

# Fitting and analyzing the dielectric spectra of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{3-x}\text{PbTiO}_3$ ceramics and single crystals

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**Abstract** The dielectric spectra of  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{3-x}\text{PbTiO}_3$  (PMN- $x$ PT) ceramics and single crystals with different  $\text{PbTiO}_3$  (PT) content were fitted and analyzed with dual mechanisms model proposed by Cheng et al. Two polarization processes were proposed in this model, one is related to flips of polar regions and the other associates with the breathing behavior of frozen polar regions. The fitted results showed that the weight factors of contribution of dielectric response from the two mechanisms near  $T_m$  varied with the different measuring frequency and PT content. These results can explain why the modeling parameters of  $T_m$  and  $\omega$  to Vogel–Fulcher relation show unlike results in different frequency regions.

**Keywords** Relaxor ferroelectrics · Dielectric spectra · PMN- $x$ PT

## 1 Introduction

Dielectric properties of relaxor ferroelectrics (RFE) were broadly investigated recently, especially in the case of model relaxors  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_{3-x}\text{PbTiO}_3$  (PMN- $x$ PT) and  $(1-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_{3-x}\text{PbTiO}_3$  (PZN- $x$ PT) due to their excellent piezoelectric and electric-optical properties. The most important feature of the RFE is a broad peak that appears in the dielectric constant as a function of

temperature. The relaxor behavior is usually attributed to the polar clusters. Based on fitting the spectra of PMN-10%PT ceramics, Cheng et al. [1, 2] proposed that there are two kinds of polarization processes in the relaxor ferroelectrics. One process is associated with the thermally activated flips of the polar regions in the materials. At temperatures much higher than the temperature of the permittivity maximum ( $T_m$ ), the dielectric constant obeys the following relation:

$$\varepsilon_{HT}(T) = \varepsilon_\infty + \exp(\alpha - \beta T) \quad (1)$$

where  $\alpha$  and  $\beta$  are constants.  $\varepsilon_\infty$  is the dielectric constant at the infinite frequency. The value of  $\beta$  is associated with the product rate of the polar regions in the materials. The other process is associated with the breathing behavior of the frozen polar regions. At temperatures much lower than the  $T_m$ , the dielectric constant can be expressed as follows:

$$\varepsilon_{LT}(T) = \varepsilon_\infty + \exp\left[\alpha_1 + (T/\beta_1)^{1+\delta}\right] \quad (2)$$

where  $\alpha_1$ ,  $\beta_1$  and  $\delta$  are constants. The value of  $\alpha_1$  is associated with the frozen rate of polar regions in the materials. The measured dielectric constant is a sum of the contribution of the two polarization processes. It can be expressed as:

$$\varepsilon_r' = \varepsilon_1 + \varepsilon_2 \quad (3a)$$

$$\varepsilon_1 = \frac{\varepsilon_{HT}(T)}{1 + C_1(\varepsilon_{HT}(T)/\varepsilon_{LT}(T))^{M_1}} \quad (3b)$$

$$\varepsilon_2 = \frac{\varepsilon_{LT}(T)}{1 + C_2(\varepsilon_{LT}(T)/\varepsilon_{HT}(T))^{M_2}} \quad (3c)$$

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where  $C_1$ ,  $C_2$ ,  $M_1$  and  $M_2$  are fitting parameters. The fitting result for PMN-10%PT ceramic [1] is of very high quality over a broad temperature range.

Viehland et al. [3] found that relaxors behave like dipolar-glass system. The relaxation in dipolar glass system can be described by Vogel–Fulcher relaxation:

$$\omega = \omega_0 \exp\left(\frac{-E_a}{k(T_m - T_f)}\right) \quad (4)$$

where  $T_f$  is the freezing temperature,  $T_m$  the temperature of the permittivity maximum,  $E_a$  an activation energy, and  $\omega_0$  the Debye frequency. Fitting the Vogel–Fulcher model to the data of PMN-10%PT ceramics, Tiwari et al. [4] found that there is a frequency above which there is a crossover to a new relaxational region, with a different  $\omega_0$  and other best-fit parameters in Eq. 4. The author can not explain this phenomenon.

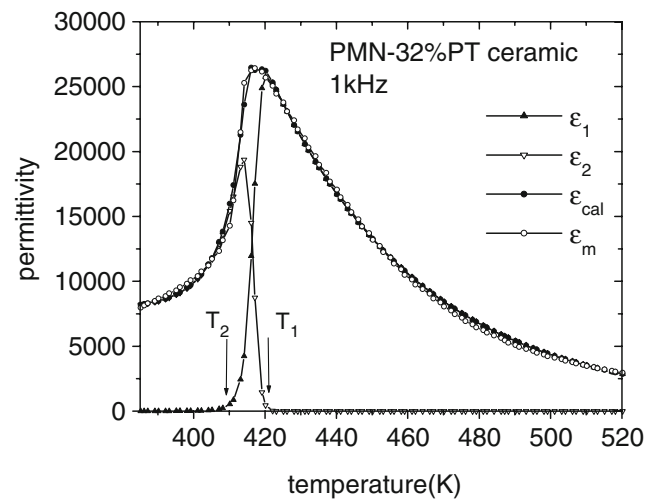
In this paper, PMN- $x$ PT ceramics and single crystal in the vicinity of the morphotropic phase boundary (MPB), were analyzed by the Cheng et al. model. Least-squares fitting of the observed data to the Eqs. 1, 2, 3a, 3b, and 3c was carried out. It was found that the weight of the two kinds polarization processes in the total of dielectric constant is different at various composition  $x$  or measuring frequencies. It is helpful to understand why the activation barrier  $E_a$  and  $\omega_0$  are different in high and low measuring frequency region.

## 2 Experimental procedure

The samples of ceramics used in this study were PMN-32% PT. They were prepared as described in literature [5]. The disk-shape samples with thickness 0.5 mm and diameter 10.0 mm were electroded with silver paste. The crystals of PMN-30%PT and PMN-32%PT were grown by a modified Bridgman method [6]. Plate-like specimens were cut into dimensions of  $0.5 \times 0.5 \times 0.1$  cm and electroded with silver paste. Dielectric measurements were operated on an automated system, which was composed of a precision LCR meter (Model HP 4284 A), an automated temperature-controlling chamber and computer automated control programme. The measuring frequencies were 1, 10, 100

**Table 1** The fitted parameters in Eqs. 1 and 2 for PMN- $x$ PT ceramics and single crystals.

	$\delta$	$\beta(10^{-3})\text{K}^{-1}$
PMN-10%PT [1]	0.95	18.20
PMN-32%PT ceramics	43.10	23.65
PMN-30%PT single crystal	5.21	30.74
PMN-32%PT single crystal	19.20	31.22



**Fig. 1** Measured ( $\epsilon_m$ ) and fitted ( $\epsilon_{cal}$ ) temperature dependence of dielectric constant for PMN-32%PT ceramic. The results of both  $\epsilon_1$  and  $\epsilon_2$  are also shown

and 1,000 kHz respectively. The dielectric spectra of sample at 1 kHz were chosen in our investigation. Measurements under weak field were made in the temperature range of 20–400 °C at heating rate of 2 °C/min.

## 3 Results and discussion

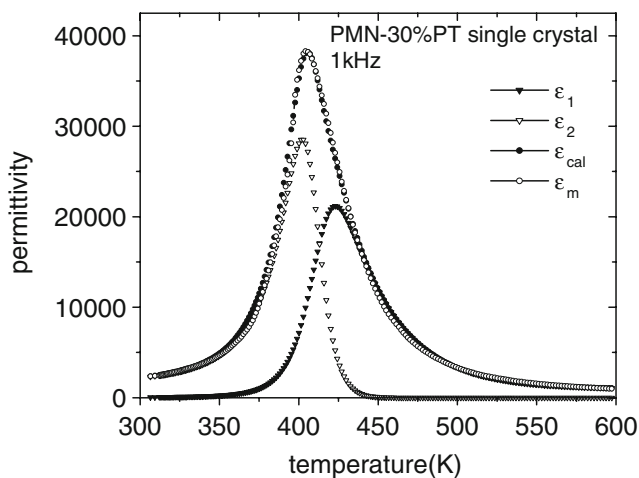
Figure 1 shows the fitting results of PMN-32%PT ceramics temperature spectrum at 1 kHz. The dielectric constant at high temperature (600 K) was chosen as  $\epsilon_\infty$ . The parameters  $\delta$  and  $\beta$  are given in Table 1. Compared to the result of PMN-10%PT in [1], it can be seen that the weight factor of dielectric constant contribution from breathing behavior ( $\epsilon_2$ ) is different for various composition  $x$ . For PMN-10%PT ceramics [1], the peak value of  $\epsilon_2$  is closed to that of  $\epsilon_1$ . But for PMN-32%PT ceramics, it is much lower than that of  $\epsilon_1$ . This indicates that the weight of  $\epsilon_1$  in the total dielectric constant increases with increasing PT content (or decreasing the degree of relaxor characteristics).

For PMN-32%PT ceramics, the parameter  $\beta$  ( $=23.65 \times 10^{-3} \text{ K}^{-1}$ ) is larger than that of PMN-10%PT ceramics ( $18.20 \times 10^{-3} \text{ K}^{-1}$ ). The concentration of dipolar region increases more rapidly with decreasing temperature than in PMN-10%PT. With decreasing temperature, the interaction among polar regions increases. Some of the polar regions with less flipping times cannot keep up with the switching of the measuring field. These polar regions become frozen polar regions. The parameter  $\tilde{a}$  ( $=43.10$ ) of PMN-32%PT ceramic is much larger than that of PMN-10%PT ceramic (0.950) [1]. This means the frozen rate of polar regions in PMN-32%PT is larger than that in PMN-10%PT because of large size and high concentration of the polar regions.

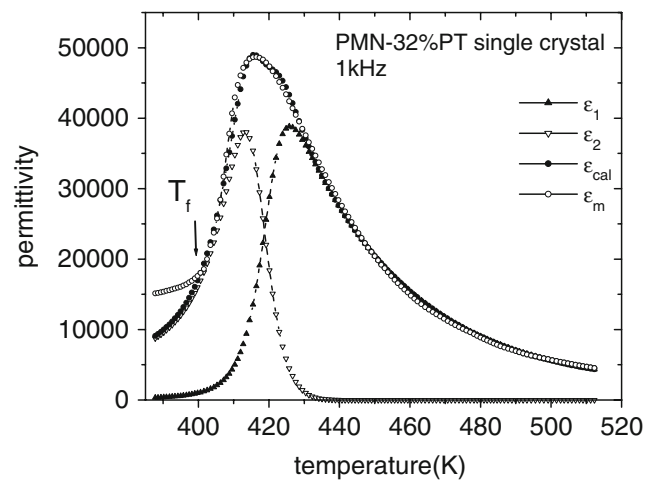
Merging of these polar regions brings about the frozen polar regions face reduced and polar regions number decreased at the temperatures below  $T_m$ . This leads the weight of the  $\epsilon_2$  decreases in the total dielectric constant.

In the temperature region between  $T_1$  and  $T_2$  as shown in Fig. 1, both two kinds of depolarization behaviors contribute to the dielectric response.  $T_1$  is near the temperature where the polar regions start to frozen. At the temperature  $T_2$ , the reversal of the polar regions is effectively frozen out. The temperature interval  $\Delta T = T_1 - T_2$  in Fig. 1 is about 15 K, whereas  $\Delta T$  is about 50 K for PMN-10%PT ceramics as shown in the Fig. 2 of [1]. This also indicates that the polar regions freeze more rapidly in PMN-32%PT ceramics.

Figure 2 shows the result of fitting Cheng et al. model to PMN-30%PT single crystal data. As Cheng expected [1], fitting of dielectric constant on single-crystal RFE gave very much the same result. The fitting result is of very high quality over a broad temperature range. The discrepancy of the fitting result in most temperature range is quite small, on the order of 0.1%. The parameters  $\beta = 30.74$  (shown in Table 1) implies density of the polar regions increases abruptly with decreasing temperature. Near temperature  $T_m$ , the breathing behavior of frozen polar regions prevails significantly. The fitted result of PMN-32%PT single crystal is shown in Fig. 3. Unacceptable discrepancy occurs at the peak of dielectric constant if the temperature region for fitting  $\epsilon_2$  extends to the temperature far below  $T_m$ . This implies that the polar region frozen process coupling with the formation of macrodomain occurs at a temperature ( $T_f$  as shown in Fig. 3) below  $T_m$  in PMN-32%PT single crystal. So, a narrow temperature region above the temperature ( $T_f$ ) in the vicinity of  $T_m$  was chosen to fit  $\epsilon_2$  for a relative good fitting result. The fitted result deviates from the experiment data below 400 K ( $T_f$ ). This divergence results from a transformation



**Fig. 2** Measured ( $\epsilon_m$ ) and fitted ( $\epsilon_{cal}$ ) temperature dependence of dielectric constant for PMN-30%PT single crystal. The results of both  $\epsilon_1$  and  $\epsilon_2$  are also shown



**Fig. 3** Measured ( $\epsilon_m$ ) and fitted ( $\epsilon_{cal}$ ) temperature dependence of dielectric constant for PMN-32%PT single crystal. The results of both  $\epsilon_1$  and  $\epsilon_2$  are also shown

from micro-domain or frozen polar region to macro-straight band domain (macrodomains).  $\epsilon_2$  can not provide good description of dielectric behavior for macrodomains. Polarized optical microscopy studies [7] revealed that in PMN-30%PT single crystal, rhombohedral phase consists of polar nanodomains (PND). The behavior of these PND is the same as frozen polar regions. Whereas for PMN-32%PT, macro-straight band domains were observed by optical microscopy [8]. The dielectric behavior of PMN-32%PT single crystal is more like normal ferroelectric at low temperatures. The absence of the frozen polar regions results in the discrepancy. But for PMN-32%PT ceramics, the transformation from micro-domain to macro-domains is frustrated by grain boundaries. Part of frozen polar region remains at low temperature. So Cheng et al. model provides a good description of dielectric behaviors for PMN-32%PT ceramics in a relative broad temperature region.

Fitted the Vogel–Fulcher Eq. 4 to the data of PMN-10%PT ceramics, V. S. Tiwari found that there is a typical frequency, about 100 kHz, above which there is a clear change in  $\omega_0$  and  $E_\alpha$ . For PMN-10%PT at low measurement frequency region, the fitting parameters  $\omega_0$  and  $E_\alpha$  are  $6.16 \times 10^{12}$  Hz and 0.021 eV respectively, but in high temperature region they are  $6.01 \times 10^6$  Hz and 0.00039 eV respectively. It is difficult to be understood why the attempt frequency of a microdipole  $\omega_0$  decreases with increasing the measuring frequency. This result can be explained using dual mechanism proposed by Cheng et al. Compared the fitted result of Cheng et al. model at different measuring frequency in the Fig. 2 of [1], one can find that the peak value of  $\epsilon_1$  decreases more quickly than that of  $\epsilon_2$  when the measuring frequency increases from 1 to 20 kHz for PMN-10%PT ceramic. This implies that the dielectric contribution of  $\epsilon_2$  increases while the contribution of  $\epsilon_1$  decreases

near  $T_m$  with increasing the measuring frequency. In low frequency region, the dielectric constant is mainly determined by the thermally activated flips of dipolar regions. The parameter  $\omega_0 = 6.01 \times 10^{12}$  Hz and  $E_a = 0.021$  eV are reasonable. The density of frozen polar region increases with increasing measuring frequency due to flips of some bigger polar regions cannot keep up with the switching of measuring field at high frequency. As a consequence, the breathing behaviors of frozen polar region play the dominant role near  $T_m$  at high measuring frequency. The fitted parameter  $\omega_0$  in high measuring frequency region is closed to the intrinsic frequency (about  $10^7$  Hz) of the frozen polar region breathing behaviors for PMN-10%PT (as shown in Fig. 6 of [1]). This result is consistent with the switch off sequence of dielectric contribution with increasing measuring frequency proposed by Bovtun et al. [9]: first polar cluster reversal contribution and then cluster bound fluctuation contribution. So, two kinds of relaxation processes result in different fitted parameters of Vogel–Fulcher relation in different measuring frequency regions.

#### 4 Conclusion

RFE of PMN-xPT ceramics and single crystals have two polarization processes proposed by Cheng et al., one is related to flips of polar regions and the other associates with the breathing behavior of frozen polar regions. The fitted results showed that in the vicinity of the temperature of the

permittivity maximum ( $T_m$ ), the weight factor of dielectric contribution from breathing behavior decreases with increasing PT content and increases with increasing measuring frequency ( $\omega$ ). At low measuring frequency, the dielectric constant of PMN-10%PT near  $T_m$  is mainly controlled by contribution from flips of polar regions. While at high measuring frequency, the contribution caused by the breathing behavior of the frozen polar region prevails near  $T_m$ .

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