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Giant electrocaloric effect in the thin film relaxor ferroelectric 0.9 $PbMg_{1/3}Nb_{2/3}O_3$ – 0.1 $PbTiO_3$ near room temperature

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We have recently observed a giant electrocaloric effect (12 K in 25 V) in 350 nm sol-gel $PbZr_{0.95}Ti_{0.05}O_3$ films near the ferroelectric Curie temperature of 242°C. Here we demonstrate a giant electrocaloric effect (5 K in 25 V) in 260 nm sol-gel films of the relaxor ferroelectric 0.9 $PbMg_{1/3}Nb_{2/3}O_3$ – 0.1 $PbTiO_3$ near the Curie temperature of 60°C. This reduction in operating temperature widens the potential for applications in novel cooling systems.

Introduction

We have recently demonstrated [OurScience] a giant electrocaloric (EC) effect in thin film $PbZr_{0.95}Ti_{0.05}O_3$ (PZT) [Sawaguchi], with a peak ΔT = 12 K at 226°C. This high working temperature could permit cooling applications in the automotive, aerospace or food industries, but a lower working temperature would open up many more possibilities, e.g. on-chip refrigeration. Lower temperatures are also attractive because thin films fatigue less quickly and possess higher breakdown fields. Here we demonstrate an EC effect in 0.9 $PbMg_{1/3}Nb_{2/3}O_3$ - 0.1 $PbTiO_3$ (0.9 PMN-0.1 PT) [Smolensky] films that peaks at the significantly lower temperature of 75°C.

Relaxor ferroelectrics could be attractive for cooling applications for three reasons. Firstly, some/many/most/all relaxor films such as 0.9 PMN - 0.1 PT show pronounced pyroelectricity [ChoiBhalla, DavisSetter], suggesting that the converse EC effect is strong. Secondly, phase transitions in relaxors are broad so the range of operating temperatures is wide. Thirdly, relaxors show low hysteresis losses. However, the potential for relaxor ferroelectric films in cooling applications has not been considered.

$PbMg_{1/3}Nb_{2/3}O_3$ – $PbTiO_3$ thin films

The PMN-PT family, based on the relaxor PMN [Smolensky], has already been proposed for many applications [YeShirane, ChoiBhalla, ViehlandLi, DavisSetter]. The PMN-rich relaxors, and compositions near the morphotropic phase boundary at 0.65 PMN - 0.35 PT, are [promising for/used in] capacitors due to their large dielectric constant, and [also] [promising for/used in] high-strain actuators/transducers and prototype microelectromechanical systems due to their piezoelectric properties [YeShirane].

Bulk 0.9 PMN - 0.1 PT is a rhombohedral (pseudocubic) relaxor ferroelectric at room temperature [YeShirane, ZekriaGlazer]. On heating above $T_C \sim 60^oC$, this structure transforms to a cubic paraelectric phase [Smolensky, YeShirane, ZekriaGlazer]. Because the material is a relaxor, the corresponding peak in the dielectric constant is frequency dependent [Smolensky], and broad due to microscopic inhomogenities [Smolensky, ChoiBhalla]. The pyroelectric properties of PMN ceramics under high DC bias fields have been studied for thermal IR detector applications [WhatmorePyro]. There is no data for PMN-PT thin films at the temperatures and high electric fields of interest, the EC effect could not be predicted from the literature.

Experimental

0.9 PMN - 0.1 PT sols were prepared from Sigma-Aldrich precursors. A mixture of $Pb(OAc)_2 \cdot 3H_2O$ and $Mg(OAc)_2$ was dissolved in acetic acid and distilled at 100^oC for 30 minutes. 20% excess Pb and 5% excess Mg were added to

compensate for losses during sintering. Separately, acetic acid and 2-methoxyethanol were added to a mixture of $Nb(OEt)_5$ and $Ti(O^nBu)_4$ and the resulting solution was stirred at room temperature for 30 minutes. The Pb/Mg and Nb/Ti based solutions were mixed and stirred at room temperature. Formamide was added to the final solution to prevent cracking during sintering.

Sols were passed through a 0.2 μm filter for spin-coating at 3000 rpm for 30 s onto Pt(111)/Ti/SiO_2/Si(100) substrates that had been rinsed with acetone, and propanol. Layers of ~50 nm were obtained by pre-firing in air on a hotplate at 350°C for 30 s, and then further annealing in a tube furnace at 750°C for 3 minutes. This procedure was repeated five times to obtain ~260 nm films.

Film structure was determined by x-ray diffraction on a Philips diffractometer using Cu Kα radiation. θ-2θ scans corresponded to a polycrystalline perovskite phase with no preferred orientations. The amount of pyrochlore phase was ~8%. Pt top electrodes of diameter 0.2 mm were sputter deposited through a mechanical mask, and the bottom Pt electrode was contacted with silver dag at a substrate edge. The dielectric constant and loss tangent were measured using a HP 4192A Impedance Analyser at 100 kHz and 100 mV ac amplitude. Hysteresis measurements were carried out at 10 kHz using a Radiant Technologies Precision Premier workstation and a low temperature (80°C to -200°C) probe station. The temperature of the sample was controlled via feedback from a thermocouple, accurate to 0.3°C, in contact with the sample.

Results and interpretation

Electrical hysteresis measurements were made roughly every T=10°C in the range 80°C to -200°C, on cooling to minimise reductions in P due to fatigue. Fig. 1 shows the expected [Smolensky] ferroelectric *P(E)* at 75°C, where the EC effect peaks as shown later. Only one loop is shown because our measurements of *P(E)* in 80°C to -200°C varied by just a few percent, and are therefore visually similar. However, we show below that this is sufficient to produce a giant EC effect. The real part of the dielectric constant ε measured on cooling has a broad peak at T_C=60°C

associated with the ferroelectric-paraelectric transition (Fig. 1, upper inset). This broadness is typical of relaxors due to microscopic inhomogeneity. It is also typical of thin films due to interfacial strain, scalar concentration gradients, or other forms of microscopic variability [Smolensky, Jim].

Reversible adiabatic temperature changes ΔT due to an applied electric field E, for a material of density ρ with heat capacity C are given [Tuttle] by:

$$\Delta T = -\frac{1}{C\rho}\int_0^E T\left(\frac{\partial P}{\partial T}\right)_{E'} dE',$$

assuming the Maxwell relation $(\partial P/\partial T)_E = (\partial S/\partial E)_T$. Values of $\partial P/\partial T$ were obtained from 6th order polynomial fits to $P(T)$ data (Fig. 2, inset). Fatigue may only reduce our values of $|\partial P/\partial T|$ since the data were taken on cooling such that P increased in successive hysteresis measurements. In the temperature range of interest, the heat capacity C = 120 J mol^{-1} K^{-1} remains sensibly constant or even decreases at low temperatures [GorevHeatCap]. We note that assuming a constant value of C despite a ~50% peak [Tuttle] resulted in excellent agreement with direct EC measurements of ΔT in bulk $Pb_{0.99}Nb_{0.02}(Zr_{0.75}Sn_{0.20}Ti_{0.05})_{0.98}O_3$ [TuttlePayne]. We assume the bulk value of ρ = 8.08 g cm^{-3} [SatoDensity].

EC temperature changes obtained with (1) are presented in Fig. 2. The largest change at T_{Peak}=75^{o}C (5 K in 25 V, i.e. 0.2 K V^{-1}) exceeds the previous best results at these temperatures obtained in bulk PMN-PT at 14^{o}C (1 K in 160 V, i.e. 0.006 K V^{-1}) and bulk $PbSc_{0.5}Ta_{0.5}O_3$ at 20^{o}C (1.5 K in 1500 V, i. e. 0.001 K V^{-1}) [Shebanov].

Our peak EC temperature change of ΔT = 5 K, determined with E = 895 kV cm^{-1}, represents a peak energy change $C\Delta T$ = 1.86 kJ kg^{-1}. The corresponding hysteresis loss was 24% of this figure, as determined from the area of the 75^{o}C hysteresis loop in E>0. Hysteresis losses may be reduced [ViehlandHystFreq] by (*i*) reducing the measurement frequency, (*ii*) introducing chemical substituents, and (*iii*) process control to modify microstructure.

Leakage current was measured at T_{Peak} = 75°C under our maximum value of E=895 kV cm^{-1} (Fig. 1, lower inset). Reliable measurements were not possible beyond 10 ms, at which time the leakage current has fallen to 4 μA. However, the graph shows that transient currents continue to fall at this measurement time. Therefore 4 μA represents an upper bound on the steady-state leakage current. A current of this magnitude generates a Joule heating of 0.1 K over one quarter of a cycle. This is negligible compared with the peak EC effect of 5 K.

We have demonstrated here a giant EC effect in the relaxor ferroelectric 0.9 PMN - 0.1 PT. The effect peaks at 75°C, which is nearer to room temperature than the giant peak found for PZT at 226°C [OurScience]. Reducing the PT content in PMN-PT is known to reduce the ferroelectric transition temperature to ~0°C in pure PMN [Smolensky]. This suggests a means by which to achieve significant EC effects at even lower temperatures.

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References

[OurScience]. A.S. Mischenko, Q. Zhang, J.F. Scott, R.W. Whatmore, and N.D. Mathur. *Science* **311**, 1270 (2006).

[Sawaguchi]. E. Sawaguchi. *J. Phys. Soc. Japan* **8,** 615-629 (1953).

[Smolensky] G.A. Smolensky. Physical phenomena in ferroelectrics with diffuse phase transitions. *J. Phys. Soc. Jpn. Suppl.* **28**, 26 (1970).

[ChoiBhalla]. S.W. Choi, T.R. Shrout, S.J. Jang, and A.S. Bhalla. Dielectric and pyroelectric properties in the $PbMg_{1/3}Nb_{2/3}O_3$ – $PbTiO_3$ system. *Ferroelectrics* **100**, 29 (1989).

[YeShirane] Z.-G. Ye, B. Noheda, M. Dong, D. Cox, and G. Shirane. *Phys. Rev. B.* **64**, 184114 (2001).

[DavisSetter] M. Davis, D. Damjanovic, and N. Setter. *J. Appl. Phys.* **96**, 2811 (2004).

[Jim] M.M. Saad, P. Baxter, R.M. Bowman, J.M. Gregg, F.D. Morrison, and J.F. Scott. Intrinsic dielectric response in ferroelectric nanocapacitors. *J. Phys.: Cond. Matt.*, **16**, L451 (2004).

[Tuttle] B. A. Tuttle. Polarization reversal and electrocaloric measurements for field – enforced transitions in the system lead zirconate – lead titanate – lead oxide: tin oxide. *PhD Thesis*, University of Illinois at Urbana – Champaign (1981).

[GorevHeatCap] M.V. Gorev, I.N. Flerov, V.S. Bondarev, and Ph. Sciau. *J. Exp. Theor. Phys. (JETP)* **96**, 531 (2003).

[TuttlePayne] [1] Tuttle, B. A. and Payne, D.A. The effects of microstructure on the electrocaloric properties of $Pb(Zr,Sn,Ti)O_3$ ceramics. *Ferroelectrics* **37,** 603-606 (1981).

[SatoDensity] Y. Sato, H. Kanai, and Y. Yamashita. *J. Am. Ceram. Soc.* **79**, 261 (1996).

[Shebanov] L. A. Shebanov, E. H. Birks, K. J. Borman, and A. R. Sternberg. *Ferroelectrics* **94**, 305 (1989).

[ViehlandHystFreq] D. Viehland and J.F. Li. *J. Appl. Phys.* **89**, 1826 (2001).

[DopingCross] W. Pan, Q. Zhuang and L. E. Cross. Direct Current Bias Aging Effects in Lead Magnesium Niobate-Lead Titanate Relaxor Ferroelectric Ceramics
J. Am. Ceram. Soc. 71, C-17 (1988).

[DopingRaevski] I.P. Raevski and S. A. Prosandeev. *J. Phys.: Cond. Matter* **13**, 15 (2001)

[WhatmorePyro] R.W.Whatmore, P.C. Osbond and N.M. Shorrocks. Ferroelectrics 76 351-367 (1987)

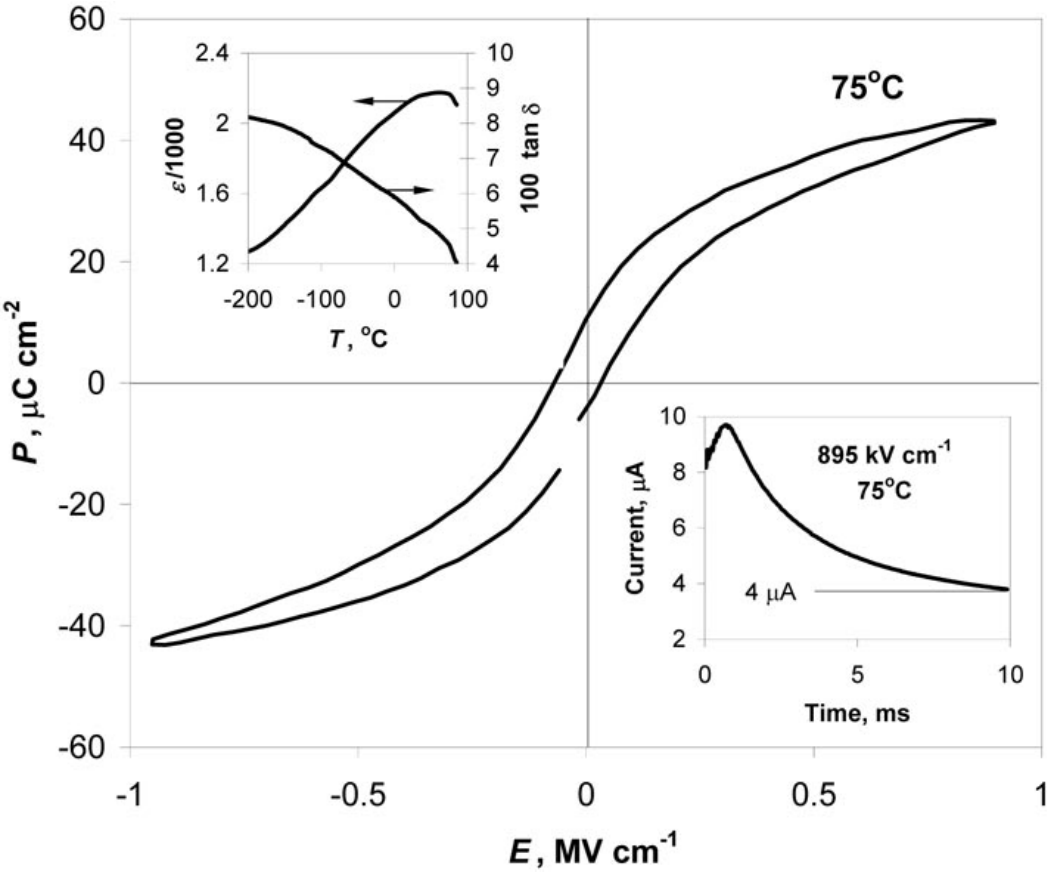

Fig. 1. Electrical measurements of 0.9 $PbMg_{1/3}Nb_{2/3}O_3$ – 0.1 $PbTiO_3$ thin films. Polarisation *P* versus applied electric field *E* at 10 kHz showing evidence of ferroelectricity in the temperature range studied (80°C to -150°C). Upper inset: the real part of the effective dielectric constant ε measured at 100 kHz shows a single broad peak at the bulk transition temperature T_C = 60°C. Loss tangent tan δ = 5% at 60°C. Lower inset: leakage current measurements at the peak working temperature T_{Peak} = 75°C.

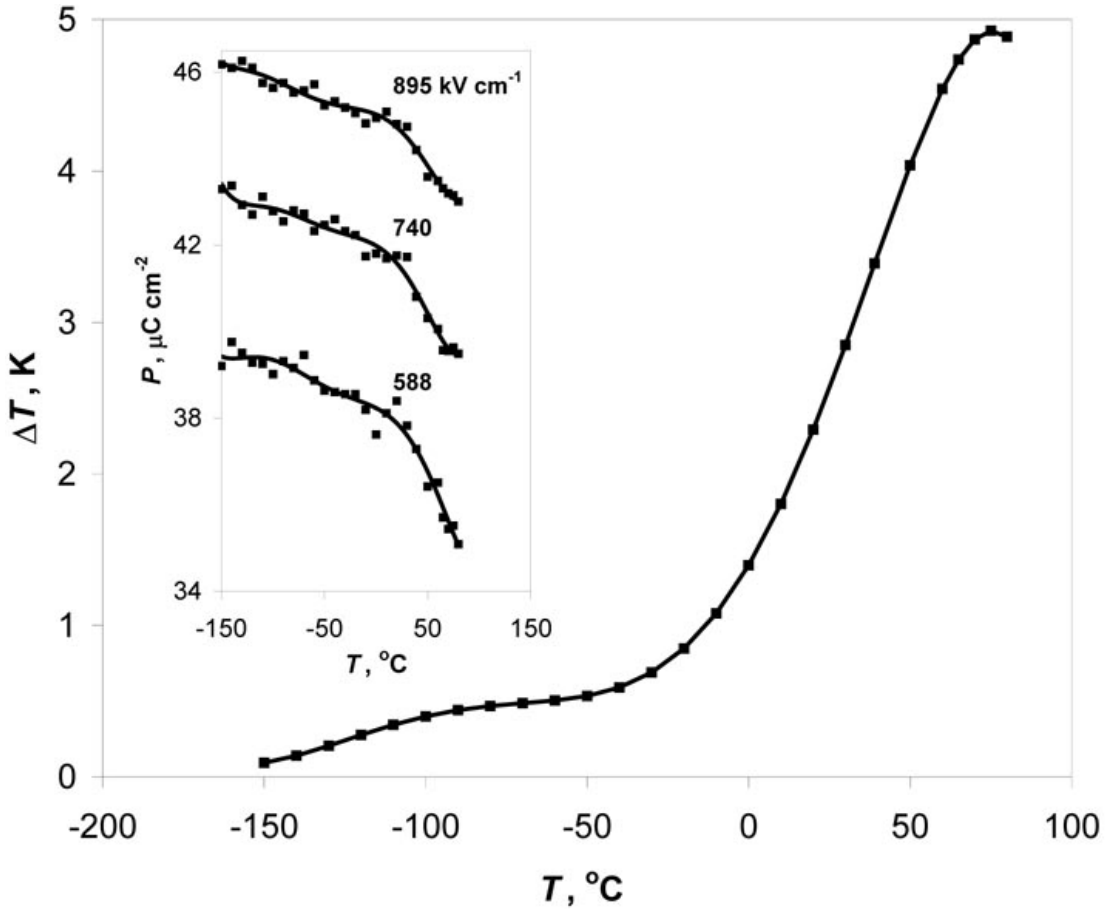

Fig. 2. Electrocaloric temperature changes. ΔT was calculated from equation (1) with applied field $E = 895$ kV cm^{-1}. The peak value of 5 K occurs at $T_{Peak} = 75^{o}$C. Inset: the temperature dependence of polarisation P at selected E. Data extracted for $E > 0$ from the upper branches of 26 hysteresis loops measured at 10 kHz in $-150^{o}\text{C} \leq T \leq 80^{o}\text{C}$. The EC effect is largest when $|\partial P/\partial T|$ is maximised at the broad paraelectric to ferroelectric transition. The lines represent 6th order polynomial fits to the data.

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