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Dielectric tunability and imprint effect in $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ceramics

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Abstract

For $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$, composition dependence of dielectric tunability under the dc bias field and dielectric hysteresis during the circle of external electric field were studied. The highest dielectric tunability of 71% (at the dc bias of 1000 V/mm) and the lowest dielectric hysteresis were observed in the 0.9PMN-0.1PT sample. The effect of circled electric field on the dielectric hysteresis was more remarkable than that on the dielectric aging. Moreover, the effect of the filed-cooled process on the ferroelectric properties was also investigated. In the polycrystalline 0.7PMN-0.3PT sample cooled under a strong dc electric field, a remarkable imprint effect was reported. The preferred direction induced by a strong external electric field was partially reserved after removing the electric field. This imprint effect and the dielectric hysteresis have been tentatively interpreted by reorientation and alignment of polar vectors.

Keywords: C. Dielectric properties; PMN-PT; Dielectric hysteresis; Imprint effect

1. Introduction

During the past several decades, lead magnesium niobate and its solid solution with lead titanate have shown great promise applications as multi-layer capacitors (MLCC) and active materials for sensors and actuators [1]. With increase of the integration degree of the circuit, these devices are subjected to a higher dc bias field. Under a high electric field, properties of materials could be induced to change. To optimize the performance of materials, it is necessary to study the responses of the materials to the electric field and to explore the mechanism of these responses.

There were lots of publications about the properties of materials under zero or a certain electric field, such as aging, field-induced phase and domain transitions [2–6]. Zhang et al. [3] investigated the aging characteristics of the $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ (PMN-PT) under dc bias field and thought that the dielectric aging was related to the change in both the 180° and non-180° polarization reorientation process. They believed that the aging in PMN-PT is mainly caused by the elastic coupling of the micro-polar regions to the defect field instead of electric coupling. Sommer et al. [5] reported the polar metastability and an electric-field-induced phase transition in the single crystal of PMN. Coarsening of polar nano-domains with decreasing temperature has been observed in rhombohedral-structured La-modified $Pb(Zr_{0.70}Ti_{0.30})O_3$. Decreasing temperature resulted in enhanced tendencies towards long-range ordering (LRO); however, the system did not transform the mixture of polar nano-domains and the para-electric matrix into a completely LRO ferroelectric. It is found that the application of an electric field is necessary to transform the relaxor to a LRO ferroelectric in rhombohedral-structured PLZT. This transition is often referred to in the literature as the field-induced micro-domain to macro-domain or induced ferroelectric transition [6]. In PMN system, those literatures about field-induced phase transition are mostly concentrated in single crystals. Researchers paid their attention to the change of dielectric properties, piezoelectric properties and domain structure under the dc or ac electric field [5,7–10]. These changes are closely related to the drifting of defect dipoles or the reorientation of polar micro-domains. However, there are few reports on the change of dielectric constant with the circle of the electric field. The field-cooling process has an obvious influence on the polarization stability. This process induces a

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preferred direction in the crystal. Field-cooling process has more obvious effects on the single crystal than on the polycrystalline ceramics, because of having more outstanding direction in the single crystal. Under an electric field, the relaxor ferroelectric can be induced to a LRO ferroelectric. There were a lot of literatures about the field-induced micro-domain to macro-domain transition. However, it is seldom reported how to do the LRO state change after the electric field was switched off. The dielectric changes are associated with the buildup and decay of macro-polarization, which has been confirmed by pyroelectric measurements using the Byer-Roundey technique. The mechanism of polarization switching has also been studied in detail for many bulk and thin-film ferroelectrics [11–13]. The P-E loops measurement could show the change of polarization with the external field, which was very important for the study of the fatigue of nonvolatile ferroelectric capacitors [11,14,15]. Imprint is the tendency of a ferroelectric memory element to develop a preferential state under certain conditions. This effect manifests itself by a shift of the hysteresis loop along the voltage axis. It is obvious that the imprint is closely related to the process that leads to aging and fatigue of materials. Imprint has been widely studied in the PZT, PLZT and SBT thin-films storage capacitors [11,16,17]. However, such effect is not reported in the PMN-based ferroelectric materials.

In this paper, we studied the dielectric responses under the different dc bias field, reported obvious imprint effect in the 0.7PMN-0.3PT sample forced by a high dc electric field for a period of time. Those results are discussed with regard to the reorientation of the polar vectors.

2. Experiment procedure

$(1-x)$PMN-xPT ($x = 0.1, 0.2, 0.3$) powders were synthesized using the Columbite precursor proceeding [18]. In this method, the formation of pyrochlore phase was eliminated. Calcination was realized at 850 °C for 2 h. The powders obtained were pressed into pellets and sintered at 1200 °C for 2 h with a 3 °C/min heating rate. To prevent PbO volatilization from the samples, the specimens were fired in a lead atmosphere.

Dielectric properties under a dc bias field were measured by the capacitance method using a LCR meter (TH2816) while the samples were placed in silicon oil. Near respective Curie temperature, the dc bias field was gradually increased to 1000 V/mm and maintained it at 1000 V/mm for 4 h, and then decreased to 0 V/mm. When the dc bias was applied in every time, it is necessary to wait during 90 s before measuring the dielectric constant.

The P-E hysteresis loops of samples were measured by a TF analyzer (Model 2000, aix ACCT Systems, Germany) at 20 °C. One surface of those selected samples was labeled with (+) as positive surface. During measuring the P-E hysteresis loops, the positive electrode of the TF analyzer was conducted on the positive surface of the sample. After three compositions were heated to 140 °C, these samples were cooled to 20 °C in 120 min without the field. These samples are referred to as zero-field-cooled (ZFC). The P-E hysteresis loops of zero-field-cooled samples were measured. Since the field-cooling process had such influence on the polarization stability, these samples were placed in silicon oil and heated to 140 °C, then cooled to 20 °C under the field of 2000 V/mm and maintained this field for 10 h at 20 °C again, respectively. The positive surface of samples was contacted to the positive electrode of the external dc voltage power supply. These samples are referred to as field-cooled (2000FC-10 h(+)). After being forced by such field-cooling process, the P-E hysteresis loops of these samples were measured again.

3. Results and discussion

For $(1-x)$PMN-xPT, with the increase of the PT content, Curie temperature of the sample also increased. To compare dielectric properties from different compositions, it is necessary to establish a reference temperature for each composition to account for this variation [3]. Taking into account these, the respective Curie temperature for each composition is chosen as the reference temperature for that composition when dielectric properties were measured. Fig. 1(a) illustrated the dc bias dependence of $(1-x)$PMN-xPT near respective Curie temperature. The nonlinear relationship was clear between the dielectric constant and dc bias. For these three compositions, the dielectric constant slightly increased at low bias level and decreased greatly at high bias level. The dielectric constant began to decrease at a point named as threshold point. The electric field corresponding with this point was looked as

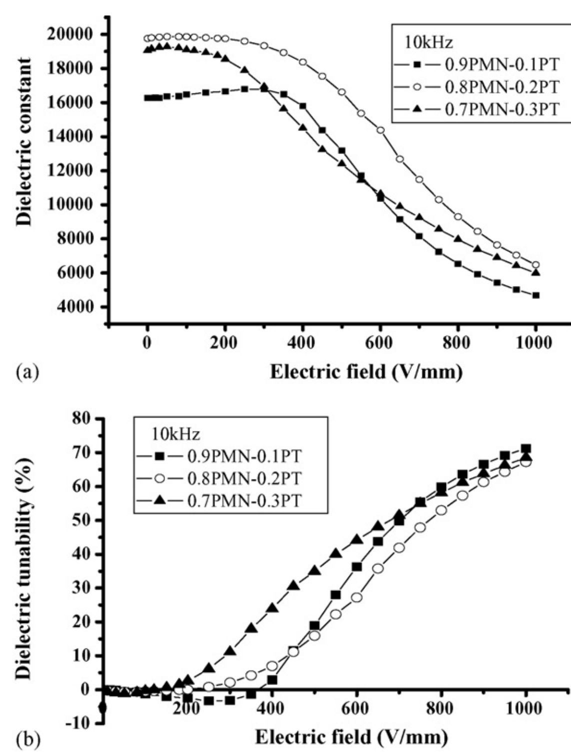

Fig. 1. Variation of the dielectric constant (a) and tunability of dielectric constant (b) with dc bias, measured near respective Curie temperature and frequencies of 10 kHz for the $(1-x)$PMN-xPT system: (1) (■) $x = 0.1$; (2) (○) $x = 0.2$; (3) (▲) $x = 0.3$.

threshold field (E_{th}). For 0.9PMN-0.1PT, the threshold field was about 300 V/mm. With increasing PT content, anisotropy in the micro-polar domains increased and the disorder of the micro-polar domains decreased. Even a lower electric field can rearrange the polar domains with the direction of external field. Hence, the E_{th} value decreased with the increase of x. Fig. 1(b) showed the dielectric constant tunability dependence for dc bias and composition near respective Curie temperature. The tunability (t) was defined as follow:

$$t = \frac{[\varepsilon_r(0) - \varepsilon_r(E)]}{\varepsilon_r(0)} \quad (1)$$

where $\varepsilon_r(0)$ and $\varepsilon_r(E)$ were the dielectric constant at zero dc bias field and at a bias of E [19], respectively. The results revealed the highest dielectric constant tunability of 71% (at the dc bias of 1000 V/mm) in 0.9PMN-0.1PT.

Fig. 2 showed the dc bias and composition dependence of the dielectric constant at a frequency of 10 kHz during the circle of alternating electric field (increased electric field then decreased electric field). For a material under a dc bias field, changes in the induced properties of the material over time will inevitably result in a phenomenon called aging. When the circle of alternating electric field was interrupted, the dielectric constant of these samples are all slightly less than primal dielectric constant of fresh samples. It shows such circle of alternating electric field resulted in aging in these samples. Otherwise, the curve of the process of increasing electric field is non-identical to that of the process of decreasing electric field. Such non-identical process can be regarded as a kind of dielectric hysteresis. The dielectric hysteresis became more severe with the increase of the PT content. For 0.7PMN-0.3PT, under a same dc bias, the dielectric constant during decreasing electric field was obviously lower than that during increasing electric field. Figs. 1 and 2 showed that there was large dielectric tunability, low dielectric hysteresis in 0.9PMN-0.1PT. Thus, it is possible to apply 0.9PMN-0.1PT in the tunable capacitors.

Fig. 3(a)–(c) showed the P-E loops of samples of being cooled without electric field (ZFC) and under the electric field of 2000 V/mm (2000FC-10 h(+)), respectively. The P_r, P_{max}, E_A and coercive field E_c values of those selected samples were listed in Table 1. P_r and P_{max} were the remanent polarization and the maximal polarization, respectively. Along the positive voltage axis, the electric field at the point A is defined as E_A when the polarization value is zero. In PMN system, we firstly revealed the P-E loop shift that is similar to the imprint effects in PZT thin-film capacitor. For $(1-x)$PMN-xPT, with the increase of PT content, the P_r value of these samples increased, the voltage shift along the voltage axis was also more and more severe. We could clearly observe such tendency from Fig. 3 and the Table 1. After being forced by such electric-field-cooled process, the P-E loops shifted along the negative voltage axis in 0.8PMN-0.2PT and 0.7PMN-0.3PT. In the 0.7PMN-0.3PT compositions, both the value of P_r and the voltage shift are the strongest. However, such voltage shift was the faintest in 0.9PMN-0.1PT. The magnitude of voltage shift shows the intensity of imprint effect. Therefore, the 0.7PMN-0.3PT

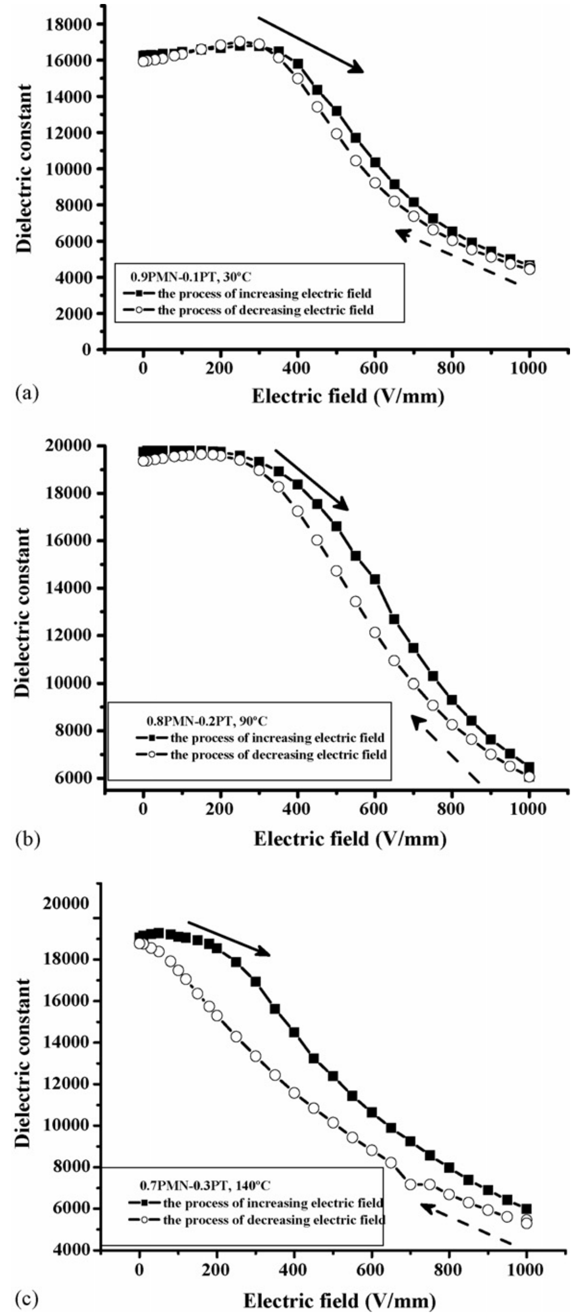

Fig. 2. Direct current bias and composition dependence of the dielectric constant at a frequency of 10 kHz during the circle of alternating electric field (increasing electric field (iE) then decreasing electric field (dE)): (a) 0.9PMN-0.1PT; (b) 0.8PMN-0.2PT; (c) 0.7PMN-0.3PT.

showed the strongest imprint effect in these three compositions. In addition, we could suppose that imprint seems to have stronger influence on the dielectric hysteresis than on the dielectric aging from the results of Fig. 2.

The dominant polarization mechanism in relaxor ferroelectrics is well known as reorientation of polar vector and domain wall broadening motion [20]. All ferroelectrics share two common features: the domains could be aligned with external electric fields exceeding the coercive field. At a certain temperature, the correlation vanishes [21]. The electric field promoted polar clusters to grow and tends to orientate them

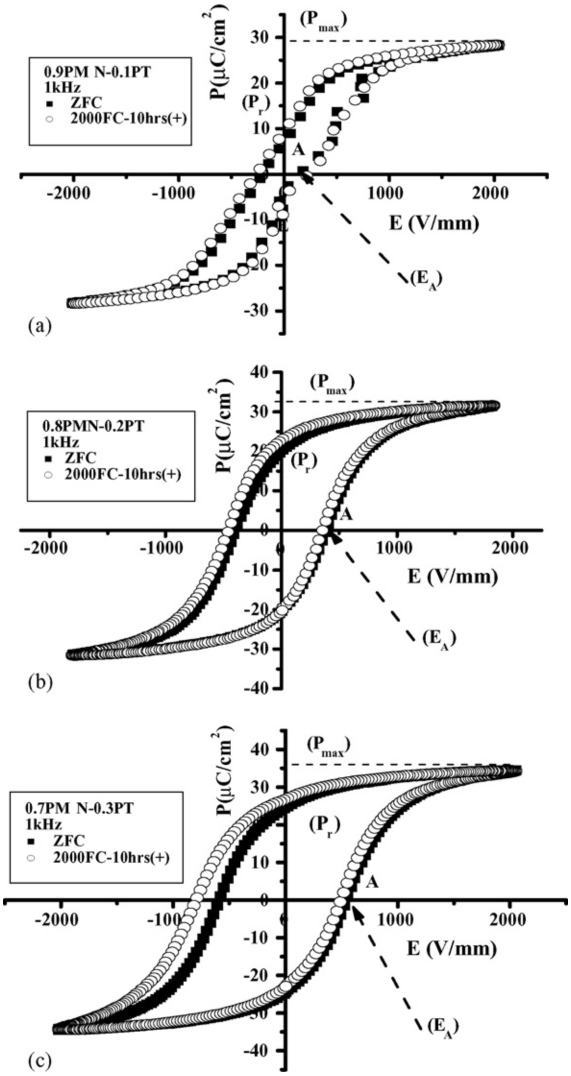

Fig. 3. The P-E loops of samples of being cooled without electric field (ZFC) and under the electric field of 2000 V/mm (2000FC-10 h(+)), respectively: (a) 0.9PMN-0.1PT; (b) 0.8PMN-0.2PT; (c) 0.7PMN-0.3PT.

Table 1
Polarization, coercive field and E_A value of samples after being cooled without electric field (ZFC) and under the electric field of 2000 V/mm (2000FC-10 h(+)), respectively

	Types		
	0.9PMN-0.1PT	0.8PMN-0.2PT	0.7PMN-0.3PT
Being cooled without electric field (ZFC)			
E_A (V/mm)	183	392	539
E_c (V/mm)	204	403	591
P_r (μC/cm^2)	7	21	25
P_{max} (μC/cm^2)	28	32	34
After being cooled under dc electric field (2000FC-10 h(+))			
E_A (V/mm)	216	357	494
E_c (V/mm)	271	541	796
P_r (μC/cm^2)	9	23	27
P_{max} (μC/cm^2)	28	32	34

parallel to the field. Field-cooling process has more obvious effects on single crystal than on polycrystalline ceramics. The polar vectors are not perfectly aligned with the direction of the electric field in the polycrystalline lattice, however likely exhibit a ''cone'' distribution with respect to the applied electric field [22]. An asymmetry of a ferroelectric hysteresis loop in ferroelectric materials is usually caused by the preference of a certain polarization state over the other. The alignment of polar vectors with a preferred direction led to the certain polarization state over the other. Field-cooling resulted in enhanced tendencies towards long-range ordering, the LRO macro-domains could stably exist below $T_{n\text{-}r}$ (the temperature of transition from the normal ferroelectric phase to the relaxor ferroelectric phase). The $T_{n\text{-}r}$ of 0.9PMN-0.1PT is lower than 20 °C, the long-range ordering induced by strong electric field was destroyed after the external electric was removed. Hence, imprint induced by the strong electric field was very faint in 0.9PMN-0.1PT. For $(1-x)$PMN-xPT, with the increase of PT content, the size and the anisotropy of the micro-polar domains is clearly increased. When the external field was removed, those larger polar domains are likely to have stronger trend of maintaining their direction according to the direction of the external field [23]. After removing the electric field, long-range ordering induced by electric field is partially reserved at room temperature because the $T_{n\text{-}r}$ of 0.8PMN-0.2PT and 0.7PMN-0.3PT are higher than 20 °C, respectively. As a result, the 0.7PMN-0.3PT showed the most remarkable imprint effect.

4. Conclusions

A strong field-cooled process could induce obvious imprint effect in the polycrystalline 0.7PMN-0.3PT ceramics. Imprint has more strong effect on dielectric hysteresis than on dielectric aging. Imprint effect is easier to appear when the anisotropy in the micro-polar domains increased. Such effect has indicated that the preferred polarization state under a strong electric field could be partially reserved in polycrystalline ceramics even when the electric field was removed. Reversal and reorientation of the polar vectors under the external field could be used to explain this effect.

Acknowledgements

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