

Investigation of the electrocaloric effect in a PMN-PT 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 ferroelectric 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 PMN-PT 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.

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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 [5], the formation of polar nano-regions (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 towards 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 at temperature T_C [4].

$\text{PbMg}_{2/3}\text{Nb}_{1/3}\text{O}_3$ (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 $(1-x)\text{PMN}-x\text{PT}$ 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, 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 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 ΔT 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 [14]. From [15], we have:

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

where ρ and c are density and specific heat capacity, respectively. Large values of ΔT 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 $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ (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) [17] and $\text{SrBi}_2\text{Ta}_2\text{O}_9$ ($T_C = 288$ °C) [18] were subsequently found to show $\Delta T_{\max} = 12$ K and

4.9 K near T_C , respectively, and the entropy (and energy) changes per cycle in the polymer could be up to 5 times larger than for PZT [14]. Although progress has therefore been reported in achieving the electrocaloric effects at lower operating temperatures [17], the large 12 °C 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 [13, 19], and the thin film was prepared by spin-coating the sol onto a Pt/Ti/TiO₂/SiO₂/Si substrate at 3000 rpm for 30 s. After being pyrolyzed at 350 °C for 1 minute, each layer was annealed at 650 °C for 5 minutes 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 (~ 15 nm) was spin-coated onto the substrate prior to 0.93PMN-0.07PT deposition using the sol-gel-based process described in [20]. Square top electrodes of Au (350 μ m $\times$ 350 μ m) were evaporated through a patterned photoresist mask.

The PZT seed layer works as a nucleation centre, such that x-ray diffraction using Cu K α 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 can not be eliminated at 650 °C [19]. Our PMN-PT thin film does not exhibit any preferred orientations, but the grain size (~60 nm from SEM) and crystallite size (15 nm estimated

by Scherrer's formula, using the standard (110) XRD reflection at 31.25° with FWHM= 0.0096°) are small with respect to similar compositions annealed at higher temperatures [3, 13].

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

At $T_m = 35^\circ\text{C}$, the permittivity reaches a broad maximum value for both ZFC and ZFH data. This observation agrees with the proposed phase diagram for PMN-PT 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 some temperature 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. 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.

Fig. 4 shows ΔT 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 Equation (1) assuming $c =$

$0.32 \text{ J K}^{-1} \text{ g}^{-1}$ and $\rho = 8.3 \text{ g cm}^{-3}$ (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 [26-28]. However, the FH data suggests the intriguing possibility of a large $\Delta T = 9 \text{ K}$ at 25°C when $E = 723 \text{ kV cm}^{-1}$ is applied. This is an interesting 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 attempt to directly evaluate ΔT 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 $T_m = 35^\circ\text{C}$, i.e. near room temperature. Thermal hysteresis, in $P(T)$ deduced from P - E loops, is evident around $T_d = 18^\circ\text{C}$. 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 $\Delta T = 9^\circ\text{C}$ near room temperature may be possible.

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Figure captions

FIG. 1. Relative permittivity and dielectric loss as a function of temperature, measured at 1 kHz under conditions of zero-field cooling (ZFC) and zero-field heating (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.

FIG. 3. Polarization as a function of temperature at selected electric fields, as deduced from P - E loops taken on field cooling (FC) and field heating (FH). Fits achieved by cubic-spline interpolation.

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

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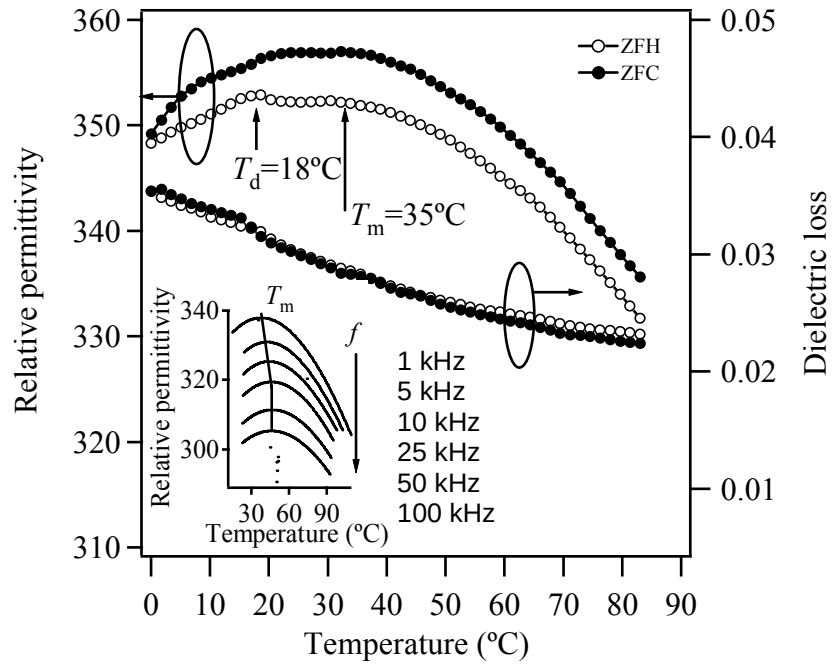


Figure 1

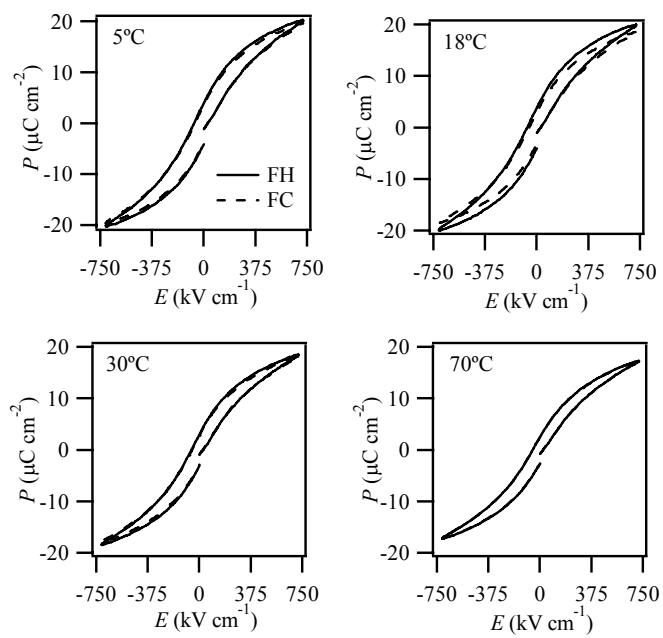


Figure 2

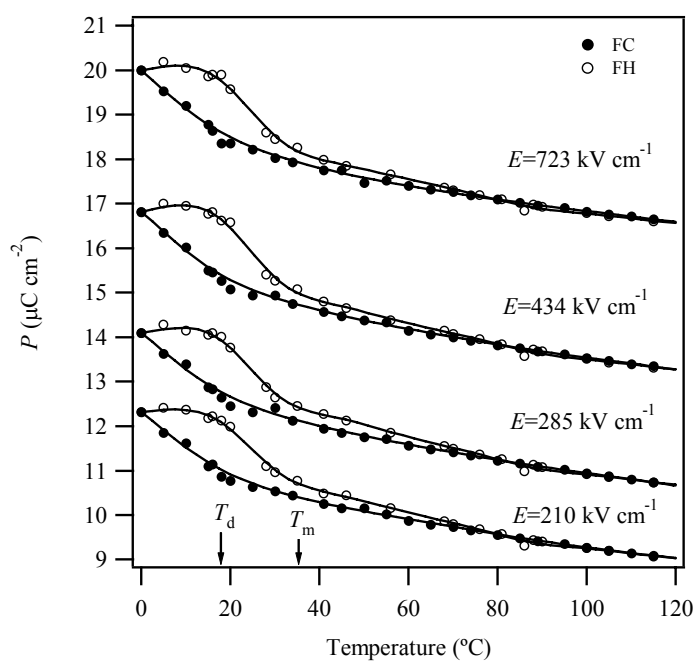


Figure 3

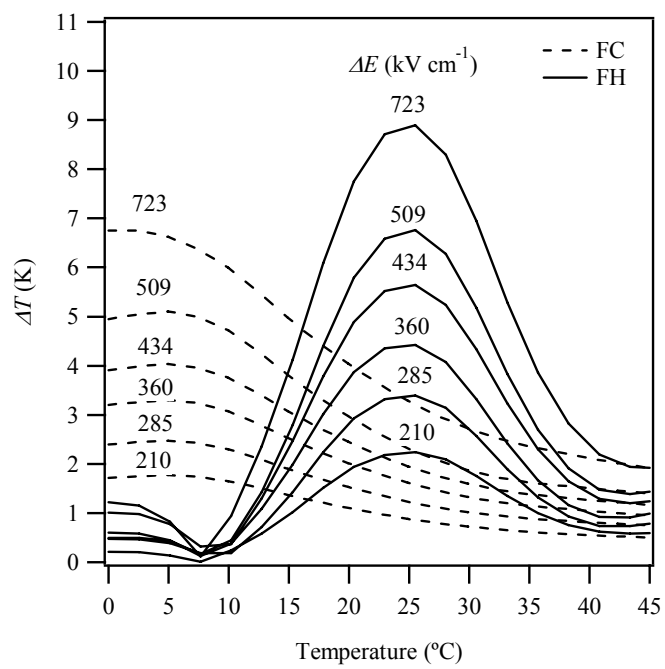


Figure 4