Electrocaloric properties in relaxor ferroelectric $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3-x\text{PbTiO}_3$ system

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Citation: *Journal of Applied Physics* **114**, 174105 (2013); doi: 10.1063/1.4829012

View online: <http://dx.doi.org/10.1063/1.4829012>

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Electrocaloric properties in relaxor ferroelectric $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $x\text{PbTiO}_3$ system

J. Peräntie,¹ H. N. Taylor,² J. Hagberg,¹ H. Jantunen,¹ and Z.-G. Ye²

¹*Microelectronics and Materials Physics Laboratories, University of Oulu, P.O. Box 4500, 90014 Oulu, Finland*

²*Department of Chemistry, Simon Fraser University, 8888 University Drive, Burnaby, British Columbia V5A 1S6, Canada*

(Received 25 September 2013; accepted 21 October 2013; published online 4 November 2013)

The electrocaloric effect (ECE) in the $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 (PMN-PT) solid solution system was investigated by means of detailed direct temperature measurements as a function of temperature, composition, and electric field. The $(1-x)\text{PMN}$ – $x\text{PT}$ ceramics of compositions $0 \leq x \leq 0.3$ were fabricated by the columbite route. In opposite to conventional ferroelectrics, the maximum of electrocaloric effect was found to shift from the proximity of depolarization/Curie temperature to higher temperatures above a certain composition-dependent electric field strengths. Especially, the compositions with low PT content showed a broadened temperature range of electrocaloric effect. With increasing PbTiO_3 concentration, the magnitude of ΔT increased, and the temperature dependence of the maximum ECE response gradually developed towards a more pronounced anomaly typical for conventional ferroelectrics. The arising high temperature electrocaloric effect in the ergodic relaxor phase was attributed to the contribution from polar nanoregions. All the compositions studied showed the highest electrocaloric activity just above the depolarization/Curie temperature close to the possible critical point, as recently predicted and observed for some compositions. The magnitude of the maximum electrocaloric temperature change was in the range of $\Delta T = 0.77$ – 1.55°C under an electric field strength of 50 kV/cm . © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4829012>]

I. INTRODUCTION

Large and reversible caloric effects, e.g., magneto-, baro-, and electrocaloric effects, found from certain ferroic materials are considered to be potential solutions for future solid-state cooling devices. Especially, ferroelectric-based thin films have been considered extensively for cooling applications due to recently found high electrocaloric temperature changes with significantly low voltage levels.^{1–3} While thin films are known to show higher maximum electrocaloric effect (ECE) than bulk materials due to a higher breakdown field, difficulties in direct measurements and intrinsically small thermal mass introduce challenges for their reliable analysis and potential use in some applications. Alternatively, bulk-type materials with high enough electrocaloric properties would offer a simpler and more straightforward route to the realization of macroscopic cooling cycles. Indeed, some direct measurements indicate that high electrocaloric effect (up to $\Delta T \sim 2.5\text{ K}$) can also be induced in the ceramics of relaxor ferroelectrics, such as the $\text{PbSc}_{0.5}\text{Ta}_{0.5}\text{O}_3$ (PST) and $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – PbTiO_3 (PMN-PT) systems.^{4,5} In addition, relaxor ferroelectrics might offer a significantly enhanced temperature range for electrocaloric effect.^{4,6}

The relaxor ferroelectric PMN-PT system shows high polarization changes as a function of electric field and temperature, which are expected to high entropy changes and, thereby, a large electrocaloric effect. The highest electrocaloric activity is generally observed close to the polar-nonpolar phase transition temperature (depolarization or Curie temperature), which can be adjusted by changing the PbTiO_3

concentration. Application of an electric field can reversibly induce a macroscopic polarization and a high entropy change in the temperature range above the highest transition temperature, especially in the case of a first-order phase transition. Some experimental results and theoretical works indicate that the characteristic relaxor ferroelectric nature with involving polar nanoregions (PNRs) within a broad temperature range has a significant contribution to the electrocaloric effect in PMN-PT and other relaxors.^{6–10} Additionally, the electrocaloric effect in relaxors seems to show maximum responsivity $R (= \Delta T/E)$ near the liquid-vapor type critical point.^{11,12}

Several studies have been laid upon the electrocaloric properties of the PMN- $x\text{PT}$ ceramics and crystals by using both direct^{4–6,11,13–18} and indirect measurements.^{19–21} Although the potentiality of this material system has been emphasized, some main characteristics of electrocaloric effect are unknown or unclear due to limited, fragmentary, and partially conflicting results. Detailed direct temperature measurements of bulk materials are thus needed especially for the verification of theoretical models for a better understanding of electrocaloric effect in general as well as for the evaluation of the technological potential.

The objective of this work is to investigate the electrocaloric response in the $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ – $x\text{PbTiO}_3$ ceramic system with $0 \leq x \leq 0.30$ by means of direct temperature measurements as a function of temperature, electric field, and composition. The development and magnitude of these effects, especially with increasing ferroelectric order through composition variation, are presented and discussed. The results of the electrocaloric behavior are

further analyzed in terms of the behavior of maximum ECE response.

II. EXPERIMENTAL

Perovskite PMN-PT ceramics were prepared following the columbite route.²² MgNb_2O_6 precursor was first formed by the calcination of mixed MgO (99.9%) and Nb_2O_5 (99.9%) at 1100 °C for 12 h. It was then mixed with PbO (99.9%) and TiO_2 (99.9%) powders in a ball mill for 24 h with acetone as a mixing vehicle. PbO , TiO_2 , and MgNb_2O_6 were mixed to produce $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{1-x}\text{Ti}_x\text{O}_3$ with $x = 0\text{--}0.30$ (0.05 intervals), and 2% of excess PbO was added to compensate the PbO evaporation during the subsequent calcination and sintering steps. The resulting powder was pressed into pellets and calcined at 900 °C for 4 h to produce a pure perovskite phase. The calcined perovskite PMN-PT powders were then crushed, mixed with a small amount of polyvinyl alcohol, and pressed into pellets. After 1 h burn-off at 650 °C, the final sintering was performed at 1200–1240 °C for 4 h. XRD studies showed that all the fabricated samples had a pure perovskite phase, and the relative density of the ceramics was >95%.

For the electrical measurements, samples were ground to a thickness of 100–130 μm and sputtered with Au/Cr electrodes ($\sim 300\text{ nm}$ in thickness). The dielectric constant was measured using a high precision LCR meter (HP/Agilent 4284A). For the thermal and polarization measurements, samples were attached to thin alumel alloy wires using a polyimide tape, and an alumel-chromel thermocouple was attached on top of the sample. The measurement of the field-induced thermal response is described in detail elsewhere.^{7,17} Each sample was poled with the highest electric field (50 or 20 kV/cm) prior to the electrocaloric measurements performed on heating. All measurements were performed in an Espec SU-261 (from -68°C to 150°C) or a Memmert

UFP-400 (from 30°C to 250°C) oven. Samples were polarized with a voltage pulse of 2.5 s in duration, and the corresponding thermal response was extracted from the measured thermocouple data.

III. RESULTS AND DISCUSSION

The measured electrocaloric effect ΔT as a function of temperature is presented in Figures 1 and 2 for PMN- x PT. All the compositions were characterized with electric fields up to 50 kV/cm because higher electric fields were found to induce significant Joule heating at high temperatures for samples with $x > 0.2$. Under relatively small applied electric fields ($< 14\text{ kV/cm}$), the electrocaloric effect shows a distinct peak close to the characteristic depolarization temperature T_d or Curie temperature T_C (see Fig. 1(a)). An additional smaller peak is also detected for PMN-30PT composition below its T_C . The major peaks occur close to the phase transition temperatures at which the applied electric field can cause significant reversible dipolar changes through the phase transition. When an electric field of 5 kV/cm is used, the electrocaloric effect shows a relatively sharp peak with $x \leq 0.2$, and its magnitude increases with increasing PT content (Fig. 1(a)). However, in PMN-25PT and PMN-30PT, this peak becomes less pronounced. According to some earlier observations, the first order phase transition to ferroelectric phase in PMN-PT solid solution shows second order character with high PT contents, especially close to this composition range.^{23,24} Additionally, first order phase transitions of PMN-PT system in general tend to be weak in nature.²⁵ The appearance of the second peak for PMN-30PT reveals the existence of the morphotropic phase transition between a rhombohedral (or a monoclinic) and a tetragonal phase at T_{R-T} (or T_{MPB}), confirming that the composition falls into the morphotropic phase boundary region.²⁶

When the electric field is increased, another broader peak in electrocaloric effect gradually arises at high

FIG. 1. (a) Electrocaloric effect in different PMN- x PT compositions with $E = 5\text{ kV/cm}$. Electrocaloric temperature change in (b) PMN, (c) PMN-5PT, and (d) PMN-10PT as a function of temperature and electric fields of 8–14 kV/cm (2 kV/cm intervals) and 18–50 kV/cm (4 kV/cm intervals). The direction of the increasing electric field is marked with arrows.

FIG. 2. Electrocaloric temperature change in (a) PMN-15PT, (b) PMN-20PT, (c) PMN-25PT, and (d) PMN-30PT as a function of temperature and electric fields of 8–14 kV/cm (2 kV/cm intervals) and 18–50 kV/cm (4 kV/cm intervals). The direction of the increasing electric field is marked with arrows.

temperatures significantly above T_d (or T_C). Although this behavior has been previously observed in direct measurements of some PMN-PT compositions,^{4,6} its presence seems to be easily missed due to lack of detailed and direct electrocaloric effect measurements. The appearance of the broad peak above the first low temperature ECE peak was suggested to originate from the entropy contribution of PNRs,^{9,10} indicating a more universal property of relaxors. In addition, the aligning PNRs may have some contribution to the “giant” electrocaloric temperature changes observed in many relaxor-based thin films under high electric fields. The value of electrocaloric temperature change ΔT varies between 0.77 °C (at 46 °C for PMN) and 1.55 °C (at 170 °C for PMN-30PT) under an electric field of 50 kV/cm.

The development of the high temperature ECE peak with electric field is described in Figure 3(a), where the temperature of maximum electrocaloric effect, T_{ECmax} , is plotted against the applied electric field. There exists a critical field strength above which the maximum ECE shifts sharply to higher temperatures, increasing efficiently the broadness of the ECE peak. This shift takes place around $E = 25$ kV/cm in PMN with T_{ECmax} being shifted from the proximity of T_d to close to the temperatures of maximum permittivity T_m . The

critical field strength for shifting T_{ECmax} gradually decreases with increasing x until no clear shift is observed in PMN-25PT and PMN-30PT. Away from the abrupt shift the field-dependence of T_{ECmax} is linear, and this trend was observed up to $E = 90$ kV/cm in PMN (Figure 3(b)). After the arising of the second ECE peak, the enhanced ECE temperature region, ranging from T_d (or T_C) to T_{ECmax} , is the broadest in PMN, and it decreases with increasing x as the relaxor nature is gradually diminished. With higher PbTiO_3 concentrations the ECE characteristics begin to resemble more of those observed in conventional ferroelectrics with first order transition, e.g., BaTiO_3 (Refs. 27 and 28), where a single sharp peak is usually observed.

The observed peculiar ECE behavior of the PMN-PT system bears some analogies to its dielectric behavior. The characteristic frequency-dependent high maximum in the temperature dependence of permittivity in relaxors is caused by dynamics of characteristic PNRs.^{29,30} When PT concentration increases in PMN-PT, the temperature of maximum permittivity T_m (although frequency-dependent) approaches T_C , as is, respectively, observed here for T_{ECmax} and T_d ($=T_C$) even under higher field strengths. It is reasonable to believe that the temperature and field evolution of ECE

FIG. 3. (a) Temperature of maximum electrocaloric effect T_{ECmax} as a function of applied electric field 4–50 kV/cm in the PMN- x PT system with $x = 0$ –0.3. (b) Electrocaloric effect as a function of temperature in PMN under electric fields of 10–90 kV/cm (4 kV/cm intervals).

above T_C in different PMN-PT compositions is related to concentration, size, and dynamics of PNRs. A perovskite B-site occupation by Ti^{4+} ion is known to favor the long-range polar order and to decrease the number of PNRs in the ergodic relaxor phase.²⁴ It is thought that a lower number of PNRs enables more free growth of individual regions around T_C where an isothermal growth of PNRs takes place.^{24,31} This effectively promotes the spontaneous formation of microdomain ferroelectric state on cooling with increasing x .²⁴ In addition, static PNRs (not reoriented by thermal motion) have been observed in PMN-PT.³² The configuration of these PNRs seems to be very stable even after the application of an external electric field. It seems that the occurrence of static PNRs is closely related to the presence of chemically ordered regions (CORs).³³ Therefore, as the size of CORs is known to be decreased in PMN- x PT with increasing x ,³⁴ it is believed that static PNRs behave in a similar way. From this viewpoint, the PMN- x PT composition with lower x has an increased difficulty for field-induced PNR growth in the ergodic phase due to a higher number of constrained PNRs (both dynamic and static). However, the higher concentration of PNRs helps the field-induced formation of critical nuclei size and activation of PNRs within wider temperature range above T_C . A disappearance of the high temperature ECE peak is therefore expected when PNRs are absent (e.g., PMN- x PT with high enough x).

Since previous theoretical work¹¹ and experiments¹² indicate that the responsivity of the electrocaloric effect (i.e., $R = \Delta T/E$) reaches its maximum value near the critical point in some relaxor compositions, the behavior of ECE responsivity was investigated in PMN- x PT system. The (E, T) point of maximum responsivity for each composition is presented in Figure 4 as a filled circle. Open circles in Figure 4 represent points where the maximum electrocaloric effect is observed. It can be seen that the maximum electrocaloric effect is slightly shifted to higher temperatures with increasing field and it finally coincides with the point of the maximum ECE responsivity. The electric field strength of the maximum responsivity point decreases greatly with increasing x , as expected if these data correspond to field-induced critical points.³⁵ However, an exception is found again in

FIG. 4. Locations of the maximum electrocaloric effect (open circles) and the responsivity $(\Delta T/E)_{\max}$ (filled circles) points represented in an E - T graph of the PMN- x PT system.

FIG. 5. Temperatures of maximum electrocaloric effect $T_{EC\max}$ ($E = 50$ kV/cm), maximum dielectric constant T_m (at 1 kHz), maximum ECE responsivity and depolarization T_d (extrapolated from Figure 4) as a function of composition x in the PMN- x PT system.

PMN-25PT composition where the corresponding electric field value is higher. This discrepancy together with a highly diffuse ECE peak (Fig. 1(a)) suggests that the first order transition is very weak or non-existing in this composition. In fact, the PMN-25PT composition lies close to a possible tricritical point where a second order phase transition arises in the x - T phase diagram.³⁶ The critical point in polycrystalline PMN- x PT system is also likely to be diffuse in nature due to the observed orientational heterogeneity or even absence of critical point depending on the electric field direction.^{35,37–40}

The temperature of the maximum ECE responsivity was observed to lie just above T_d ($=T_C$) (extrapolated from Figure 4) which is reflected in their similar concentration dependence (Figure 5). When the ferroelectric nature of PMN-PT is strengthened with increasing x , it is expected that T_C is approaching T_m ($T_C = T_m$ for ordinary ferroelectrics),^{30,41} as shown in Figure 5. The temperature of maximum electrocaloric effect (shown for $E = 50$ kV/cm in Figure 5) also shows a linear behavior with increasing x in this composition range. The slope of $T_{EC\max}(x)$ was practically independent of electric field strength after the shift to high temperatures. This means that basically all the studied PMN- x PT compositions exhibit similar variation of the high temperature electrocaloric effect as a function of electric field at least up to $E = 50$ kV/cm. The contribution of PNRs to the ECE is expected to continue to significantly higher temperatures with increasing electric field since the characteristic temperatures, T^* and T_B , related to the PNR formation, are observed at around $\sim 230^\circ\text{C}$ and $\sim 350^\circ\text{C}$, respectively.^{42,43}

IV. CONCLUSIONS

Electrocaloric effect in a polycrystalline $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $x\text{PbTiO}_3$ solid solution system was investigated in terms of temperature, electric field, and composition by means of direct temperature measurements. The maximum electrocaloric temperature change was observed in the vicinity of the thermal depolarization temperature or the Curie temperature with low electric fields. An additional electrocaloric maximum was found to appear at high temperatures when higher electric fields were applied. This effect was very clear in PMN- x PT with low x ,

and a more continuous development of electrocaloric maximum was observed with increasing x . The evolution of electrocaloric effect as a function of temperature, electric field, and composition indicates that a field-induced additional contribution from aligning and growing polar nanoregions arises in the high temperature ergodic relaxor phase. The maximum electrocaloric temperature change ΔT varied between 0.77°C (at 46°C for PMN) and 1.55°C (at 170°C for PMN-30PT) under an electric field of 50 kV/cm . These electrocaloric results suggested that this type of materials could be utilized in solid-state cooling applications on a wide temperature range significantly above their intrinsic Curie temperature.

ACKNOWLEDGMENTS

The author J.P. gratefully acknowledges the Graduate School in Electronics, Telecommunications and Automation (GETA), the Nokia Foundation, the Jenny and Antti Wihuri Foundation, the Tauno Tönnning Foundation, the Ulla Tuominen Foundation, the Riitta and Jorma J. Takanen Foundation, the Seppo Säynäjäkangas Science Foundation, the Kaute Foundation, and the Finnish Cultural Foundation for the financial support of this work. The work at Simon Fraser University was supported by the U.S. Office of Naval Research (Grant Nos. N00014-11-1-0552 and N00014-12-1-1045) and the Natural Science & Engineering Research Council of Canada (NSERC).

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