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Electrocaloric effect in $(1-x)$PIN-xPT relaxor ferroelectrics

G. Ramesh [a, **], M.S. Ramachandra Rao [b], V. Sivasubramanian [c], V. Subramanian [a, *]

[a] Department of Physics and Microwave Laboratory, Indian Institute of Technology Madras, Chennai 600 036, India
[b] Department of Physics and Nano Functional Materials Technology Centre, Indian Institute of Technology Madras, Chennai 600 036, India
[c] Condensed Matter Physics Division, Indira Gandhi Centre for Atomic Research, Kalpakkam 603 102, India

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ABSTRACT

The electrocaloric effect (ECE) is investigated in both relaxor as well as morphotropic composition of $(1-x)Pb(In_{1/2}Nb_{1/2})O_3$-$xPbTiO_3$ system. The ECE is analyzed by evaluating the electrocaloric temperature change (ΔT) using thermodynamic Maxwell equation. The relaxor phase ($x = 0.15$) show an anomalous broadening in ECE and the maximum of ΔT is found to shift from the proximity of depolarization temperature (T_d) to around T'_m with increase in electric field. However, for morphotropic composition ($x = 0.33$) a region with negative ΔT is observed below T_d along with anomalous broadening in positive ΔT in the proximity of T_{RT}. The maximum value of ΔT obtained for relaxor phase is 0.37 K whereas 0.12 K is observed for morphotropic composition at 225C. The electrocaloric responsivity ξ_{max} is 0.21 mmK/kV for relaxor phase whereas 0.06 mmK/kV is obtained for the morphotropic composition at 18 kV/cm electric field.

1. Introduction

Electrocaloric effect (ECE) is the adiabatic temperature change (ΔT) and isothermal entropy change (ΔS) when an electric field applied to the polar materials [1–3]. ECE in dielectric materials has great potential for reliable solid state cooling device for a broad range of applications such as on-chip cooling and temperature regulations for sensors, electronic devices, and medical specimens. Furthermore, refrigeration based on the ECE approach is more environmental friendly and hence may also provide an alternative to the existing vapor-compression approach [4]. Though the ECE is known from early 70's the recent discovery of giant ECE in some organic and inorganic ferroelectric materials has revived the interest on solid state refrigeration through the ferroelectric materials [3]. For instance, thin film of PZT and P(VDF-TrFE-CFE) tripolymers shows the giant adiabatic temperature change of 12 K above room temperature at high fields [5–7]. Saranya et al. reported colossal adiabatic temperature change of 31 K for PMN-PT think film at 120 °C for the applied field of 747 kV/cm [8]. However for practical applications, electrocaloric (EC) materials should possess high cooling power. As the cooling power of bulk is two order of magnitude higher than of the thin films, in practical terms, the bulk ceramics has a decisive advantage over the thin films Even in terms of electrocaloric responsivity, $\xi_{max} = \Delta T_{max}/\Delta E_{max}$ bulk ceramics is preferred, as Matjaz et al. showed that the ξ_{max} of bulk ceramics is an order of magnitude higher than the thin films and polymers [3].

Among the bulk ferroelectric ceramics, lead based relaxor systems has large ξ_{max} and wide operating temperature range of ΔT due to the existence of polar nano regions (PNRs) and morphotropic phase region (MPR) [9–11]. A reversible adiabatic temperature change of 2.4 K is observed for ordered PST ceramic around the ordered paraelectric to ferroelectric transition [12]. Further, high ΔT (>2 K) have been achieved over a board temperature range, from 80 °C to 160 °C, for 70 PMN-30PT single crystal [11]. The very high electrocaloric responsivity of 0.45 mK/V is observed for the 60PNN-40PT single crystal [13]. Rozic et al. demonstrated that the enhanced electrocaloric response can be achieved around the liquid–vapor type critical point of relaxor-PT system [14]. Though relaxor could be the most suitable candidate to realize the solid state refrigeration the ECE studies on relaxors are far and few.

$Pb(In_{1/2}Nb_{1/2})O_3$ (PIN) belongs to the relaxor class of material that has received considerable attention owing to the controllable nature of cation ordering in its octahedral position [15]. Depending on the cation ordering, ordered PIN exhibits anti-ferroelectric behavior with a sharp peak at 168 °C, while the disordered PIN

* Corresponding author.
** Corresponding author.
E-mail addresses: ramesh.mwl@gmail.com (G. Ramesh), manianvs@iitm.ac.in (V. Subramanian).

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showing relaxor behavior with maximum dielectric constant at 40 °C for 1 kHz [16,17]. The MPR for PIN-PT system occurs between $x = 0.3$ and 0.38 exhibiting phase coexistence of rhombohedral(R) + tetragonal(T) ($0.30 \leq x \leq 0.33$) and monoclinic(M) + tetragonal(T) ($0.33 \leq x \leq 0.38$) phase [18]. The electromechanical characteristic of PIN-PT is comparable with that of PMN-PT along with enhanced T_{RT} and T_C [19]. The present work discusses the ECE investigation on PIN-PT ceramic in relaxor ($x = 0.15$) and near MPR ($x = 0.33$) composition.

2. Experimental

Polycrystalline $(1 - x)Pb(In_{1/2}Nb_{1/2})O_3–PbTiO_3$ ($x = 0.15$, 0.33) pellets are prepared by conventional solid state reaction and the details are given elsewhere [20]. For electrical characterization, circular pellets of 8 mm diameter and 1 mm thickness are used. The phase confirmation is done using XRD and it reveals the rhombohedral phase for $x = 0.15$ and coexistence of rhombohedral and tetragonal phase for $x = 0.33$. The density of the pellets is measured by Archimedes principle. Temperature dependence of dielectric response is measured in heating mode at a rate of 3 °C/min from 30 °C to 300 °C using Nova control broadband impedance analyzer in the frequency range of 100 Hz to 1 MHz. Temperature evolution of polarization-electric field hysteresis loop is recorded by precision premier II ferroelectric loop tracer (Radiant Technologies, USA) with a maximum field of 30 kV/cm in the temperature range of 30 °C–225 °C. P-E loop is recorded in heating mode with the temperature interval of 5 °C and temperature is kept constant for 10 min before each measurement performed. The electric field is applied with triangular bipolar waveform with the frequency of 50 Hz. Thermal characteristics of the PIN-PT pellets are obtained by using differential scanning calorimetry (Netzsch, DSC 200 PC). The electrocaloric effect is investigated by indirect method, using Maxwell relation, with accuracy in adiabatic temperature change, ΔT, of 0.001 °C.

3. Results and discussion

Temperature dependence of dielectric response measured at different frequencies for poled PIN-PT ceramics are given in Fig. 1. For $x = 0.15$, dielectric spectrum shows the broad dielectric anomaly at temperature of the dielectric constant maximum, T'_m and the strong dielectric dispersion below T'_m. As frequency increases the maximum dielectric constant decreases and T'_m shifts to higher temperature, from 155 °C for 1 kHz to 162 °C for 100 kHz, while tan δ increases with increase in frequency confirming the relaxor behavior. On the other hand, dielectric spectrum of $x = 0.33$ shows the anomaly at 187 °C and maximum at 298 °C with diffuse character. The structural analysis reveals that the former is associated with rhombohedral-tetragonal transition (T_{RT}) and the later is attributed to the tetragonal–cubic transition (T_C). In addition, the frequency variant in dielectric constant appears in the proximity of 100 °C. In relaxor-PT system, the long range ferroelectric order can often be induced by sufficiently large electric field. Upon heating, the long range order decays above the depolarization temperature that results the frequency variation in the dielectric spectrum.

In order to estimate the EC temperature change in PIN-PT ceramics, the temperature dependant *P-E* loop is measured from 30 to 220 °C at different electric field. Temperature variation *P-E* loop for 0.85PIN-0.15 PT ceramic is given in Fig. 2(a). At room temperature, it shows a closed and saturated loop similar to normal ferroelectric. The corresponding saturation polarization (P_s) and remnant polarization (P_r) is measured to be 28.7 μC/cm^2 and 22 μC/cm^2 respectively. The squareness of hysteresis loop strongly deteriorates with temperature and attains slim loop behavior above

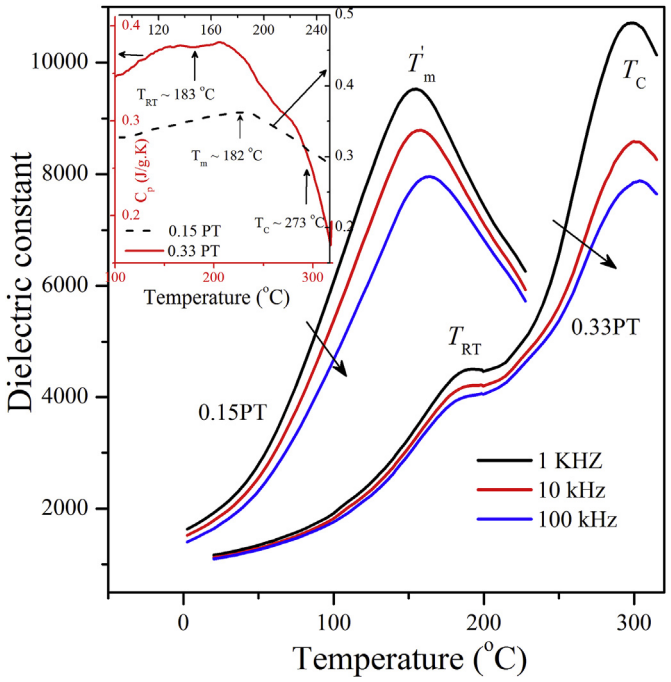

Fig. 1. Temperature dependence of dielectric constant of poled $(1 - x)$PIN-xPT measured at various frequencies. Inset shows the heat capacity of unpoled PIN-PT ceramic.

the T'_m with non-zero P_r. It implies that the PNRs exists at temperatures much higher than T'_m. It corroborates the relaxor nature of 0.85PIN-0.15PT. Upon heating, the variation in P_s is small up to 110 °C whereas corresponding P_r decreases rapidly. On the other hand, above T'_m, significant changes are observed in P_m while negligible change is observed in P_r. This can be clearly seen in the inset of Fig. 2(a) (Shows the temperature dependence of P_r, P_s and E_c). As the temperature increases to 110 °C, P_s decreases by 9% to the value of 26 μC/cm^2 while the P_r reduces by 39% to the value of 8.5 μC/cm^2. P_r decreases faster than P_m up to 110 °C then follows a gradual fall and approaches the lowest value above T'_m. It indicates that the thermal depolarization occurs in the proximity of 100 °C. In relaxor, unlike normal ferroelectric, the polarization decreases continuously above depolarization temperature (T_d) which is lower than T'_m. Above T_d, the macrodomains break into microdomains causing the decrease in polarization [21]. This is further confirmed by fitting P_r with Landu equation, $P_r = A(T_d - T)^{1/2}$ where A is constant and T_d is depolarization temperature [21]. The fitting shows $T_d = 116$ °C and above T_d, P_r and squareness of the loop decrease rapidly.

Temperature dependence of P-E loop for 0.67PIN-0.33PT ceramic is given in Fig. 2(b). Unlike 0.85PIN-0.15PT the square loop is observed up to 200 °C. In addition, P_m shows the negligible change while the P_r decreases continuously as depicts in the inset of Fig. 2(b). The close examination shows that P_m increases slightly up to 100 °C while P_r maintained constant and both decrease below 100 °C. The decrease in polarization may be due to the depolarization phenomena and it corroborates with the frequency variation of dielectric constant near 100 °C. Further, E_c decreases almost linearly followed by the plateau region around 180 °C then decreases with temperature.

Temperature dependence of polarization at different electric fields is given in Fig. 3. Polarization is obtained from the first quadrant of the hysteresis loop. For $x = 0.15$, the polarization decreases rapidly with temperature for the lower electric fields while