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# Investigation of the electrocaloric effect in a $PbMg_{2/3}Nb_{1/3}O_3$-$PbTiO_3$ relaxor thin film

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# Investigation of the electrocaloric effect in a PbMg$_{2/3}$Nb$_{1/3}$O$_3$-PbTiO$_3$ relaxor thin film

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Permittivity measurements of a 0.93PMN-0.07PT thin film show a broad maximum near 35 °C, and an anomaly at the depolarizing temperature $T_d = 18$ °C on heating only, suggesting a dipolar glass-relaxor phase transition. No structural phase transition at 18 °C is apparent from ferro-electric hysteresis loops taken on field cooling and field heating. These loops show the thermal hysteresis expected for ferroelectric relaxors, which has not hitherto been experimentally verified in PbMg$_{2/3}$Nb$_{1/3}$O$_3$-PbTiO$_3$ thin films. Our data suggest the intriguing possibility of a giant electrocaloric effect ($\Delta T = 9$ K, $\Delta E = 720$ kV cm$^{-1}$) at and near room temperature. © *2009 American Institute of Physics.* [doi:10.1063/1.3257695]

Ferroelectric relaxors are characterized by a broad and frequency-dependent permittivity maximum at $T_m$, a slim *P-E* loop and a spontaneous polarization well above $T_m$.[1–4] According to Burns and Dacol,[5] the formation of polar nanoregions (PNRs) occurs at $T_B$, which may be up to several hundred degrees higher than $T_m$. PNRs can be understood as regions with a Curie temperature $T_C$ higher than the bulk average. Therefore, below $T_B$, a relaxor is a mixed system where PNRs exist within a nonpolar matrix. Upon cooling toward $T_m$, the number and size of PNRs increase and their dynamics slow down. Upon further cooling, PNRs may freeze at temperature $T_f < T_m$, or even undergo a structural phase transition.[4]

PbMg$_{2/3}$Nb$_{1/3}$O$_3$ (PMN) is a well-known relaxor that develops long-range dipolar order by adding a certain amount of the ferroelectric perovskite PbTiO$_3$ (PT).[6–8] The phase diagram of the mixed solid solution $(1-x)$PMN-$x$PT has generated some controversy, particularly in $x < 0.3$ where relaxor compositions form. The existence of a structural phase transition in relaxor PMN-PT is debatable. By means of high-resolution x-ray diffraction (XRD), Ye *et al.*[6] observed that for $x > 0.05$ an orthorhombic phase occurs below $T_m$. However, there is no evidence of any structural phase transition in zero-field cooling (ZFC) and zero-field heating (ZFH) dielectric measurements.[3,7–9] Some authors have explained this apparent contradiction by suggesting that some PNRs undergo a cubic-orthorhombic phase transition below $T_m$ while the average symmetry of "PNR+nonpolar matrix" remains globally cubic.[4]

PMN-PT thin-film processing is a challenge due to the persistence of a pyrochlore phase and high porosity. These features are rather difficult to eliminate fully owing to the fact that at high annealing temperatures perovskite degradation occurs quickly and before porosity can be eliminated.[3] Pyrochlore phases and porosity have been pointed out as the

main factors contributing to the decrease of dielectric and ferroelectric properties. Consequently many studies have focused on developing processing methodologies to avoid them.[10–13] We show here that the introduction of a PbZr$_{0.95}$Ti$_{0.05}$O$_3$ (PZT) seed layer permits a purely perovskite 0.93PMN-0.07PT film to be grown at lower annealing temperature (650 °C) with a lower porosity.

Using our film, we investigate here the electrocaloric effect (ECE), i.e., a temperature change $\Delta T$ in an insulating material that is driven by the application or withdrawal of an electric field $E$. The nature of this effect is controversial in textbooks, as discussed in Ref. 14. From Ref. 15, we have

$$\Delta T = -\frac{1}{\rho c} \int_{E_1}^{E_2} T \left( \frac{\partial P}{\partial T} \right) dE, \tag{1}$$

where $\rho$ and $c$ are density and specific heat capacity, respectively. Large values of $\Delta T$ are expected using high electric fields, when operating near phase transitions, i.e., in ferroelectric materials near $T_C$. Bulk materials show a small ECE due to the fact that it is difficult to apply a high electric field without causing electrical breakdown. Consequently bulk electrocaloric materials are not suitable for cooling applications.

We have previously demonstrated that a giant ECE could be obtained for thin films because it is possible to apply a higher $E$.[14,16] $\Delta T_{max} = 12$ K for PZT thin films near $T_C = 226$ °C,[14] and $\Delta T_{max} = 5$ K for 0.9PMN-0.1PT thin films near 60 °C,[16] were determined by indirect measurements using Eq. (1). Some lead-free films, like the poly(vinylidene fluoride-trifluoroethylene) copolymer ($T_C = 70$ °C) (Ref. 17) and SrBi$_2$Ta$_2$O$_9$ ($T_C = 288$ °C) (Ref. 18) were subsequently found to show $\Delta T_{max} = 12$ and 4.9 K near $T_C$, respectively, and the entropy (and energy) changes per cycle in the polymer could be up to five times larger than for PZT.[14] Although progress has therefore been reported in achieving the ECEs at lower operating temperatures,[17] the large 12 °C

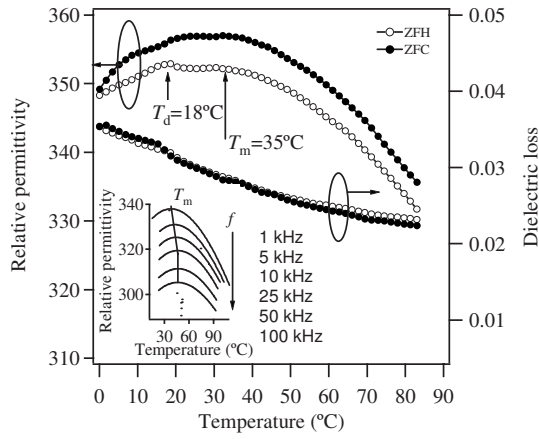a)Electronic mail: q.zhang@cranfield.ac.uk.

FIG. 1. Relative permittivity and dielectric loss as a function of temperature, measured at 1 kHz under conditions of ZFC and ZFH. The inset shows the relative permittivity as a function of frequency and temperature. $T_m$ shifts to higher temperatures as frequency increases.



FIG. 2. FH and FC *P-E* loops at selected temperatures and 100 Hz.

effects[14,17] have not previously been demonstrated at or very near room temperature.

In this paper, we predict a significant ECE at and near room temperature, from data taken on our 0.93PMN-0.07PT film. The ECE was determined from isothermal *P-E* data using Eq. (1) for data taken on heating, and separately for data taken on cooling. The influence of PNR dynamics on the ECE is discussed.

A 0.93PMN-0.07PT sol was prepared according to the method described in Refs. 13 and 19 and the thin film was prepared by spin-coating the sol onto a $Pt/Ti/TiO_2/SiO_2/Si$ substrate at 3000 rpm for 30 s. After being pyrolyzed at 350 °C for 1 min, each layer was annealed at 650 °C for 5 min on a hotplate. This process was repeated until the thickness was 210 nm. To enhance the crystallization of the PMN-PT layers, a thin PZT30/70 seed layer ($\sim$15 nm) was spin-coated onto the substrate prior to 0.93PMN-0.07PT deposition using the sol-gel-based process described in Ref. 20. Square top electrodes of Au ($350 \times 350$ $\mu m^2$) were evaporated through a patterned photoresist mask.

The PZT seed layer works as a nucleation center, such that XRD using Cu $K\alpha$ radiation ($\lambda=1.54$ Å) indicated that pure perovskite PMN-PT was grown on top, even at a low annealing temperature (650 °C). Without this PZT layer, pyrochlore cannot be eliminated at 650 °C.[19] Our 0.93PMN-0.07PT thin film does not exhibit any preferred orientations, but the grain size ($\sim$60 nm from SEM) and crystallite size (15 nm estimated by Scherrer's formula, using the standard (110) XRD reflection at 31.25° with full width at half maximum=0.0096°) are small with respect to similar compositions annealed at higher temperatures.[3,13]

Figure 1 shows the temperature dependence of the relative permittivity and dielectric loss for our 0.93PMN-0.07PT thin film, using both the ZFC and ZFH approaches. Given that our 0.93PMN-0.07PT film is significantly thicker than the PZT seed layer, and given an expected PZT permittivity[20] of 365 at 1 kHz, our measured permittivity reflects the true 0.93PMN-0.07PT permittivity to within $\sim$5%. The measured loss tangent is low compared with other reports,[3,7] but in the context of a multilayer dielectric system of this type, it is not possible to say whether this reflects the intrinsic loss of the 0.93PMN-0.07PT layer, or if it is dominated by the PZT seed layer, which would be expected[20] to have a loss tangent of
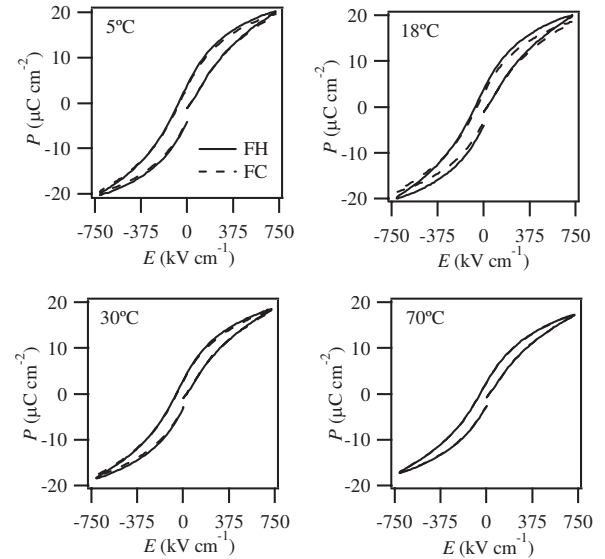
$\sim$0.025 at 1 kHz. Variation of $T_m$ with frequency, well known in relaxors, is shown in the inset of Fig. 1. Failure of the dielectric behavior above $T_m$ to collapse to a single frequency-independent curve could be simply due to sampling in a small temperature window, or due[21] to space charge associated with low crystallinity, or due[21–23] to inhomogeneity such that the transition is smeared out. The discrepancy in the absolute value of the calculated permittivity at 1 kHz ($\sim$5%) (between Fig. 1 and inset) is due to small (<5%) thickness variations across the film.

At $T_m=35$ °C, the permittivity reaches a broad maximum value for both ZFC and ZFH data. This observation agrees with the proposed phase diagram for 0.93PMN-0.07PT solid solutions.[9] At 18 °C, the permittivity displays a reproducible anomaly in the ZFH data that is not readily apparent in the ZFC data (the loss data is not smooth enough to read in this way). This suggests that no structural phase transition takes place on cooling, which in turn suggests no structural transition on heating, despite observations to the contrary.[6] We suggest that during cooling, PNRs freeze at $T_f$, and depolarize on heating through the depolarizing temperature $T_d=18$ °C. The dipole glass model proposed by Viehland *et al.*[24] describes relaxors by analogy with dipole glasses, in which dipole-dipole interactions (or PNR interactions) become stronger at low temperatures. The different thermal dependences of ZFC and ZFH permittivity are due to the coexistence of stable and metastable polar and nonpolar nanoregions. The values of $T_m$ and $T_d$ in the present work corroborate the observation found for 0.93PMN-0.07PT ceramics.[9] This thermal hysteresis has not been previously observed in relaxor thin films.

*P-E* loops were taken in 0–130 °C during field cooling (FC) and then field heating (FH) (Fig. 2). The slim and S-shaped nature of the *P-E* loops, the variation of permittivity on frequency and temperature (inset, Fig. 1) and the persistence of ferroelectricity above $T_m$, confirm the relaxor nature of our 0.93PMN-0.07PT thin film. The *P-E* loops obtained via FC and FH were transformed to show polarization as a function of temperature (Fig. 3), revealing thermal hysteresis around $T_d$. Zhang *et al.*[25] have reported that relaxors, namely PMN-PT, exhibit a prominent aging effect.
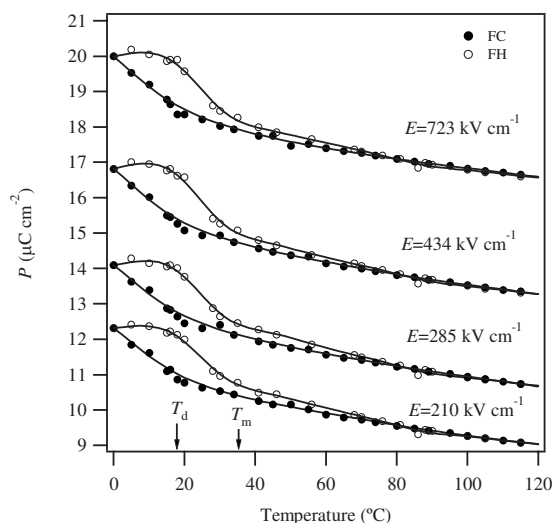
FIG. 3. Polarization as a function of temperature at selected electric fields and 100 Hz, as deduced from *P-E* loops taken on FC and FH. Fits achieved by cubic-spline interpolation.

Therefore, in order to clarify the origin of anomaly at 18 °C, five FC-FH cycles were performed. The results obtained (not shown) have revealed that the anomaly at 18 °C does not disappear after several cycles, and therefore confirms that the effect is not due to aging, but instead originates from PNR depolarization upon heating.

Figure 4 shows $\Delta T$ for $\Delta E = E_1 - E_2 = 723$, 509, 434, 360, 285, and 210 kV cm$^{-1}$ ($E_1 = 0$) for the FC and FH data, as obtained from Eq. (1) assuming $c = 0.32$ J K$^{-1}$ g$^{-1}$ and $\rho = 8.3$ g cm$^{-3}$ [data are only shown up to 45 °C, in order to zoom in on the peak ECE predictions where $dP/dT$ (Fig. 3) is largest]. Given that the indirect method[15] assumes the equilibrium value for $P(E,T)$, it is not possible to interpret the predictions in Fig. 4 literally, as relaxors are never formally in thermal equilibrium.[22,26,27] However, the FH data suggests the intriguing possibility of a large $\Delta T = 9$ K at 25 °C when $E = 723$ kV cm$^{-1}$ is applied. This is an interest-
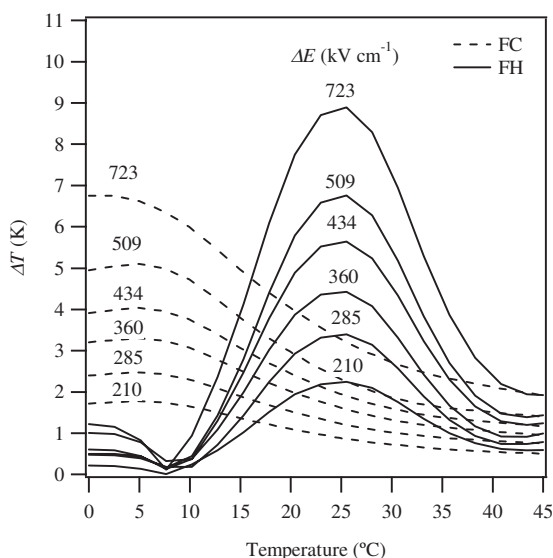


FIG. 4. Predictions of electrocaloric temperature change $\Delta T$ in the 0.93PMN-0.07PT thin film, as a function of starting temperature, due to selected $\Delta E$ ($E_1 = 0$). Results were obtained using the indirect method separately for the FC and FH data in Fig. 3.

ing outcome because no dielectric material has shown or been predicted to show such a large ECE at room temperature. Further work is in progress in an attempt to directly evaluate $\Delta T$ in thin films.

In summary, an all-perovskite thin film of 0.93PMN-0.07PT was produced using a PZT seed layer, and maximum permittivity occurred at $T_m = 35$ °C, i.e., near room temperature. Thermal hysteresis, in $P(T)$ deduced from $P$-$E$ loops, is evident around $T_d = 18$ °C. The cubic-orthorhombic phase transition at low temperatures reported by several authors could not be reconciled with this work. Instead a dipole-glass model for relaxors can explain well the observed thermal hysteresis. Anomalies at $T_d$ both in permittivity and polarization are observed only on heating and correspond to the PNR depolarizing process. $T_m$ and $T_d$ are in good agreement with the previously reported phase diagram.[9] Using the indirect method to process the data, the ECE of the film cannot formally be determined in the absence of thermal equilibrium, but large effects of $\Delta T = 9$ °C near room temperature may be possible.

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