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Enhanced cooling capacities of ferroelectric materials at morphotropic phase boundaries

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The electrocaloric properties of $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (PZT) epitaxial films and $0.7\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - 0.3PbTiO_3 (0.7PMN-0.3PT) single crystals are measured and demonstrated enhanced low temperature refrigeration at morphotropic phase boundary compositions. The results reveal large adiabatic cooling figures in ~ 260 nm PZT films (11 K in 15 V) and 200 μm thick 0.7PMN-0.3PT single crystals (2.7 K in 240 V) at Curie transition temperatures and secondary cooling peaks at lower temperatures, near critical points. This is a very useful aspect of ferroelectric cooling elements to attain effective cooling over wide range of working temperatures in solid-state devices. © 2011 American Institute of Physics. [doi:10.1063/1.3595344]

Electrocaloric (EC) refrigeration of ferroelectric materials is of high interest for solid-state cooling applications. The cooling method is often described as a clean, robust, and efficient process due to its intriguingly simple design and operation. Despite of its technical advantages, the developments were relatively slow compared to other solid-state techniques such as magnetocaloric refrigeration¹ or thermoelectric cooling.² The resurgence of EC cooling is spotlighted only after the notable findings of adiabatic temperature changes (ΔT) in $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ and poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] ferroelectric thin-films.^{3,4} The discoveries revealed that the giant ΔT values in thin-films are due to the large isothermal entropy changes (ΔS) near ferroelectric-paraelectric (FE-PE) phase transitions. The sharp rise in EC effects are also attributed to the improved breakdown strengths of the materials in thin-films form compared to their bulk counter parts. Later, the field of research is quickly animated by several groups with the addition of various thin-film systems with huge cooling capabilities to the materials treasure.^{5–10} This has revived the possibilities of materials selection over range of working temperatures for solid-state cooling applications. Albeit of the progressive developments in materials, there are very few dedicated works involved in implementation of the EC materials into practical cooling devices.^{11–13} The hitches in device designs are, being thin-film structures, the materials are capable of imbibing only small portions of huge heat fluxes from the loads and second, the maximum ΔT values are mostly confined to Curie temperatures (T_c) alone. These are some serious limitations to achieve high refrigeration capacities (RCs) in materials with sharp and narrow cooling peaks.

Effective cooling over wide temperatures is a coveted property of any coolant material for efficient cooling process. For practical cooling devices, the EC materials must possess large ΔS values along with large ΔT values to achieve high uniform cooling throughout the working temperatures.¹⁴ It is well realized that the materials with discontinuous phase transition exhibit higher ΔT values than those with continu-

ous phase transitions,^{3,8} which is due to the abrupt changes in total polarization/entropy values at T_c . Besides, some earlier works suggest that the change in order phase transition from first order to second order greatly reduces the temperature dependence of ΔT at a cost of its peak cooling values (ΔT_{max}).¹⁵ For instance, in recent works of Li *et al.* described that by changing the nature of the phase transition from first order to second order in P(VDF-TrFE) polymers, ΔS reduces nearly to half of its original value.¹⁶ Even though the first-order phase transition is preferred (while considering ΔT_{max}) to the second-order transition, the later one offers consistent cooling over wide working temperatures due to its minimal temperature dependence. This poses some orthogonal difficulties to attain high ΔS and ΔT values at the same time.

Here, we establish a hypothesis to improve the cooling capacities of ferroelectric capacitors by improving the ΔS values at lower temperatures without sacrificing ΔT_{max} at FE-PE phase transitions. It is believed that the phase boundaries act as potential resources of high ΔS values due to more lattice entropy contributions from phase transformations induced by applied electric fields (ΔE). A continuous phase boundary along the entire cooling line below T_c [e.g., morphotropic phase boundary (MPB)] can originate high entropy changes than the values in single ferroelectric phases. So it is possible to achieve high EC cooling values in ferroelectrics at lower temperatures, below T_c by selecting the materials with MPB compositions. To validate the postulation, we have investigated PZT [001] oriented epitaxial films and 0.7PMN-0.3PT single crystals with [111] orientations at MPBs and demonstrated improved EC effects in both thin-films and bulk materials. The results show that the ΔT values induced by critical points and FE-FE phase boundaries are equally as effective as FE-PE transition and stretch the cooling range down to lower working temperatures.

Experimental details of samples preparation and characterization are presented in the supporting online information.²⁷ Figure 1(a) depicts representative plots of 0.7PMN-0.3PT single crystal hysteresis loops measured at different temperatures during cooling process to minimize reductions in total polarization (P) values due to fatigue. Typical hysteresis characteristics of single crystals are seen

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FIG. 1. (Color online) (a) Representative hysteresis loops of 0.7PMN-0.3PT single crystals measured at 1 kHz in cooling temperatures. (b) Temperature dependence of dielectric constant during ZFH and ZFC and frequency dependent relaxor behavior (in inset) are shown. (c) Polarization variation induced by temperature changes $P(T)$ data are extracted from the series of P - E hysteresis loops and fit to seventh-order polynomials. (d) The EC temperature changes as a function of sample temperature from 40 to 160 °C at an applied field 12 kV cm⁻¹. The $\Delta T_{max}=2.7$ K occur at $T_c=127$ °C and the secondary peak $\Delta T_{critl}=2.2$ K appear at $T_{critl}=93$ °C due to critical phase transitions.

as the temperature descends. The temperature dependence of polarization, $P(T)$ at different electric fields is presented in Fig. 1(c). We observed an anomalous behavior of $P(T)$ in 0.7PMN-0.3PT single crystals poled along [111] direction. The deviations in $P(T)$ data near critical point temperature ($T_{critl} \sim 93$ °C) are identified in a similar way to Kutnjak *et al.* reports^{17,18} and the irregularities are described as, the result of multiphase transitions between tetragonal (T) and rhombohedral (R) ferroelectric states in applied bias. The dielectric measurements shown in Fig. 1(b) also display similar anomaly at T_{critl} and the results cross-confirm the crossover of multiphase transitions during heating and cooling cycles. The real part of the dielectric constant ϵ measured during ZFH and ZFC show a maxima at 127 °C, which is claimed as Curie temperature, T_c in our studies. The strong frequency dependence of T_c (inset) indicates relaxor-ferroelectric behavior of 0.7PMN-0.3PT single crystals. Also, the T_c display phase transition degradation during ZFC which is due to reorientation of nanopolar-domains during structural transitions at MPB.^{4,19} The existence of broad phase transition at lower temperatures and the T dependence of ϵ are push to achieve large ΔS and ΔT values in relaxor-ferroelectrics at MPBs.

The $(\partial P / \partial T)_E$ data were derived from seventh-order polynomial fits to $P(T)$ to closely account the P variations near T_{critl} at different fields. The adiabatic temperature change, isothermal entropy change, and RC of the materials determined using Maxwell's relations,

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

$$\Delta S = -\frac{1}{\rho} \int_{E_1}^{E_2} \left(\frac{\partial P}{\partial T} \right)_E dE, \quad (2)$$

$$RC = \int_{T_1}^{T_2} \Delta S dT, \quad (3)$$

where $C=0.34$ (J g⁻¹ K⁻¹) is the specific heat capacity and $\rho=8.01$ g cm⁻³ the mass density of 0.7PMN-0.3PT single crystals assumed as constant values²⁰ in the testing temperature range. The EC temperatures obtained from Eq. (1) along the working temperatures are presented in Fig. 1(d). The maximum temperature change, $\Delta T_{max}=2.7$ K was detected at $T_c=127$ °C when $\Delta E=12$ kV cm⁻¹ is applied. It is also interesting to notice very high cooling values throughout the working temperatures from 125 to 75 °C (>2 K up to 75 °C). The ΔS values derived using Eq. (2) at FE-PE transition, $\Delta S_{max}=2.3$ J kg⁻¹ K⁻¹ and at critical point transition, $\Delta S_{critl}=2.04$ J kg⁻¹ K⁻¹ claim that the critical points are equally effective as FE-PE transitions in PMN-PT crystals at MPB compositions. Even though the FE-FE phase boundary considered inferior to FE-PE boundaries, the presence of orthorhombic (O), monoclinic (M_B, M_C) phases between R and T transitions at critical point according to Kutnjak *et al.*¹⁷ makes the lattice more frustrated and causes huge ΔS values even in small applied fields. The RC=206 J kg⁻¹ estimated in the limits of 40 to 160 °C at an applied field 12 kV cm⁻¹ and the ΔT_{max} observed are larger than the previous best reported results in PMN-PT ceramics.^{21,22}

Furthermore, we carried out similar studies in PZT thin-films to verify the EC properties of ferroelectric systems at MPB compositions for the role of universality. Electrical hysteresis measurements made at 10 kHz by varying the external temperature at 10 °C steps. Differential scanning calorimetry (DSC) measurements were conducted at a ramp rate of 1 °C/min [inset Fig. 2(a)] during heating cycle in N₂ atmosphere. The exothermic peak observed at 195.7 °C indicates the crystallographic transformation in PZT. Based on earlier reports, the phase transitions are described as the tri-critical transition between R, M_A , and T phases.^{23,24} The

FIG. 2. (Color online) (a) The isothermal entropy changes ΔS as a function of sample temperature in PZT thin-films. Upper inset: DSC data show an exothermic peak at 195 °C during heating at a ramp rate 1 °C/min corresponds to tricritical transition point. (b) The adiabatic temperature changes ΔT in applied bias ΔE . The peak $\Delta T_{max}=11.1$ K occurs at Curie point 387 °C and a secondary peak $\Delta T_{crit}=1.4$ K at $\Delta E=577$ kV cm⁻¹. Lower inset: polarization as function temperature $P(T)$ at different electric fields fit to sixth-order polynomials.

specific heat capacity ($C=0.37$ J g⁻¹ K⁻¹) deduced from DSC data of PZT thin-films and density ($\rho=7.8$ g cm⁻³) values used to calculate ΔT from Eq. (1). The $(\partial P/\partial T)_E$ data was derived from sixth order the polynomial fits of $P(T)$.

The results in Fig. 2 exhibit similar EC characteristics as 0.7PMN-0.3PT single crystals. The peak adiabatic temperature $\Delta T_{max}=11.1$ K detected at $T_c=387$ °C and a secondary cooling peak $\Delta T_{crit}=1.4$ K at tricritical temperature, $T_{crit}=195$ °C in $\Delta E=577$ kV cm⁻¹ [Fig. 2(b)]. The ΔT_{max} observed exceeds the earlier reports at any other compositions in PZT films.^{21,25} Inclusion of unsymmetrical phases at T_{crit} such as M_A to T and R transitions enhanced the ΔS values, minimize the temperature dependence of ΔT and broadened the cooling range. The isothermal entropy changes derived from Eq. (2) represented in Fig. 2(a). The critical isothermal entropy, $\Delta S_{crit}=1.1$ J kg⁻¹ K⁻¹, and the $\Delta S=0.49$ J kg⁻¹ K⁻¹ at $T=285$ °C are substantially less than the $\Delta S_{max}=6.17$ J kg⁻¹ K⁻¹ at T_c . The RC estimated in the limits of 100–420 °C at an applied field 577 kV cm⁻¹ is given as 688 J kg⁻¹. But when we look at the RC contributions from major and minor peaks independently, RC=474 J kg⁻¹ in the temperature range 285–420 °C and RC=213 J kg⁻¹ in 100–285 °C were observed. Even though the ΔT values differ significantly at T_c and T_{crit} , the secondary cooling peak still contributes ~30% to the total RC. It is highlighted that the critical points are equally important as FE-PE transformations in ferroelectrics to achieve large RCs.

We note that in recent work²⁶ of Valant *et al.* demonstrated a similar EC characteristics in

0.92Pb(Zn_{1/3}Nb_{2/3})O₃-0.08PbTiO₃ single crystals ($\Delta T=0.25$ K at $T_c=180$ °C in 1.2 MV m⁻¹) at MPB. Although their works did not emphasize much on critical point effects or low temperature phase boundary contributions to ECE, it provides a strong support to the hypothesis we made.

In summary, we have investigated EC properties of ferroelectric systems at MPB in view of accessing materials with broad working temperature ranges below T_c . The results presented from both 0.7PMN-0.3PT single crystals and PZT thin-films demonstrate the potential to achieve large ΔS and ΔT values at the same time in ferroelectric materials at MPBs. The relaxor-ferroelectric single crystals show prominent RCs than the ferroelectric thin-films at MPB. This is because of the excess lattice entropy generated from the field induced nanopolar-to-polar transitions in relaxor-ferroelectrics contribute to the overall ΔS values and thereby ΔT values. It is very attractive for high performance solid-state cooling devices.

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