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Critical slowing down in lead magnesium niobate–zirconate ceramic

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Abstract Dielectric relaxation behaviour of (1 – x) PMN – xPZ, for x = 0.10, 0.30 and 0.40 have been studied. The nature of relaxational behaviour was found to change with PZ concentration. A crossover from a static freezing to critical slowing down like behaviour is observed with increase in Zr^{4+} concentration. We have used Glazounov and Tangastev criterion to distinguish freezing and critical slowing down like behaviour.

Introduction

Lead magnesium niobate (PMN), $PbMg_{1/3}Nb_{2/3}O_3$, is the archetypal relaxor ferroelectric (RFE). It is characterized by a broad and rather strongly frequency-dependent maximum in its dielectric response in the radio-frequency regime. A solid solution of PMN with ferroelectric lead titanate ($PbTiO_3$) [PT] is thoroughly investigated system. It shows a relaxor ferroelectric like behaviour for $x < 0.30$ and normal ferroelectric for $x > 0.35$. A crossover from relaxor to normal ferroelectric is sharp and studied by many authors in past [1–5]. On the other hand, a solid solution of lead magnesium niobate (PMN) with an antiferroelectric lead zirconate (PZ) gives rise to a system which behaves like a relaxor ferroelectric for $x < 0.50$, beyond which it behaves as a normal ferroelectric [6]. The crossover from the relaxor behaviour to the normal ferroelectric is gradual and reflected in the heat capacity as well as dielectric measurements [6, 7]. We have carried out a detailed structural analysis of PMN-PZ in the crossover region [8] and found that the rhombohedral *(R3m)* phase on nano-scale in relaxor phase gets stabilized on microscopic level by increasing Zr^{4+} content. This crossover behaviour can be studied using dielectric relaxation data in the composition range where the crossover takes place.

Several models have been proposed to explain the RFE behaviour [9–14]. However, a thorough understanding of the behaviour is still awaited. In-spite of contradictions, the dielectric behaviour of RFE provides decisive support in favour of dipolar glass model [11]. According to this model RFE consists of nano-meter scaled polar clusters and a frustrated correlation between them [9] results a dipolar glass like behaviour. It was proposed by Viehland [11] that these polar clusters have a freezing temperature and their relaxation time follows a Vogel–Fulcher relation similar to observed in canonical glasses.

$$\omega^{-1} = \omega_o^{-1} \exp\left[E_a/k_B(T_{max} - T_f)\right]. \tag{1}$$

Equation 1 relates the temperature of dielectric maximum (T_{max}) to the measured frequency $\omega(T_{max})$. ω_o, T_f and E_a are fitting parameters better known as attempt frequency, freezing temperature and activation energy of the clusters. It can be arranged as

$$1/\ln(\tau_c/\tau_o) = k_B/E_a(T_{max} - T_f), \tag{2}$$

where $\omega^{-1} = \tau_c$ and $\omega_o^{-1} = \tau_o$. The Eq. 2 is written in the form of characteristic relaxation time ($\tau_c = 1/\omega$) which tend to infinity at $T = T_f$ i.e. the width of relaxation time spectrum diverges at freezing temperature.

Glazounov and Tangastev [15, 16] proposed that a similar condition may arise if the static dielectric constant

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peaks at $T = T_{f.}$ In this respect the relaxation spectrum may broaden due to a critical slowing down of relaxation time. They suggested a method to distinguish between critical slowing down and a static freezing. According to them, the temperature dependence of maximum relaxation time (τ_{max}) follow a relation similar to that of $\omega^{-1}(T_{max})$ (Eq. 1) during relaxational freezing. i.e.

$$\tau_{max} = \tau_o \exp\left[E_a/k_B(T - T_f)\right] \tag{3}$$

or

$$1/\ln(\tau_{max}/\tau_o) = k_B/E_a(T - T_f) \tag{4}$$

However, for freezing-free or critical slowing down [13] this dependence, near T_f, can be given as

$$1/\ln(\tau_{max}/\tau_o) = a[1 + b(T - T_f)] \tag{5}$$

The difference between Eqs. 4 and 5 is that Eq. 4 represents a straight line passing through the origin, which is not true with Eq. 5. The value of τ_o and T_f can be calculated from the dielectric spectrum and using Eq. 1. This criterion has been used by Glazounov and Tangastev [15] to understand the freezing behaviour in PMN and PST.

The purpose of the present study is to understand the crossover from glassy to normal ferroelectric behaviour with varying PZ concentration in $(1 - x)$PMN – xPZ using the same criteria.

Experimental

Lead magnesium niobate-zirconate [$(1 - x)$PMN – xPZ] ceramics for $x = 0.10, 0.30, 0.40$ were prepared by mixed oxide method using columbite precursor [17]. Sintered samples were in the form of disks of 13 mm diameter and 1 mm in thickness. Single perovskite phase was confirmed by x-ray diffraction. High temperature curing silver paste was applied on both the surfaces as electrode. The dielectric measurements at different temperatures and frequencies were carried out using automated HP4194A impedance analyser. The detail procedure for powder synthesis and dielectric measurement is published elsewhere [6, 7].

The temperature dependence of τ_{max} was calculated by method adopted by Glazounov and Tangastev [15]. The τ_{max} is the relaxation time above which no frequency dependence will be observed. The temperature corresponding to the τ_{max} was determined from the plots of temperature dependence of dielectric constant. The point of splitting of dielectric curves for different frequencies from the high temperature side give the temperature dependence of maximum relaxation time, see inset of Fig. 1. For accurate determination of the onset temperature we used non-linear fitting to the dielectric data.

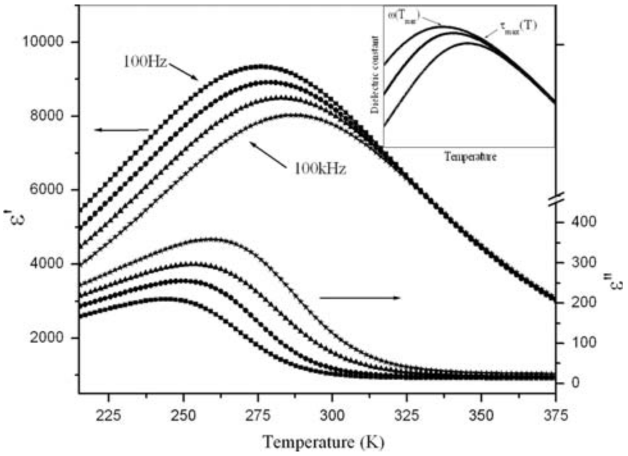


Fig. 1 Dielectric response for $x = 0.10$. The inset explains the way to determine $\omega(T_{max})$ and $\tau_{max}(T)$ from dielectric plots

Results and discussion

The dielectric data for all the compositions have been given in our earlier publications [6, 7] and are not being repeated here. For illustration, a representative dielectric response for one of the composition, $x = 0.10$ is shown in Fig. 1. Figure 2 shows Vogel–Fulcher fittings to the dielectric data where $\ln \omega$ is plotted against T_{max}, for all the compositions. The solid line represents the fitting of Eq. 1 to the experimental data. The best fitted values of the parameters τ_o, E_a, and T_f, obtained by Levenberg-Marquadt non-linear analysis program, are summarized in Table 1. All the three parameters were found to increase with PZ content. The same dielectric data was used to plot $1/\ln(\tau_{max}/\tau_o)$ against $T - T_f$ to verify the relations 4 and 5, shown in Fig. 3. The value of the parameters T_f and τ_o were used from Table 1. For comparison, we plotted the data of $1/\ln(\tau_c/\tau_o)$ and $T_{max} - T_f$ using the relation 2 and the parameters values from Table 1 on the same scale represented by close circles in Fig. 3. It is evident from these plots that for $x = 0.10$, both the lines pass through the origin, representing a freezing like behaviour. On the other hand, the lines corresponding to $x = 0.30$ and 0.40, represented by open circles, deviate from the origin giving a signature of critical slowing down.

The dielectric response of a relaxor ferroelectric is strongly affected by dynamics of the polar clusters. Mainly two kind of cluster dynamics, thermally activated and domain wall like, contribute to the relaxational spectrum. Thermally activated dynamics leads to a dipolar glass like behaviour with a finite freezing temperature [11]. The

Fig. 2 Fitting of Vogel–Fulcher equation (Eq. 1) for $x = 0.10$, 0.30 and 0.40

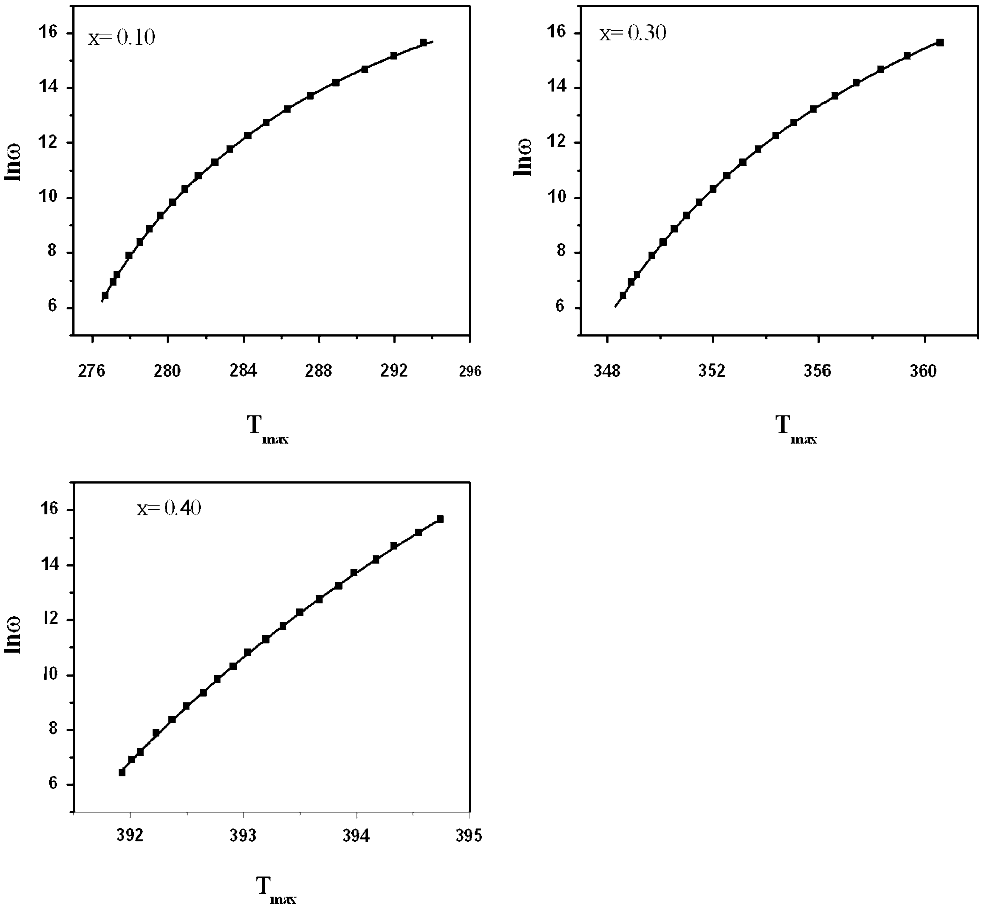


Table 1 Best fitted parameters for Vogel–Fulcher equation (Eq. 1)

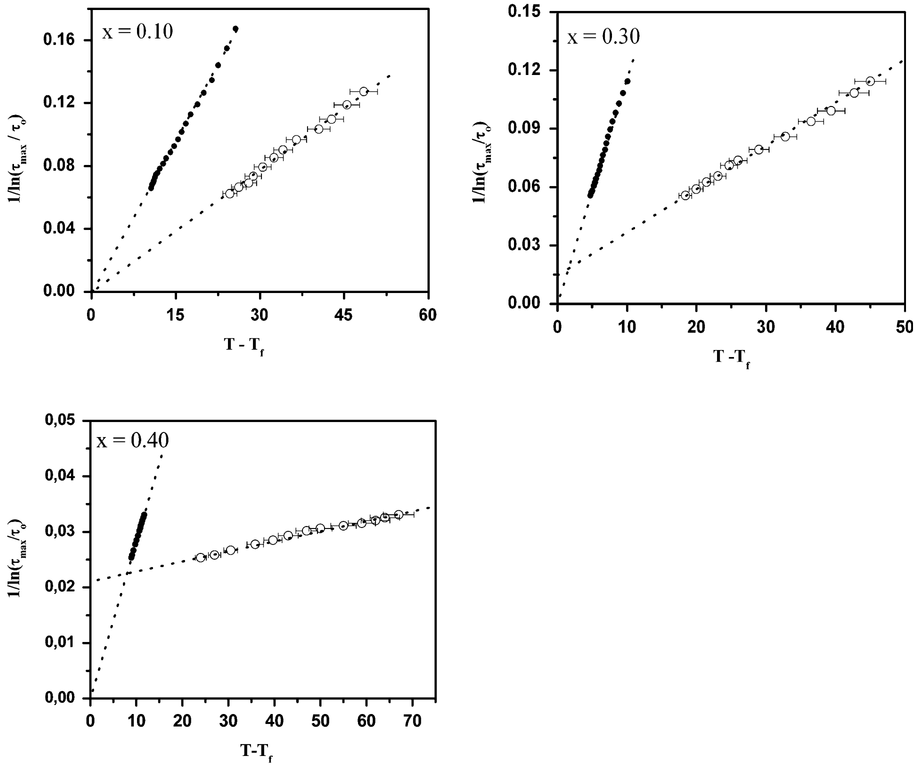
x	E_a (eV)	ω_o (Hz)	τ_o (s)	T_f (K)
0.10	0.020	1.41×10^{10}	7.09×10^{-11}	262.27
0.30	0.026	5.82×10^{11}	1.72×10^{-12}	333.81
0.40	0.028	1.35×10^{19}	7.41×10^{-20}	383.18

domain wall like dynamics, resulted from the motion of interface boundary of the polar-regions, correspond to a critical slowing down rather than freezing [12].

A crossover from a glassy phase to a ferroelectric behaviour depending on composition is observed in proton glasses [18, 19]. Recently, an evidence of co-existence of long range ferroelectric domains and short range glassy regions during the freezing process has been observed in dielectric behaviour of $Rb_{1-x}(NH_4)_xH_2PO_4$ [20]. Similar kind of co-existence of polar and glassy regions was also observed in $K_{1-x}(NH_4)_xI$ and $K_{1-x}Li_xTaO_3$ [21–23]. The dynamics of dipolar cluster will show a glass like or critical slowing down, strongly depends on the concentration of active ions present in the region, like NH_4 and Li for above systems. Similar crossover from glassy to domain like dynamics was observed by others [24, 25] in $(1 - x)$ PMN – xPT system, near x~0.30. The domain structure becomes notably larger in this range of x, increasing from polar nano-regions to micron size ferroelectric domains. However, for lower PT content this dynamics was observed at high ac-drive field [24].

A similar analogy can be extended for PMN-PZ also. PMN is a classic relaxor ferroelectric. It has random distribution of Mg^{2+} and Nb^{5+} ions at B-site. For either occupancy, there is a deviation from the value 4+ required for charge balancing in the perovskite unit cell. In order to compensate the charge imbalance, small polar regions, extended over 2–10 nm, with 1:1 ordering [13] are formed. These regions are thermally activated and leads to a glass like behaviour in PMN. The doping of B-site with Zr^{4+} stabilizes the 1:1 short range polar order by neutralizing charge imbalance. The increasing concentration of Zr^{4+} increases the cluster volume which is reflected in the increase of activation energy of V–F like fitting (see Table 1). With increase in Zr^{4+} concentration the correlation length of dipolar cluster increases and the dynamics is more like a domain wall type rather than freezing type. This crossover of the cluster dynamics from a glassy to a critical slowing down is continuous and clearly reflected in the relaxation spectrum of dielectric response. Therefore,

Fig. 3 Investigation of freezing and freezing-free relaxation in PMN-PZ for x = 0.10, 0.30 and 0.40



the plot of 1/ln(τ_{max}/τ_o) vs. $T - T_f$ for higher concentration of Zr^{4+} are not passing through the origin because at higher concentration of Zr^{4+}a domain like cluster dynamics is more significant than the thermally activated dynamics.

Cheng et al. [26] has argued that the dipolar clusters can not be completely frozen below any non-zero T_f, and suggested a power law which provides a relation between ω^{-1} and T_{max}

$$\omega^{-1} = \tau_o[-(E_a/k_B T_{max})^p] \tag{6}$$

Different type of dielectric response is sought to be reflected with this relation. For $p^{-1} = 1$ it describes a Debye relaxation, for $p^{-1} = 0$ a normal ferroelectric and for $p^{-1} = 2$ glassy type relaxational behaviour. We fitted our experimental data to the Eq. 6. The values of the parameters obtained from the fitting are summarized in Table 2. The activation energy and attempt frequency obtained from V–F and the relation given by Cheng are comparable and realistic. However, for x = 0.40 we found that V–F fitting gives unrealistic value for attempt frequency. This again supporting the fact that freezing free model is more reliable especially for higher concentration Zr, than the freezing one.

Table 2 Best fitted parameters for equation of Cheng et al. (Eq. 4)

x	E_a (eV)	ω_o (Hz)	τ_o (s)	p^{-1}
0.10	0.025	6.24×10^7	1.60×10^{-8}	0.0384
0.30	0.031	3.48×10^8	2.87×10^{-9}	0.0256
0.40	0.034	8.34×10^{11}	1.12×10^{-12}	0.0125

Conclusion

Similar to $Rb_{1-x}(NH_4)_xH_2PO_4$, $K_{1-x}Li_xTaO_3$ and $(1 - x)$ PMN – xPT the dielectric relaxation behaviour of $(1 - x)$ PMN – xPZ shows a crossover from glassy behaviour to critical slowing down with increasing PZ concentration. Higher concentration of Zr^{+4} stabilizes the nano-polar clusters by decreasing the charge imbalance. This leads to change in the nature of the relaxation from a static freezing to a critical slowing down like behaviour.

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