



Electro-caloric effect in relaxor and ferroelectric compositions of $\text{Pb}(\text{Mg}_{(1-x)/3}\text{Nb}_{2(1-x)/3}\text{Zr}_x)\text{O}_3$ ceramics

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ABSTRACT

Solid solution of relaxor PMN and antiferroelectric PZ, $[\text{Pb}(\text{Mg}_{(1-x)/3}\text{Nb}_{2(1-x)/3}\text{Zr}_x)\text{O}_3]$, behaves like ferroelectric with increasing PZ content following a wide composition range of diminishing relaxor properties. Electro-caloric measurements on three relaxor and one ferroelectric composition of this solid solution have been carried out by indirect method. All the compositions give a maximum temperature change of ~ 0.33 K on application of 1 kV/mm electric field. This value is higher than the PLZT or PMN-PT based relaxors. A shift of $\sim 35^\circ\text{C}$ in the temperature of electro-caloric maximum was observed with application of electric field, for relaxor compositions, attributed to the field induced effect on the transition temperature. Similar shift for ferroelectric composition is significantly lower ($\sim 8^\circ\text{C}$).

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1. Introduction

Electro-caloric effect (ECE) is a change in temperature (ΔT) in a dielectric material by virtue of change in entropy (ΔS) on application of electric field [1,2]. Electric field aligns the polarization in the dielectric media leading to change in entropy. A large polarization change is desirable to achieve a large ECE, which makes the ferroelectric materials as primary candidates for electro-caloric studies. The ECE in ferroelectric material is maximum near the phase transition temperature because a huge change in polarization in vicinity of the transition temperature. Several ferroelectrics materials have been investigated in past, but their commercial exploitation are missing due to low ECE values [2–5]. However, a recent report on $\text{PbZr}_{0.95}\text{Ti}_{0.05}\text{O}_3$ (PZT) thin film of by Mishchenko et al. [6] has stimulated the search for new ferroelectric based electro-caloric materials. They have observed a temperature change of $\Delta T \sim 12$ K under an electric field of 48 kV/mm, near anti-ferroelectric to paraelectric phase transition temperature ($T_c = 500$ K). Saranaya et al. [7] have also reported a temperature change of 31 K in 0.65PMN–0.35PT thin films by applying an electric field of ~ 80 kV/mm at 413 K. But device application needs maximum ECE near room temperature (300 K). In view of this, ferroelectric materials especially relaxor ferroelectrics and polymers having transition temperature near 300 K are under investigation. Neese et al. [8] and Lu et al. [9] have observed that thin films of

PVDF and PLZT exhibit a temperature change as large as $\Delta T \sim 30$ K under an electric field of 125 kV/mm, near room temperature. Correia et al. [10] have also observed a temperature change of ~ 10 K at 300 K in 0.93PMN–0.07PT thin film. Most of these thin films show a temperature change (ΔT) of ~ 0.25 K with application of 1 kV/mm electric field. This value is much higher compared to PZT (0.021 K per 1 kV/mm) thin films [6] at room temperature. The EC effect has been also investigated on anti-ferroelectric material [11,12]. Field induced transition from anti-ferroelectric to ferroelectric phase is expected to give higher electro-caloric effect. Parui and Krupanidhi [11] have observed a temperature change of 0.29 K with application of 1 kV/mm electric field in antiferroelectric lead zirconate (PZ) which is higher than many ferroelectric materials. This stimulate to explore electro-caloric effect in anti-ferroelectric materials. In addition to thin films, the electro-caloric effect was also studied in single crystals and ceramics of relaxor ferroelectrics [13–18]. In most of the published results the maximum temperature change is ~ 1.0 K with application of 4 kV/mm electric field. The large temperature change in thin films as compared to bulk materials is because thin films can withstand larger electric fields. However, the value of temperature change with application of unit electric field ($\Delta T/E$) is nearly the same for bulk as well as thin-films. Therefore, study of bulk material will be helpful in understanding many mechanisms involved in electro-caloric effect. It is important to note that both direct [19] and indirect [6] method have been employed in past to study the electro-caloric effect. For direct measurements a high precision calorimetry is used, while in indirect measurements the thermo-dynamical Maxwell relations have been used to calculate the temperature change. Although a difference in the values of ECE

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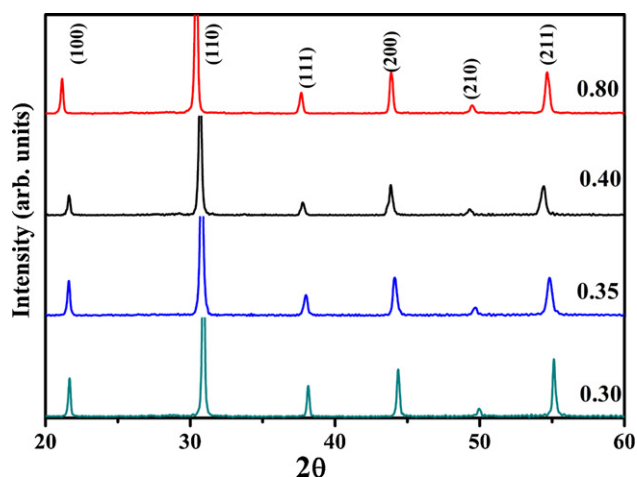


Fig. 1. Powder X-ray diffraction of $\text{Pb}(\text{Mg}_{(1-x)/3}\text{Nb}_{2(1-x)/3}\text{Zr}_x)\text{O}_3$ for different compositions.

was observed by Lu et al. [20] for direct and indirect method measurements in PVDF, but both the methods are equally exploited by the researchers in past [1,6,8,18,19].

In the present investigation we have studied electro-caloric effect in $\text{Pb}(\text{Mg}_{(1-x)/3}\text{Nb}_{2(1-x)/3}\text{Zr}_x)\text{O}_3$ called as $(1-x)\text{PMN}-x\text{PZ}$ solid solution by indirect method. It is a solid solution of typical relaxor ferroelectric (PMN) and antiferroelectric (PZ) materials. As mentioned, relaxor and anti-ferroelectrics produce quite high electro-caloric effect therefore it will be interesting to study the solid solution of relaxor with antiferroelectric material. $(1-x)\text{PMN}-x\text{PZ}$ has been investigated by us earlier for its relaxor behaviour [21,22]. It shows relaxor ferroelectric like behaviour for $x < 0.50$ and normal ferroelectric nature for $0.50 < x < 0.90$. A relaxor to normal ferroelectric crossover was observed near $x = 0.44$. Relaxor ferroelectrics are known to have [23] anomalously high electro-mechanical properties just below the crossover regions. In view of this we have considered three relaxor compositions i.e. $x = 0.30, 0.35, 0.40$ for electro-caloric investigation. A pure ferroelectric composition with $x = 0.80$ is also investigated.

2. Experimental

Lead magnesium niobate-zirconate, $\text{Pb}(\text{Mg}_{(1-x)/3}\text{Nb}_{2(1-x)/3}\text{Zr}_x)\text{O}_3$, $x = 0.30, 0.35, 0.40$ and 0.80 were prepared by dry method using the columbite precursor route [24]. First, a columbite (MgNb_2O_6) precursor was synthesized using reagent-grade MgO and Nb_2O_5 in stoichiometric proportions. The powders were thoroughly mixed in a ball mill for 10 h, using acetone as a grinding medium. The mixed powder was calcined at 1100°C for 2 h, and again at 1150°C for 2 h, with an intermediate ball-milling. The columbite precursor was mixed with PbO (99% purity), and ZrO_2 (99% purity) and calcined at 900°C for 4 h. Single-phase formation was confirmed by X-ray diffraction (Fig. 1). Powders were compacted in form of disks of diameter 15 mm and thickness ~ 1 mm. These disks were sintered in PbO -rich atmosphere at 1150°C for 2 h. The densities of the sintered samples were measured to be $\sim 95\%$ of the theoretical values.

The sintered specimens were electroded using high-temperature-curing silver paste. Dielectric measurements were carried out using an automated HP4194A impedance analyser over a frequency range of 0.1–1000 kHz, at different temperatures. The temperature was measured at an accuracy of $\pm 0.1^\circ\text{C}$ using Eurotherm 902 programmable temperature controller. The polarization versus electric field (P - E) hysteresis loops were recorded at 100 Hz frequency with Radiant Technology's Precision Material Analyzer Workstation based on virtual ground system. The P - E hysteresis measurements were made roughly every 10°C in range of 30 – 200°C during cooling.

3. Results and discussion

Fig. 2 shows the dielectric response of all the compositions i.e. $x = 0.30, 0.35, 0.40$ and 0.80 . For first three compositions the dielectric constant (ϵ') and dielectric loss (ϵ'') show a frequency

dependent shift in the dielectric maximum-temperature (T_m). A shift in ' T_m ' is a typical feature of relaxor-ferroelectric like-behaviour. However, for $x = 0.80$ no such shift is observed, implies normal ferroelectric like nature of this composition. The temperature of dielectric maximum also shifts to higher temperature side with increase in ' x '. The increase in the transition temperature is attributed to the incorporation of Zr in octahedral cage as explained by Singh and Tiwari [22].

In order to evaluate the electro-caloric effect, P - E hysteresis loop at 100 Hz were measured at different temperatures. The measured hysteresis loop at four different temperatures for one of the relaxor composition i.e. $x = 0.35$ is shown in Fig. 3. The figure shows that polarization decreases with temperature, implies that sign of $\partial P/\partial T$ is negative. The hysteresis loop exists even above the temperature of dielectric maximum. In addition to the frequency dependence of dielectric maximum temperature, the square to slim hysteresis loop transition corroborate relaxor behaviour for $x = 0.30, 0.35$ and 0.40 . Fig. 4 shows the temperature dependence of polarization under different electric fields. Polarization at different fields was calculated using the upper branches of the hysteresis loops as stated by Mischenko et al. [6].

Reversible adiabatic temperature change ΔT due to an applied electric field E , for a material of density ' ρ ' with specific heat capacity ' c_p ' is given by [6]:

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

where P is the polarization, E_1 and E_2 are the starting and final applied fields, respectively. The values of $(\partial P/\partial T)_E$ were obtained from P versus T data by fitting a fourth order polynomial (see Fig. 4). The specific heat capacity ' c_p ' of the material is also temperature dependent. For most of earlier studies the value of ' c_p ' for material under investigation was taken as a constant value [6–11]. It is known that near phase transition temperatures the specific heat capacity (c_p) of a material shows a jump in its values. It is therefore, imperative to consider temperature dependence of ' c_p ', while calculating electro-caloric effect. For compositions under investigations the temperature dependence of heat capacity was taken from our earlier investigation [25]. It lies from 0.27 to 0.30 J/g K at room temperature for all the samples. The density ' ρ ' for each sample was measured by Archimedes's principle which comes between 7.77 and 7.80 g/cm³. Fig. 5a–d shows the ΔT as a function of temperature for $\Delta E (= E_2 - E_1)$ 0.5, 1.0, 1.5 and 2.0 kV/mm as obtained using Eq. (1). Since, there was no temperature dependent anti-ferroelectric to ferroelectric phase transition observed in PMN–PZ, the E_1 can be set as low as zero, which is sufficient to ensure the criterion $(\partial P/\partial T) < 0$ as mentioned by Mischenko et al. [6]. A broad anomaly in ΔT was observed in all the relaxor compositions compared to a sharp change in ferroelectric composition. It is interesting to note that at low field (0.5 kV/mm) measurement the largest temperature change (ΔT) was observed near the temperature of dielectric loss maximum (ϵ''). It is clear from Fig. 5a–c that the temperature of electro-caloric maximum (T_{EC}) shifts toward higher temperature side with increase in electric field for relaxor compositions. A shift of $\sim 35^\circ\text{C}$ was observed as the electric field increased from 0.5 kV/mm to 2 kV/mm. However, this shift in T_{EC} for ferroelectric composition ($x = 0.80$) was much lower ($\sim 8^\circ\text{C}$) (see Fig. 5d). Similar shift was also observed in relaxor ferroelectrics by Luo et al. [14] and Bai et al. [18]. But the origin of such shift was not discussed by them. The shift in T_{EC} can be attributed to the field induced shift in the phase transition temperature as observed in PMN and PLZT [26,27]. To further elucidate this we plotted $(\partial P/\partial T)$ at 0.5 and 2.0 kV/mm field for all the compositions in Fig. 6. It is clear from this figure that maximum in $(\partial P/\partial T)$ shifts towards higher temperature with increase in electric field. This shift is reasonably large for the relaxor

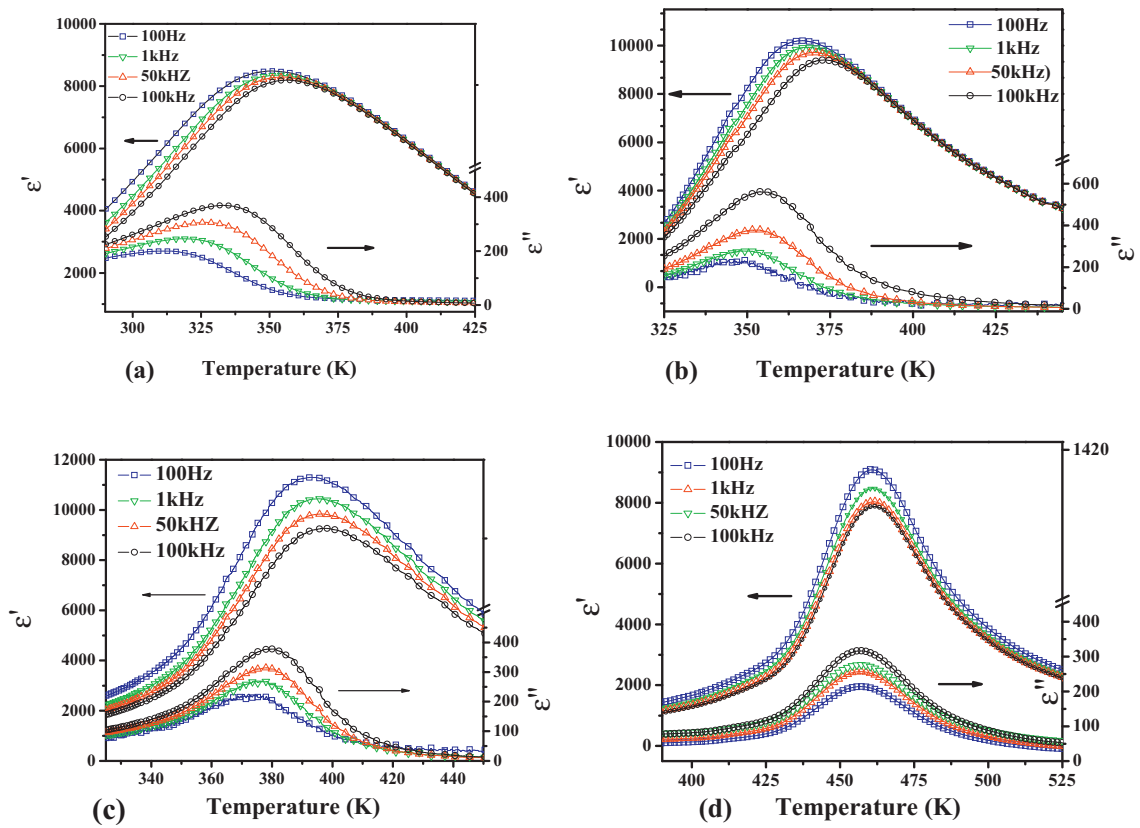


Fig. 2. Temperature dependent dielectric behaviour of (a) $x=0.30$, (b) $x=0.35$, (c) $x=0.40$ and (d) $x=0.80$.

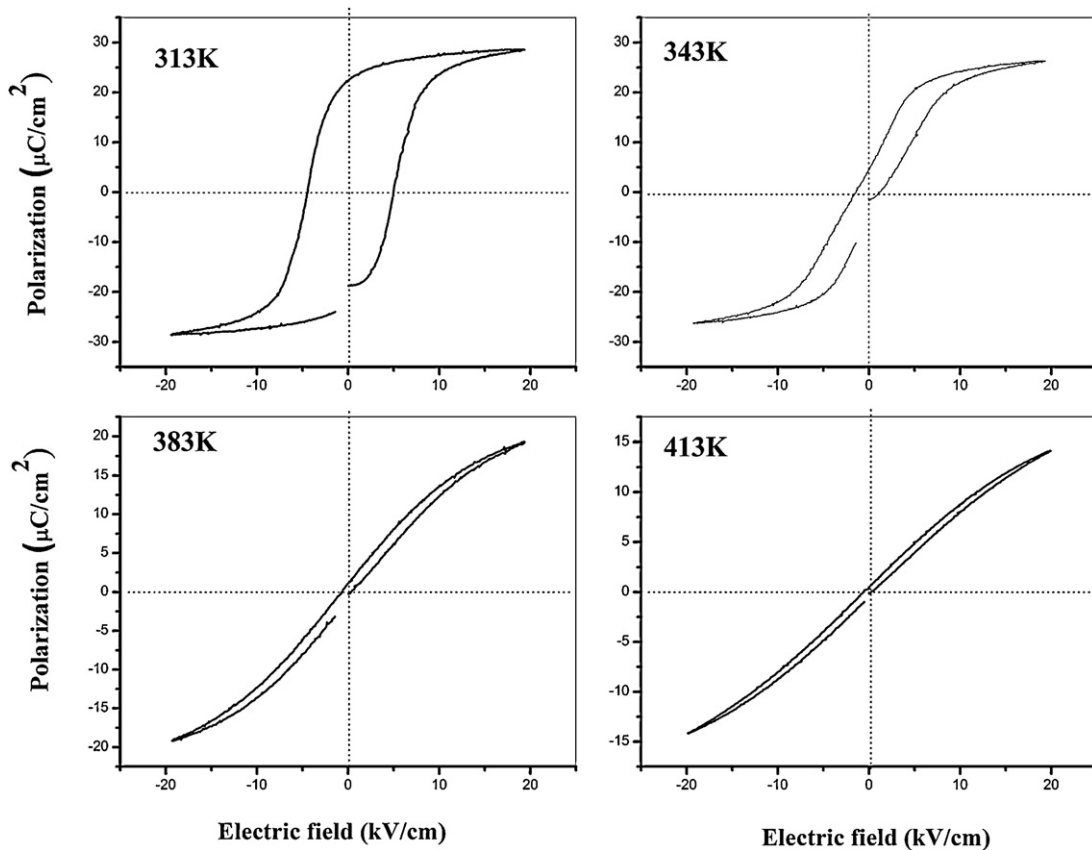


Fig. 3. P - E hysteresis loops of 0.65PMN–0.35PZ at different temperatures.

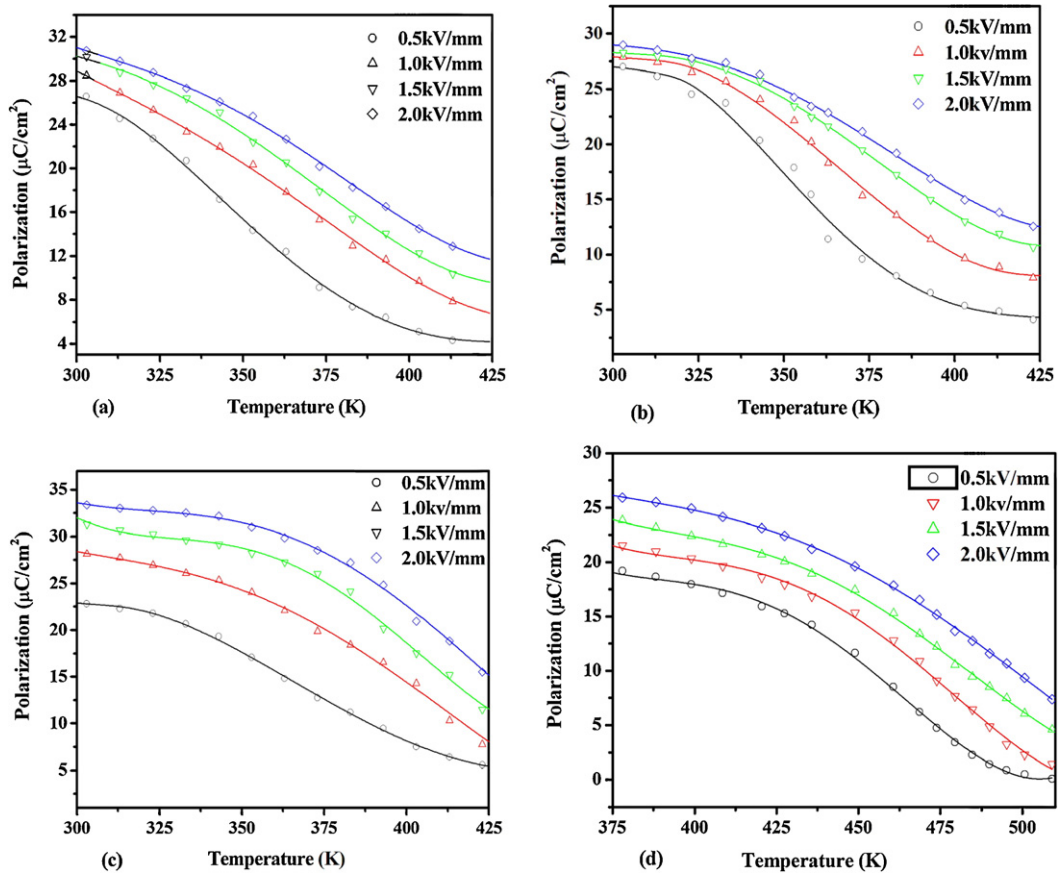


Fig. 4. Temperature dependent polarization behaviour at different electric fields of (a) $x = 0.30$, (b) $x = 0.35$, (c) $x = 0.40$ and (d) $x = 0.80$; symbols are the experimental point and solid line is fitted curve.

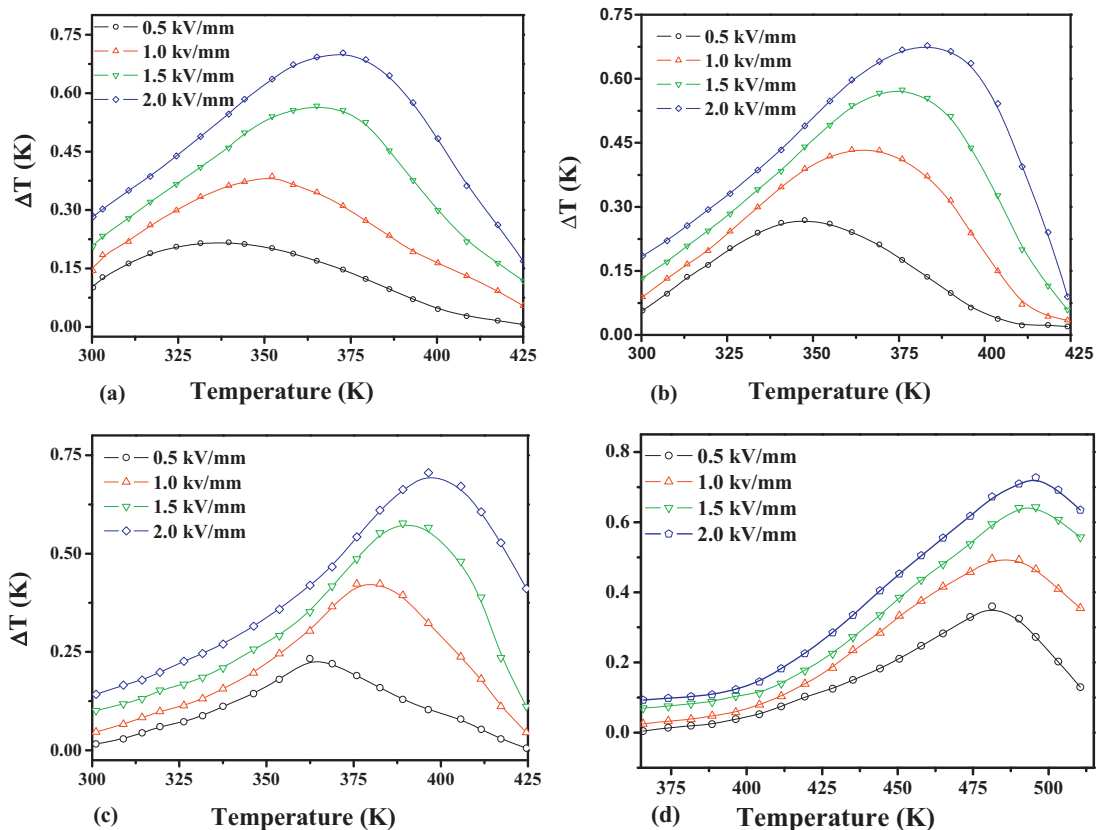


Fig. 5. Electro-caloric temperature change (ΔT) as a function of temperature at different applied electric field for (a) $x = 0.30$, (b) $x = 0.35$, (c) $x = 0.40$ and (d) $x = 0.80$.

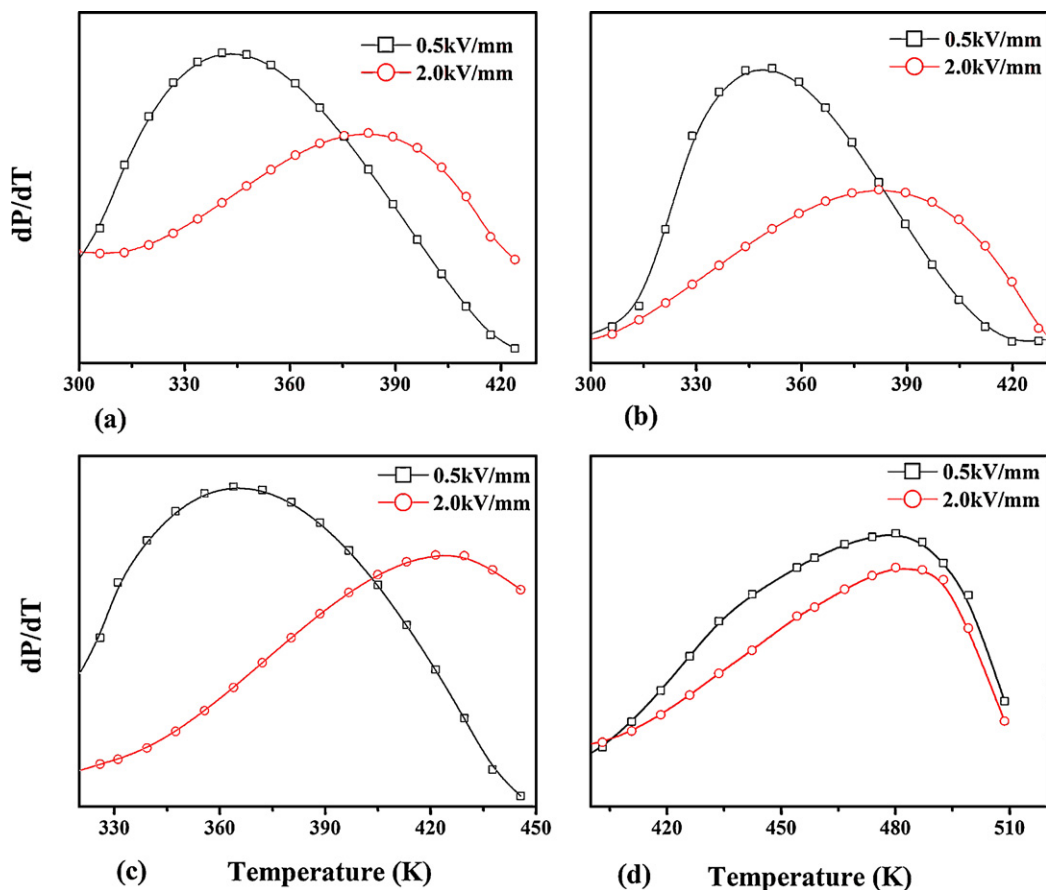


Fig. 6. Variation of dP/dT with temperature at electric fields of 0.50 and 2.0 kV/mm for (a) $x=0.30$, (b) $x=0.35$, (c) $x=0.40$ and (d) $x=0.80$.

compositions ($x=0.30$, 0.35 , and 0.40) and less for ferroelectric composition ($x=0.80$). For PLZT based ceramic samples Vodopivec et al. [27] have observed similar shift for maximum of $(\partial P/\partial T)$ in pyroelectric measurements under electric field. However, in relaxor thin films no such shift was observed [9,10]. It can be due to broadening of phase transition in thin films the field induced shift in temperature of electro-caloric maximum is will masked. The temperature of electro-caloric maximum (T_{EC}) at 2 kV/mm, maximum electro-caloric coefficient (ξ_{max}) and electro-caloric coefficient (ξ) at 300 K are summarized in Table 1. Here, electro-caloric coefficient is defined as change of temperature with application of unit (1 kV/mm) electric field. It is clear from table that ' T_{EC} ' shifts toward higher temperature side with increase in ' x '. This shift is due to shift in the phase transition temperature of $(1-x)$ PMN- x PZ with increase in PZ content [23]. Moreover, the electro-caloric coefficient (ξ_{max}) at T_{EC} lies between 0.33 and 0.35 Kmm/kV for all the compositions and significantly higher than well known relaxors like PLZT and PMN-PT [14–17]. At room temperature ' ξ ' is maximum for $x=0.30$ and could be related to large change in room temperature polarization with application of electric field. With increase in ' x ' the decrease in ' ξ ' is observed. It implies that with decrease in relaxational character the electrocaloric coefficient at

Table 1
Temperature of electro-caloric maximum and electro-caloric coefficients for different compositions.

x	T_{EC} (at 2.0 kV/mm) (K)	ξ_{max} (Kmm/kV)	ξ (at 300 K) (Kmm/kV)
0.30	371	0.35	0.142
0.35	388	0.33	0.980
0.40	404	0.34	0.075
0.80	492	0.35	0.040

room temperature is decreasing. This suggest that large number of polar nano-regions in relaxor ferroelectrics can lead to large change in entropy on application electric field and provide a scenario for achieving large ECE, compared to normal ferroelectrics.

4. Conclusions

The electro-caloric effects of $(1-x)$ PMN- x PZ solid solution with " x " being, 0.30, 0.35, 0.40 and 0.80, respectively, were measured. These ceramics possess large electro-caloric coefficient ($\xi_{max} \sim 0.33$) compared to other known relaxors ($\xi_{max} \sim 0.25$). At room temperature electro-caloric coefficient decreases with increase in PZ content. For relaxor compositions a shift in temperature of electro-caloric maximum was observed and related to the field induced shift in the transition temperature. This shift is very weak in ferroelectric composition.

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