Non-linear dielectric dispersion in PMN relaxor system

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1. Introduction

In recent years the investigation of relaxor ferroelectrics has been very intense because relaxors are promising materials for various applications. In spite of intensive investigations, the nature of relaxor freezing properties is still not completely understood. Recently, the studies of non-linear dielectric properties of relaxors became intense because it is believed that the non-linear dielectric data could be significant in discriminating between existing models of relaxors.

Relaxors provide a conceptual link between dipolar glasses and ferroelectrics. In zero bias electric field relaxors, as dipolar glasses, show the transition into the non-ergodic phase [1–3], on the other hand if relaxors are cooled in an electric field higher than critical, a long range ferroelectric phase is formed [4,5]. A recently introduced spherical random bond random field (SRBRF) model [6,7] can describe well this behaviour. The quasistatic non-linear dielectric ratio $\beta = \varepsilon_3/\varepsilon_1^4\varepsilon_0^3$ was recently used to confirm the validity of the model [8,9]. The SRBRF model explains the crossover in the temperature dependence of β from decreasing into the increasing behaviour when approaching the freezing transition T_f from above [8,9] in zero bias electric field and the crossover from the glass-like behaviour of β into the ferroelectric-like monotonous decreasing behaviour under the bias electric field higher than critical $E > E_C$ [8,9]. The SRBRF model predicts also the peak of the temperature dependence in the static dielectric non-linearity β

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at the freezing transition [7]. Because of dispersions in ε_1 and ε_3, in which characteristic relaxation times rapidly increase with decreasing temperature at temperatures much above T_f, it is experimentally not feasible to determine the static non-linear susceptibility in the vicinity of the freezing temperature.

In the present work we present the measurements of $\varepsilon_1^*(\omega, T)$ and $\varepsilon_3^*(\omega, T)$ in PMN single crystals measured along the $\langle 0\,0\,1\rangle$ and $\langle 1\,1\,1\rangle$ axes and show that ε_1^*, ε_3^* and the dielectric non-linearity β are functions of the frequency and temperature in the temperature interval between 270 and 220 K. The experimental data are compared with the results of the phenomenological model of the dynamic non-linear response of relaxors, introduced recently by Glazounovand Tagantsev[10], and the predictions of the static non-linear dielectric response of the SRBRF model [6,7] are tested.

2. Experimental procedure

Plates, cut perpendicular to the $\langle 0\,0\,1\rangle$ and $\langle 1\,1\,1\rangle$ axes of PMN single crystals and covered with sputtered gold electrodes, were used for measurements. The methods of simultaneous measurements of ε_1^* ($\varepsilon_1 \propto P_1/E$) and ε_3^* ($\varepsilon_3 \propto P_3/E^3$), were already described before [3,11]. The dielectric response was measured in the frequency interval of 10^{-2}–9×10^3 Hz. The amplitudes of measuring ac electric field applied on samples along $\langle 0\,0\,1\rangle$ and $\langle 1\,1\,1\rangle$ axis were 260 and 170 V/cm, respectively. The measuring electric field was low enough to perform measurements of ε_1^* and ε_3^* in the regime where contributions of higher harmonics were negligible [12,13]. Prior to each measurement, the samples were annealed for 1 h at 410 K in order to eliminate the effects of previous treatments and to ensure equal conditions for all measurements. All measurements were done on cooling with a cooling rate of -0.5 K/min.

3. Results and discussion

Figs. 1 and 2 show $|\beta| = |\varepsilon_3(\omega)|/|\varepsilon_1(\omega)|^3|\varepsilon_1(3\omega)|\varepsilon_0^3$ measured along $\langle 1\,1\,1\rangle$ and $\langle 0\,0\,1\rangle$ axes as a function of the temperature at five frequencies, where $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m. The temperature dependence of dielectric non-linearity $|\beta|$ measured along both axes shows similar temperature dependence with prominent dispersion below $\approx$260 K. Similar dielectric dispersion in $|\beta|$ close to the glass transition was also observed in PLZT ceramics [8,9]. These observations are in contradiction to the recently introduced phenomenological model for non-linear dynamic response in relaxor ferroelectrics [10], where the non-linear dielectric constant is proportional to the product $\varepsilon_3(3\omega) \propto$

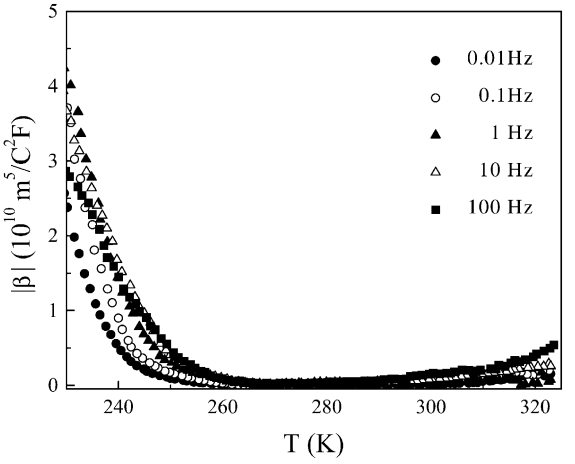

Fig. 1. The temperature dependence of $|\beta|$ measured along $\langle 1\,1\,1\rangle$ axis at five frequencies.

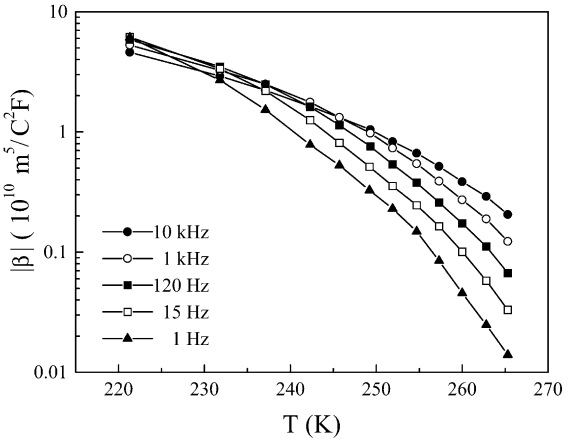

Fig. 2. The temperature dependence of $|\beta|$ measured along $\langle 0\,0\,1\rangle$ axis at five frequencies.

$\varepsilon_1(\omega)^3\varepsilon_1(3\omega)$, which implies a frequency and temperature independent parameter β. The model supposes that the dispersion of the non-linear response in relaxors is determined with the dispersion of the linear response. In Figs. 1 and 2 is also shown that $|\beta|$ increases with decreasing temperature when approaching the glass transition temperature at 227 K [3,10], which means, that the dielectric non-linearity $|\beta|$ shows a crossover from decreasing paraelectric-like to rapidly increasing glass-like temperature behaviour which was predicted by the SRBRF model for relaxors [6,7].

The temperature and frequency dependence of the third harmonic polarization P_3^* measured along $\langle 001 \rangle$ axis are plotted in Figs. 3 and 4. The solid lines connect the data measured at the same frequency. The real part (P_3'), which is plotted in Fig. 3, shows a maximum as a function of temperature which shifts to the higher temperatures and its maximum value decreases with increasing frequency. At lower temperatures the values of P_3' at all frequencies became negative, the temperature at which P_3' changes sign decreases with decreasing frequency. At high frequencies the values of P_3' are negative in the studied temperature interval. The temperature and frequency dependence of P_3' exhibits some similarities to the frequency and temperature dependence of the real part of the first harmonics (P_1') which shows a well-known diffusive phase transition typical for relaxor type ferroelectrics [1–3]. In contrast to the behaviour of P_3', which becomes negative at lower temperatures, the first harmonic P_1' is always positive. It should be noted that similar behaviour was reported before in spin glasses [11] and liquid crystals [14].

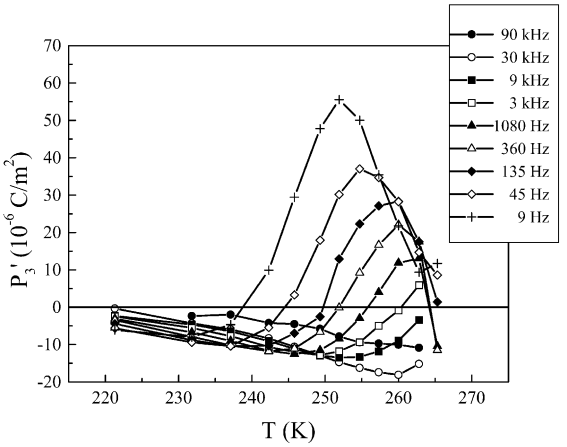

Fig. 3. The temperature dependence of P_3' measured along $\langle 001 \rangle$ axis at various frequencies.

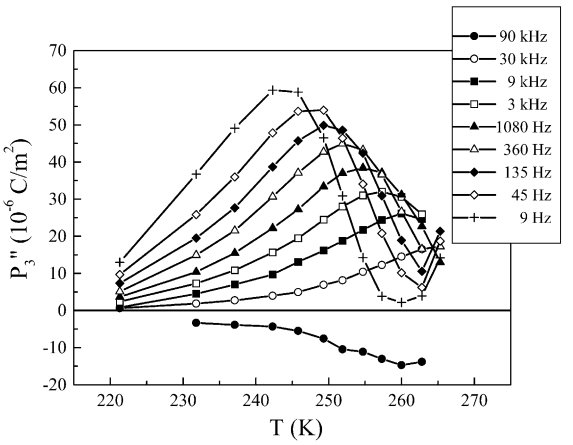

Fig. 4. The temperature dependence of P_3'' measured along $\langle 001 \rangle$ axis at various frequencies.

The temperature dependence of the imaginary part of the third harmonic polarization (P_3''), which is plotted in Fig. 4, also shows a maximum which shifts to higher temperatures and its maximum value becomes smaller with increasing frequency, as real part P_3' does. The values of P_3'' are always positive at all temperatures except values measured at 90 kHz which are negative in the whole studied temperature interval. The temperature and frequency dependence of P_3'' is not similar to the frequency and temperature dependence of the imaginary part of the first harmonics (P_1''). Temperature dependencies of P_3'' show maxima for which the temperature positions increase with increasing frequency, but maximum values become smaller with increasing frequency, in contrast to P_1'' where maximum values increase with increasing frequency. A substantial difference in data presented in Figs. 3 and 4 and the temperature in frequency dependence of the real and imaginary part of the first harmonic polarization P_1^* leads to the conclusion that the dynamics in the non-linear response in relaxors $\varepsilon_3^*(\omega, T)$ are not a simple reflection of the dynamics in the linear dielectric response $\varepsilon_1^*(\omega, T)$ as recently suggested [10].

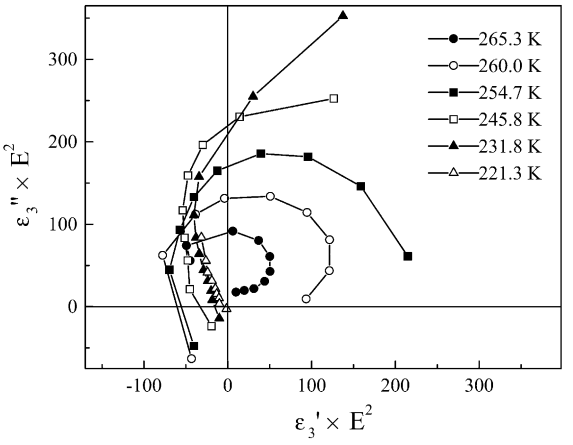

Fig. 5. $\varepsilon_3'' \times E^2$ plotted vs $\varepsilon_3' \times E^2$ measured along $\langle 0\,0\,1 \rangle$ axis at six temperatures between 265 and 221 K.

Fig. 5 shows measured values of $\varepsilon_3'' \times E^2$ plotted vs $\varepsilon_3' \times E^2$ in PMN measured along $\langle 1\,1\,1 \rangle$ axis at six temperatures in the temperature interval 265–221 K. Values of ε_3' and ε_3'' are calculated by using experimental values of P_3' and P_3'' plotted in Figs. 3 and 4 from equations $P_3'(\omega) = \varepsilon_3'(\omega)\varepsilon_0 E^3$ and $P_3''(\omega) = \varepsilon_3''(\omega)\varepsilon_0 E^3$. The solid lines connect the data measured at the same temperature. Fig. 6 shows measured values of $\varepsilon_3'' \times E^2$ plotted vs $\varepsilon_3' \times E^2$ in PMN measured along $\langle 0\,0\,1 \rangle$ axis at several temperatures in the temperature interval 260–210 K with the temperature step of 5 K. The Cole–Cole plots below freezing temperature T_f ($T_f \approx 227$ K [3,15]) are denoted by (•) and the plots above T_f by (○). The solid lines connect the data measured at the same temperature and use as a guide for the eye. Cole–Cole plots presented in Figs. 5 and 6 a similar except that the values measured along $\langle 1\,1\,1 \rangle$ axis have higher maximum values of ε_3'' [15] in comparison with ε_3'. Since the permittivity of the vacuum ε_0 is introduced in the definition of ε_3, the quantities $\varepsilon_3' \times E^2$ and $\varepsilon_3'' \times E^2$ are dimensionless and thus can be easily compared with the values of ε_1. Cole–Cole plots of the non-linear dielectric constant presented in Figs. 5 and 6 are not similar to Cole–Cole plots of the linear dielectric constant [3]. For example, ε_3' has negative values at high frequencies in contrast to ε_1', which is always positive at any frequency or temperature. The comparison between Cole–Cole plots of linear $\varepsilon_1^*(\omega, T)$ and non-linear $\varepsilon_3^*(\omega, T)$ dielectric constant shows that the dynamics of the non-linear dielectric constant are not only a reflection of the dynamics of the linear dielectric constant, as proposed in the model of Glazounovand Tagantsev[10].

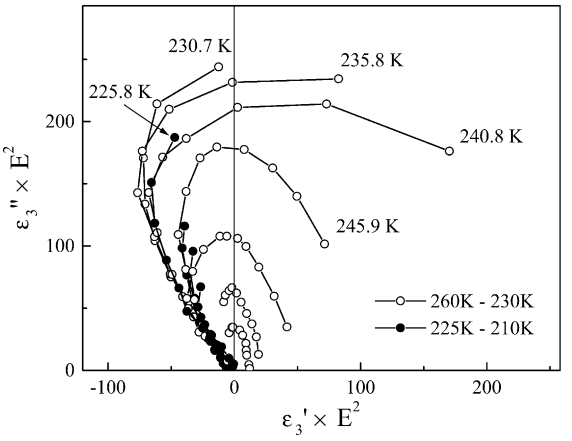

Fig. 6. $\varepsilon_3'' \times E^2$ plotted vs $\varepsilon_3' \times E^2$ measured along $\langle 1\,1\,1 \rangle$ axis in the temperature range of 260–210 K.

In the sample measured along the $\langle 1\,1\,1 \rangle$ axis the extrapolation $\omega \to 0$ was made with a linear plot through the measured points at low frequencies (Fig. 6), thus giving the static non-linear dielectric constant ε_{3s} [15]. The temperature dependence of ε_{3s} increases with decreasing temperature in the temperature interval between 265 and 240 K, which also implies the increase of static dielectric non-linearity $\beta_s = \varepsilon_{3s}/\varepsilon_{1s}^4 \varepsilon_0^3$ with decreasing temperature, where ε_{1s} denotes the static value of the linear dielectric response [3]. Figs. 5 and 6, which show dispersion in ε_3^*, also demonstrate a rapid increase of the characteristic relaxation time with decreasing temperature at temperatures much above T_f. Therefore it is experimentally not possible to determine the static non-linear susceptibility in the vicinity of the freezing temperature. This makes confirmation of the existence of the peak in β at T_f predicted by the SRBRF model impossible by the present experimental technique.

4. Conclusions

The first and the third harmonic complex dielectric constants of the PMN single crystal along

the $\langle 0\,0\,1\rangle$ and $\langle 1\,1\,1\rangle$ axes were studied as a function of the frequency and temperature. ε_1^*, ε_3^* and the dielectric non-linearity β show distinct dielectric dispersion in the temperature interval between 270 and 220 K. It is also shown that the dielectric non-linearity β shows a crossover from a decreasing paraelectric-like to a rapidly increasing glass-like temperature behaviour which was predicted by the SRBRF model for relaxors.

Acknowledgements

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