

## dc bias-induced dielectric anomalies in $\langle 111 \rangle$ -oriented $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3)-0.1\text{PbTiO}_3$ single crystals

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dc bias dependence of small signal dielectric response was measured on  $\langle 111 \rangle$ -oriented  $0.9\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3)-0.1\text{PbTiO}_3$  single crystals at various temperatures. It was shown that at different temperature ranges, the dielectric responses were quite different, implying different natures of the polar nanodomains. It was found that the freezing occurred effectively below freezing temperature  $T_o$ . Between  $T_o$  and  $T_m$ , the dielectric constant peak temperature, the reversible dielectric peaks under bias were explained by the mechanism of polarization rotation, revealing a possible presence of multiple polar orders in nanodomains. © 2006 American Institute of Physics. [DOI: 10.1063/1.2186102]

In recent years, intensive research works have been devoted to relaxor  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3)$  (PMN). The main features of a relaxor include a strong frequency dispersion of the dielectric permittivity, a broad transition peak, and an absence of spontaneous ferroelectric long range order at the peak temperature  $T_m$ .<sup>1</sup> The peculiar dielectric properties of relaxors are related to the presence of polar nanoregions (PNRs).<sup>2</sup> These PNRs have been described by several models, including superparaelectric,<sup>1</sup> dipole glass freezing,<sup>3</sup> random fields,<sup>4</sup> and interface-roughening models.<sup>5</sup> Their major distinction lies in advocating either flipping of the thermally activated local dipole moments under ac fields or vibration of boundaries of the PNRs in accounting for the dielectric responses.

The solid solutions  $(1-x)\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3}\text{O}_3)-x\text{PbTiO}_3$  with low concentration of  $\text{PbTiO}_3$  (PT) ( $x < 0.15$ ) show similar relaxor behaviors at room temperature.<sup>6</sup> In  $0.9\text{PMN}-0.1\text{PT}$  a spontaneous ferroelectric long range order can be established<sup>7-9</sup> at  $T_C = 285 \pm 5$  K. The puzzling point is that this phase transition is smeared on the dielectric constant versus temperature curve. This can be understood by the fact that the dielectric constant of a relaxor is mainly dominated by the response of the PNRs. Recent Raman<sup>10</sup> and scanning probe microscopy studies<sup>11</sup> have found that the PNRs can be embedded in a ferroelectric phase. Our previous work<sup>12</sup> on the mechanical properties of the PMN/PT suggests that the structural phase transition corresponds actually to the paraelectric to ferroelectric transition of the matrix.

In this work, in order to study the nature of the PNRs in PMN-PT, we performed dc bias dependence of dielectric measurements in  $\langle 111 \rangle$ -oriented  $0.9\text{PMN}-0.1\text{PT}$  single crystal at various temperatures. We found quite a distinctive behavior of the PNRs through observing dielectric anomalies in different temperature ranges.

The  $0.9\text{PMN}-0.1\text{PT}$  single crystals were grown by a Bridgman method at Shanghai Institute of Ceramics. The

crystal for measurement has a rectangular shape with an area of  $16 \text{ mm}^2$  and a thickness of  $0.2 \text{ mm}$ , with  $\langle 111 \rangle$  axis perpendicular to the large surfaces of the crystal. The polished crystal was sputtered with gold as electrodes. Small signal dielectric permittivity  $\epsilon_{33}$  as well as loss tangent measurement was carried out with a Stanford Research LCR meter SR720. The amplitude of the ac drive was  $0.5 \text{ V}$ . The sample was placed in a liquid nitrogen cryostat (Oxford Optistat<sup>DN</sup>). The measurement was performed between the temperature range of  $323-213 \text{ K}$ . The temperature of the sample was controlled within a precision of  $\pm 0.1^\circ \text{C}$  by means of an Oxford ITC 601 temperature controller. For measurement performed under dc bias, a blocking circuit was used to protect the LCR meter in case of sample break down.

Figure 1 shows the temperature dependence of the small signal dielectric constant  $\epsilon_{33}$  and loss tangent  $\tan \delta$  of the  $0.9\text{PMN}-0.1\text{PT}$  single crystal measured at frequencies of 1, 10, and 100 kHz. The measurement was taken under zero-field-cooling conditions. Since it is well known that the dielectric properties of a relaxor depends strongly on its ther-

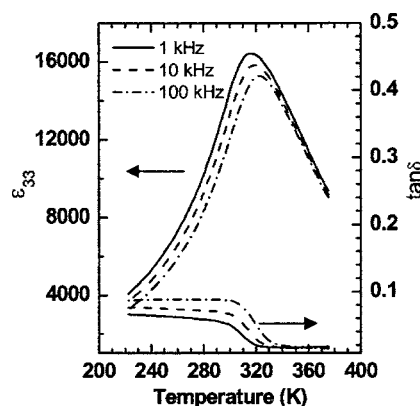


FIG. 1. Temperature dependence of dielectric constant  $\epsilon_{33}$  and loss tangent  $\tan \delta$  of the  $0.9\text{PMN}-0.1\text{PT}$  single crystal measured at frequencies of 1, 10, and 100 kHz.

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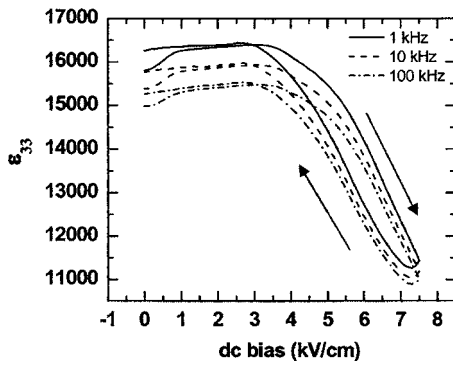


FIG. 2. dc bias dependence of  $\epsilon_{33}$  measured at 323 K, with frequencies of 1, 10, and 100 kHz.

mal history,<sup>13</sup> the sample was annealed at 373 K for 1 h before cooling. For each frequency, a broad transition peak is observed,  $\epsilon_{33}$  reaches a maximum at the temperature  $T_m$ , which is frequency dependent. Strong frequency dispersion is exhibited below  $T_m$ . The  $T_m$  at 1 kHz is 315 K, the molar fraction  $x$  of the lead titanium is determined as 0.104, according to the empirical formula  $T_m = 5x - 10$  (where  $T_m$  is in degrees Celsius).<sup>14</sup> The frequency dependence of the  $T_m$  can be interpreted by the dipole glass model<sup>4</sup> and fitted with the well known Vogel-Fulcher relation:  $f = f_0 \exp[-U/(T_m - T_o)]$ , where the freezing temperature  $T_o$  can be best fitted to the value of 284 K. It coincides with the  $T_{R-F}$ .<sup>7,8,15</sup> These results are in good agreement with the literature.

The dc bias dependence  $\epsilon_{33}$  measurements were carried out at constant temperature between 323 and 213 K. Before each measurement, the sample was first annealed at 373 K for 30 min to insure that all previous poling effects were canceled. Then the sample was cooled to the prefixed temperature under the zero-field condition. For each bias field applied, the measurement started after a waiting time of 3 s. The measurements can be grouped into three temperature ranges: (i) above  $T_m$ , (ii) between  $T_m$  and  $T_o$ , and (iii) below  $T_o$ .

Figure 2 shows the dc bias field dependence of  $\epsilon_{33}$  measured at 323 K, which is above  $T_m$ , with frequencies of 1, 10, and 100 kHz. During the increasing bias field run, there is a slight increase (about 6%) in  $\epsilon_{33}$  at low bias level (<1 kV/cm). It displays a plateau at intermediate bias field. A further increase in the bias field results in a decrease in  $\epsilon_{33}$ . At a bias field of 7 kV/cm, the change of  $\epsilon_{33}$  is about 25%. It should be mentioned that dielectric dispersion occurs in the whole bias field range. In the decreasing bias run,  $\epsilon_{33}$  increases and regains the plateau level. The dielectric constant does not return to the exact initial value, at zero bias fields.

Figures 3(a)–3(c) show the dc bias dependence of  $\epsilon_{33}$  measured at 303, 293, and 288 K, respectively, with frequencies of 1, 10, and 100 kHz. We see that they all exhibit some common features in this temperature range: an initial increase in  $\epsilon_{33}$  at small bias (<1 kV/cm), followed by a large increase in  $\epsilon_{33}$  at intermediate bias field, then a decrease, forming a peak. Further increase in bias field results in rapid decrease in  $\epsilon_{33}$ , which seems to saturate at  $\sim 7$  kV/cm. Comparing to the zero bias value, the maximum change of  $\epsilon_{33}$  is more than 50%. It can be also observed that the frequency dispersion remains strong all the way but becomes strongly attenuated at high bias fields where  $\epsilon_{33}$  are strongly dimin-

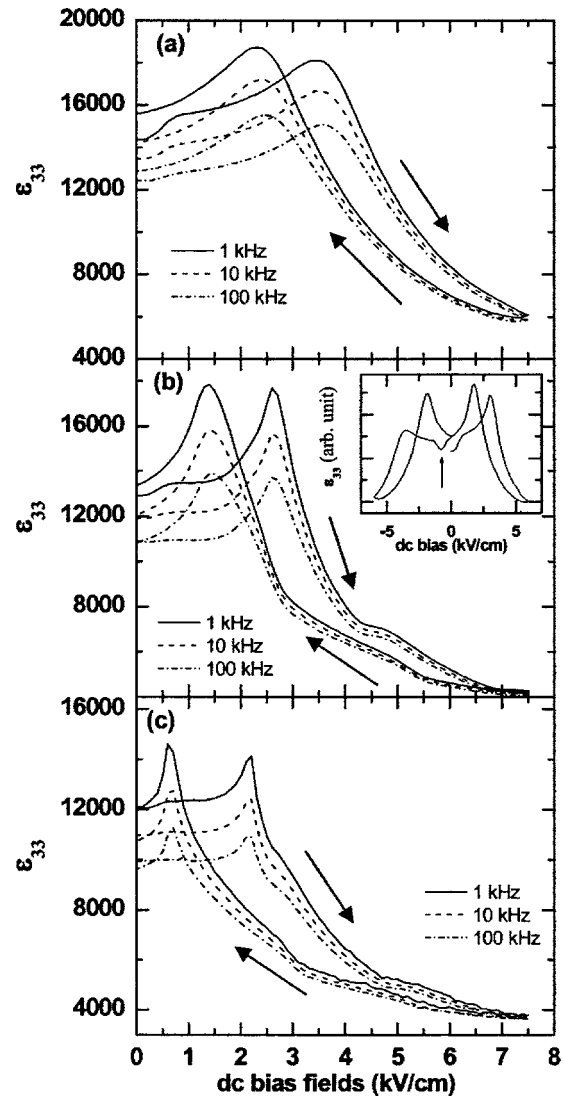


FIG. 3. dc bias dependence of  $\epsilon_{33}$  measured at fixed temperatures of (a) 303, (b) 293, and (c) 288 K, with frequencies of 1, 10, and 100 kHz, respectively.

ished. In the decreasing bias field run, the peak of the  $\epsilon_{33}$  reappears at a lower bias field.

The inset of Fig. 3(b) shows the  $\epsilon_{33}$  measurements performed at 293 K with a frequency of 1 kHz, under bipolar dc bias fields. We see that the double peak can be reproduced in reverse bias as well. An important feature to note here is that, in the reverse bias direction,  $\epsilon_{33}$  continues to decrease and reaches the initial zero-bias value before increasing again (see arrow).

Figure 4 shows the measurements performed below  $T_o$ , at 253 and 213 K, respectively. Here we see regardless of the temperatures and frequency  $\epsilon_{33}$  shows a step-like drop at a threshold bias field. The relaxor characteristics, i.e., the frequency dispersion (shown only for the 253 K data) disappear after the stepwise drop. During decreasing bias,  $\epsilon_{33}$  remains almost constant.

Before interpreting these results, we first consider the effect of dc bias on small signal dielectric response. Tagantsev<sup>5</sup> has shown that in single crystal PMN, the dielectric response is affected by dc bias in two ways: (i) it reorients the local polarization vectors in the direction of the applied field and (ii) it provides a coalescence of neighboring PNRs resulting in the diminishing of the total area of their

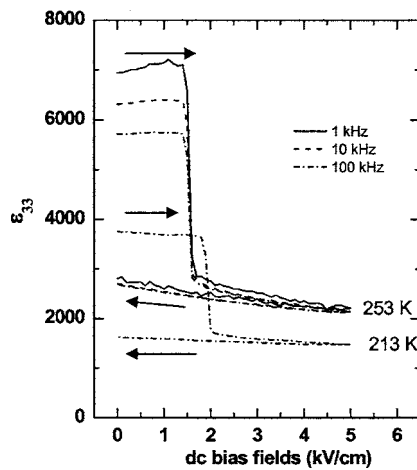


FIG. 4. dc bias dependence of  $\epsilon_{33}$  measured at fixed temperatures of 253 and 213 K.

interfaces. In terms of (i), if the crystal is oriented in the  $[111]$  direction, reorientation of local polar vectors from other equivalent  $\langle 111 \rangle$  directions should result in an increase in  $\epsilon_{33}$ . For (ii), a decrease of the interface area should decrease  $\epsilon_{33}$ .

By x-ray and neutron studies, it was shown<sup>8</sup> that the PNRs in 0.9PMN–0.1PT exhibit a multiple polar order at room temperature: (i) a local rhombohedral polar order with Ti/Nb/Mg oxygen atoms shift in the  $\langle 111 \rangle$  direction and (ii) a local tetragonal polar order within the same unit cell formed by  $\langle 001 \rangle$  shift of Pb atom. The competition between the two orders results in a monoclinic distortion at the local level. The multiple polar orders have been predicted by the spherical random bond random field model.<sup>16</sup>

The most striking feature is the double peak in  $\epsilon_{33}$  for measurements performed between  $T_m$  and  $T_o$ , as shown in Fig. 3. It can be interpreted with the multiple polar orders model. First we assume that the increase in  $\epsilon_{33}$  at small bias should be due to the reorientation of the rhombohedral polar vectors from other equivalent  $\langle 111 \rangle$  directions. It is based on the fact that the increase in  $\epsilon_{33}$  at low bias is not reversible and a reverse bias is needed to recover the original value [inset of Fig. 3(b)].

Next the peak of  $\epsilon_{33}$  at higher bias is assigned to the polarization rotation of PNRs from tetragonal to rhombohedral distortions. The main reason for this suggestion is the reversibility of this peak in the decreasing bias run. Since the Pb atom has a natural off-center shift in the  $\langle 001 \rangle$  direction, its  $[111]$  reorientation under dc bias is highly unstable. The tetragonal polar order should be recovered on the removal of external field. Previously it has been shown that electric fields can induce macroscopic polarization rotations between tetragonal and rhombohedral ferroelectric lead zirconate titanate.<sup>17,18</sup> The present result provides a possible evidence of polarization rotation in PNRs of relaxor ferroelectrics.

In both Figs. 2 and 3 the large decreases in dielectric constant at high bias are due to the coalescence of PNRs. This leads to transformation of the whole matrix into a long range order ferroelectric. It is also noticed that polarization rotation is absent for temperatures above  $T_m$ . This suggests

that  $T_m$  might correspond to a transition temperature through which both tetragonal and rhombohedral distortions exist in PNRs. Last, the model of thermally activated dipole flipping can not explain the present results since in that case the polar vectors will be clamped by dc bias and  $\epsilon_{33}$  should not show any increase.

In Fig. 4, the relaxor behavior persists before reaching a threshold bias. So the effect of bias is to transform the PNRs into the symmetry of the matrix. The flatness of the  $\epsilon_{33}$  implies that there was no field induced polar vectors reorientation. This confirms that freezing occurs in 0.9PMN–0.1PT below  $T_o$ . The stepwise drop of  $\epsilon_{33}$  and the disappearance of the relaxor behavior after exceeding the threshold bias field indicate the destruction of the glassy state of the PNRs and the dielectric response is contributed by the matrix alone.

In summary, in this work we report the observation of dielectric anomalies of  $\langle 111 \rangle$  0.9PMN–0.1PT single crystal under dc bias. We show that the polar nanoregions exhibit quite distinctive natures at different temperature ranges. The reversible dielectric peaks under bias between  $T_m$  and  $T_o$  suggest a possible presence of polarization rotation mechanism.  $T_m$  might correspond to an “underlying” phase transition temperature through which multiple local polar orders are formed. We confirm that freezing took place below  $T_o$  where spontaneous long range ferroelectric order occurred also in the matrix.

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