba}_{0.06}\text{TiO}_3$ lead-free ferroelectric ceramics by La_2O_3 addition. *Materials Research Bulletin*. Elsevier Ltd; 2016; 74: 57–61. Available at: DOI:10.1016/j.materresbull.2015.10.010
 48. Patel S., Chauhan A., Kundu S., Madhar NA., Llahi B., Vaish R., et al. Tuning of dielectric, pyroelectric and ferroelectric properties of $0.715\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3$ - 0.065BaTiO_3 - 0.22SrTiO_3 ceramic by internal clamping. *AIP Advances*. 2015; 5(8): 87145. Available at: DOI:10.1063/1.4929328
 49. Hungria T., Galy J., Castro A. Spark plasma sintering as a useful technique to the nanostructuration of piezo-ferroelectric materials. *Advanced Engineering Materials*. 2009. pp. 615–631. Available at: DOI:10.1002/adem.200900052
 50. Dudina D V., Mukherjee AK. Reactive spark plasma sintering: Successes and challenges of nanomaterial synthesis. *Journal of Nanomaterials*. 2013; 2013. Available at: DOI:10.1155/2013/625218
 51. Mudinepalli VR., Leng F., Reddy MP., Lin WC., Murty BS. Structural, dielectric and ferroelectric properties of lead-free $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ ceramics prepared by spark plasma sintering technique. *Indian Journal of Physics*. Springer India; 2015; 90(October): 0–7. Available at: DOI:10.1007/s12648-015-0743-3
 52. Abo, Jiro Kobune M., Nishimura T., Yazaw T., Nakai Y. Effects of manganese addition on pyroelectric properties of $(\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3)_{0.94}(\text{BaTiO}_3)_{0.06}$ ceramics. *Integrated Ferroelectrics*. 2006; 80(1): 87–95. Available at: DOI:10.1080/10584580600656502
 53. Suchanicz J., Lewczuk U. KKDEM. Effect of Ba addition on the structural ,

- dielectric and. Materials Science-Poland. 2015; 33(September 2014): 414–417. Available at: DOI:10.1515/msp-2015-0056
54. Shannigrahi SR., Tay FEH., Yao K., Choudhary RNP. Effect of rare earth (La, Nd, Sm, Eu, Gd, Dy, Er and Yb) ion substitutions on the microstructural and electrical properties of sol-gel grown PZT ceramics. Journal of the European Ceramic Society. 2004; 24(1): 163–170. Available at: DOI:10.1016/S0955-2219(03)00316-9
 55. Craciun F., Galassi C., Birjega R. Electric-field-induced and spontaneous relaxor-ferroelectric phase transitions in $(\text{Na}_{1/2}\text{Bi}_{1/2})_1 - \text{XBa}_x\text{TiO}_3$. Journal of Applied Physics. 2012; 112(2012). Available at: DOI:10.1063/1.4770326
 56. Lau ST., Cheng CH., Choy SH., Lin DM., Kwok KW., Chan HLW. Lead-free ceramics for pyroelectric applications. Journal of Applied Physics. 2008; 103(10): 10–13. Available at: DOI:10.1063/1.2927252
 57. Cho J-H., Jeong Y-H., Nam J-H., Yun J-S., Park Y-J. Phase transition and piezoelectric properties of lead-free $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3\text{--BaTiO}_3$ ceramics. Ceramics International. 2014; 40: 8419–8425. Available at: DOI:10.1016/j.ceramint.2014.01.051
 58. Guo F., Yang B., Zhang S., Wu F., Liu D., Hu P., et al. Enhanced pyroelectric property in $(1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3\text{--}x\text{Ba}(\text{Zr}_{0.055}\text{Ti}_{0.945})\text{O}_3$: Role of morphotropic phase boundary and ferroelectric-antiferroelectric phase transition. Applied Physics Letters. 2013; 103(18): 182906. Available at: DOI:10.1063/1.4828675.

11 Conclusions and Recommendations for Future Work

11.1 Conclusions

The general conclusions of this study can be listed as:

1. The lead-free NBT-0.06BT ceramic materials were synthesised using a conventional solid-state route and show good pyroelectric properties.
2. The pyroelectric properties of NBT-0.06BT ceramic were significantly enhanced in response to the variations in the conditions of its preparation. The composition subjected to 24 hrs ball milling, calcination at 850 °C/ 3 hrs., and sintering at 1150 °C/ 2 hrs., exhibited the highest pyroelectric properties, with a pyroelectric coefficient (p) $\sim 3.14 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ and figure of merit F_D around $9.08 \mu\text{Pa}^{-1/2}$ at room temperature (RT).
3. The $(1-x)\text{NBT}-x\text{BT}$ ($0.05 \leq x \leq 0.08$) ceramics manufactured by the same conventional route showed that the structure of NBT-0.06BT and NBT-0.07BT compositions were in the close proximity to a MPB, whereas the structure of NBT-0.05BT and NBT-0.08BT compositions at expected were further away.

The depolarization temperature (T_d), identified for $(1-x)\text{NBT}-x\text{BT}$ ($0.05 \leq x \leq 0.08$) compositions were around 130 °C, 115 °C, 100 °C, and 120 °C by dielectric method . However, only the NBT-0.07BT composition had a T_d that would be estimated by the maximum pyroelectric coefficient (p) at ~ 80 °C.

At room and higher temperatures, NBT-0.06BT composition possessed the maximum p values compared to the other compositions, which were around $\sim 3.14 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ at RT and $24 \times 10^{-4} \text{ C.m}^{-2} \cdot ^\circ\text{C}^{-1}$ at 90 °C. The figures of merit (F_i , F_v and F_D) also presented higher values than the other compositions. They are $\sim 1.12 \times 10^{-10} \text{ m.v}^{-1}$, $\sim 0.021 \text{ m}^2 \cdot \text{C}^{-1}$ and $\sim 9.10 \mu\text{Pa}^{-1/2}$ at RT respectively. Similarly, F_i , F_v and F_D showed the maximum values of $8.6 \times 10^{-10} \text{ m.v}^{-1}$, $0.19 \times 10^{-10} \text{ m}^2 \cdot \text{C}^{-1}$ and $65.5 \mu\text{Pa}^{-1/2}$ respectively, at 90 °C.

4. Modifying NBT-0.06BT compositions, by increasing Ba^{2+} content from $x=0.0$ to $x= 0.01$, and 0.02 . shifted T_d from ~ 125 °C to ~ 85 °C. However, at

$x=0.03$, the T_d rose to ~ 125 °C. T_d was observed in both NBT-0.6B_{1.01}T, and NBT-0.6B_{1.02}T compositions at a temperature of ~ 85 °C. An exact value of T_d was not identified in either NBT-0.6B_{1.00}T or NBT-0.6B_{1.03}T compositions when using the pyroelectric coefficient method.

The NBT-0.6B_{1.02}T composition showed higher values of pyroelectric properties than all other compositions at both RT and T_d , with $p \sim 3.54 \times 10^{-4}$ C.m⁻². °C⁻¹ and 741×10^{-4} C.m⁻². °C⁻¹ at room and depolarization temperatures respectively. Also, the FOMs (F_i , F_v and F_D) for this composition at T_d were $\sim 260 \times 10^{-10}$ m.v⁻¹, ~ 1.64 m².C⁻¹ and ~ 915 μPa^{-1/2}, respectively, much higher than all the other compositions.

Also, changing N_xB_yT-0.06B_zT ceramic compositions by modifying one or two, or all of the A-site element contents demonstrated considerable effects on both the T_d and the pyroelectric properties.

The T_d decreased from ~ 115 °C in NBT-0.06BT to around 85 °C, 55 °C, and 65 °C for N_{0.52}B_{0.52}T-0.06BT, N_{0.5}B_{0.534}T-0.06BT, and N_{0.5}B_{0.534}T-0.06B_{1.02}T respectively. These temperatures were identified by a dielectric method. However, they were around 83 °C, 60 °C, and 61 °C for N_{0.52}B_{0.52}T-0.06BT, N_{0.5}B_{0.534}T-0.06BT, and N_{0.5}B_{0.534}T-0.06B_{1.02}T respectively by pyroelectric method.

This study also revealed that the nonstoichiometric N_{0.52}B_{0.52}T-0.06BT composition showed the maximum p , F_i , F_v , F_D , and F_C values ($\sim 7.00 \times 10^{-4}$ C.m⁻². °C⁻¹, $\sim 2.50 \times 10^{-10}$ m.v⁻¹, ~ 0.05 m².C⁻¹, ~ 16.3 μPa^{-1/2} and $\sim 2.6 \times 10^{-9}$ C.cm⁻². °C⁻¹ (at 100 Hz) and $\sim 75 \times 10^{-4}$ C.m⁻². °C⁻¹, $\sim 27 \times 10^{-10}$ m.v⁻¹, ~ 0.40 m².C⁻¹, and ~ 139 μPa^{-1/2} in both room and depolarization temperatures respectively.

Pyroelectric properties of nonstoichiometric compositions were considerably improved due to the change of A-site element contents.

5. The depolarization temperature and the pyroelectric properties of NBT-0.06BT were affected by doping A-sites with different xLa concentrations ($x=0.0, 0.2, 0.5$, and 1.00 (mole%)). The T_d which was found from the dielectric properties (ϵ_r and $\tan\delta$) was around ~ 115 °C, ~ 73 °C, ~ 70 °C, and ~ 28 °C for NBT-0.06BT, 0.002La-NBT-0.06BT, 0.005La-NBT-0.06BT, and

0.01La-NBT-0.06BT respectively. However, T_d was identified from the p vs. temperature plots for the given compositions as; $> 90^\circ\text{C}$, $\sim 67.9^\circ\text{C}$, $\sim 73.5^\circ\text{C}$, and $\sim 46.8^\circ\text{C}$ respectively. From both methods, the depolarization temperature was shifted toward a lower temperature by doping the NBT-0.06BT with different amounts of lanthanum.

The pyroelectric properties of the NBT-0.06BT were highly enhanced by La^{3+} doping. 0.005La-NBT-0.06BT demonstrated the highest pyroelectric properties ($\sim 7.42 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$, $\sim 2.65 \times 10^{-10} \text{ m.v}^{-1}$, $0.048 \text{ m}^2.\text{C}^{-1}$, and $2.1 \times 10^{-9} \text{ C.cm}^{-2}.\text{C}^{-1}$ (at 33 Hz)) for p , F_i , F_v , and F_C at RT respectively, whereas for 0.002La-NBT-0.06BT the maximum properties were found to be around $105 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$, $38 \times 10^{-10} \text{ m.v}^{-1}$, and $0.56 \text{ m}^2.\text{C}^{-1}$ for p , F_i , and F_v , respectively at T_d .

6. Likewise, doping the material with different amounts of Ta^{5+} greatly enhanced the pyroelectric coefficient and the values of the figures of merit at RT and T_d , but reduced the T_d for the B-site doped compositions. According to the dielectric method, the T_d decreased from $\sim 115^\circ\text{C}$ in the undoped composition to $\sim 95^\circ\text{C}$, $\sim 55^\circ\text{C}$, and $\sim 60^\circ\text{C}$ (average values) in the Ta^{5+} doped compositions with $x=0.002$, 0.05 , and 0.01 . The depolarization temperature as identified by the pyroelectric method was at temperatures of around $> 90^\circ\text{C}$, 79°C , 49°C , and 57°C in NBT-0.06BT, 0.002Ta-NBT-0.06BT, 0.005Ta-NBT-0.06BT, and 0.01Ta-NBT-0.06BT compositions, respectively.
7. The co-doping of NBT-0.06BT with a wide range of dopant concentrations ($x\text{La}$ and $y\text{Ta}$) affected both the depolarization temperature and the pyroelectric properties.

The dielectric method used to determine the T_d of undoped and doped compositions revealed that a depolarization temperature was observed in all compositions with the values of around 115°C , 45°C , 40°C , and 45°C for compositions NBT-0.06BT, 0.002La-NBT-0.06BT-0.002Ta, 0.005La-NBT-0.06BT-0.002Ta, and 0.01La-NBT-0.06BT-0.002Ta respectively.

From the maximum pyroelectric coefficient value T_d was found at temperatures $\sim 61^\circ\text{C}$, $\sim 55^\circ\text{C}$, and $\sim 33^\circ\text{C}$ in the co-doped compositions,

but this method did not provide exact values of the T_d value for undoped compositions. The depolarization temperature seemed to be shifted towards lower temperatures with doping of A-and B-sites of the NBT-0.06BT with xLa ($x=0.005$), and yTa ($y=0.002, 0.005$ and 0.01). The T_d was found at the temperatures of ~ 115 °C, ~ 40 °C, ~ 45 °C, and < 40 °C using the dielectric method, while the pyroelectric vs. temperature plot shows T_d at the temperature of around 55 °C, 35 °C, and 36 °C for the co-doped compositions. This method did not reveal the precise value of depolarization temperature for the NBT-0.06BT composition.

Two doping ranges of $(0.002-0.01)\text{La-NBT-0.06BT-0.002Ta}$ and $0.005\text{La-NBT-0.06BT-(0.002-0.01)Ta}$ were investigated and it was found that $0.005\text{La-NBT-0.06BT-0.002Ta}$ shows the highest p , F_i , and F_v values at both room and depolarization temperatures, which are $\sim 12.9 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$, $4.6 \times 10^{-10} \text{ m.v}^{-1}$, and $0.08 \text{ m}^2.\text{C}^{-1}$ at RT. Further, the pyroelectric coefficient and the FOM values at T_d were sharply increased to $\sim 54 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$, $19 \times 10^{-10} \text{ m.v}^{-1}$, and $0.28 \text{ m}^2.\text{C}^{-1}$.

8. Depolarization temperature and pyroelectric properties were significantly changed by forming CPCPM. Generally, the T_d shifted towards lower temperature to around 41.5 °C in the CPCPM. Composite pyroelectric ceramic material synthesized using two xLa-NBT-0.06BT, ($x=0.002$, and 0.005) compositions presented the maximum pyroelectric properties, with p and F_D values $\sim 5.9 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$ and $7.1 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$ and $23 \mu\text{Pa}^{-1/2}$, $25 \mu\text{Pa}^{-1/2}$ at RT and T_d respectively.

Furthermore, comparing p and F_D values of the unmodified and undoped NBT-0.06BT ($p \sim 3.15 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$ and $F_D \sim 9.8 \mu\text{Pa}^{-1/2}$) and those of the best CPCPM ($p \sim 5.9 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$ and $F_D \sim 23 \mu\text{Pa}^{-1/2}$) indicates that this composite pyroelectric ceramic material possessed higher pyroelectric properties than the NBT-0.06BT at RT. However, the NBT-0.06BT presented the higher p and F_D values, which are around $24 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$, and $66 \mu\text{Pa}^{-1/2}$ respectively than the CPCPM ($p \sim 7.1 \times 10^{-4} \text{ C.m}^{-2}.\text{C}^{-1}$ and $F_D \sim 25 \mu\text{Pa}^{-1/2}$) at T_d .

11.2 Recommendations for Future work

In the current study, unmodified and undoped $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ -0.06 BaTiO_3 and modified and A- or/and B- sites doped ceramic materials were synthesized by the solid-state route. Further, in this study the CGPCs were manufactured using spark plasma sintering (SPS), for all these compositions the microstructure, depolarization, dielectric, and pyroelectric properties were then investigated. The following recommendations are made for extending the present current study:

- Modify the B-site element (Ti^{4+}) concentration of NBT-0.06BT and study the effects the B-site variation on the microstructure, depolarization temperature, dielectric and pyroelectric properties.
- Doping NBT-0.06BT with other lead-free perovskite compositions such as: $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$ (KNN), BaZrTiO_3 (BZT), $\text{K}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (KBT) etc., and investigate the microstructure, depolarization temperature, dielectric, and pyroelectric properties of the new compositions.
- Synthesize undoped and A or/and B-sites doped NBT0.06BT compositions using SPS and compare the microstructure, depolarization temperature, dielectric, and pyroelectric properties of the new compositions with compositions made using the solid-state synthesis route as in this study.
- Synthesize other composite pyroelectric ceramic materials, which will be made from merging two doped A and B-sites of NBT-0.06BT compositions and compare the properties of the new CPCM with those that were manufactured in this study.

APPENDICES

Appendix A

Publication list:

1. Balakt AM., Shaw CP., Zhang Q. The effects of Ba^{2+} content on depolarization temperature and pyroelectric properties of lead-free $0.94\text{Na}0.5\text{Bi}0.5\text{TiO}_3 - 0.06\text{Ba}_{1+x}\text{TiO}_3$ ceramics. *Journal of Materials Science: Materials in Electronics*. 2016; 27: 12947–12954. Available at: DOI:10.1007/s10854-016-5433-1.
2. Balakt AM., Shaw CP., Zhang Q. Enhancement of pyroelectric properties of lead-free $0.94\text{Na}0.5\text{Bi}0.5\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ ceramics by La doping. *Journal of the European Ceramic Society*. 2017; 37(4): 1459–1466. Available at: DOI:10.1016/j.jeurceramsoc.2016.12.021.
3. Balakt AM., Shaw CP., Zhang Q. The decrease of depolarization temperature and the improvement of pyroelectric properties by doping Ta in lead-free $0.94\text{Na}0.5\text{Bi}0.5\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ ceramics. *Ceramics International*. December 2017; 43: 3726–3733. Available at: DOI:10.1016/j.ceramint.2016.12.004
4. Balakt AM., Shaw CP., Zhang Q. Large pyroelectric properties at reduced depolarization temperature in A-site nonstoichiometry composition of lead-free $0.94\text{Na}_x\text{Bi}_y\text{TiO}_3\text{-}0.06\text{Ba}_z\text{TiO}_3$ ceramics. *Journal of Materials Science*. 2017; 52(12): 7382–7393. Available at: DOI:10.1007/s10853-017-0973-1
5. Balakt AM., Shaw CP., Zhang Q. Giant pyroelectric properties in La and Ta co-doped lead-free $0.94\text{Na}_x0.5\text{Bi}_y0.5\text{TiO}_3\text{-}0.06\text{BaTiO}_3$ ceramics. *Journal of Alloys and Compounds*. 2017; 709: 82–91. Available at: DOI:10.1016/j.jallcom.2017.03.143.
6. Improvement of pyroelectric properties of lead-free NBT-0.06BT ceramics at a wide temperature range by co-doping La and Ta.
This paper is currently under review in the *Journal of Materials Science*.

7. A novel method to extend the temperature range of pyroelectric response near room temperature by two compositions coexisting in one La-doped 0.94NBT-0.06BT ceramic material. This paper is currently under writing.