Electric field effects on the phase transitions in [001]-oriented \((1-x)\)Pb\((\text{Mg}_{1/3}\text{Nb}_{2/3})\)O\(_3\)-xPbTiO\(_3\) single crystals with compositions near the morphotropic phase boundary

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Dielectric behavior and phase transitions of [001] oriented \((1-x)\)Pb\((\text{Mg}_{1/3}\text{Nb}_{2/3})\)O\(_3\)-xPbTiO\(_3\) single crystals with \(x=29, 31, 32,\) and 33% were investigated by impedance measurements and high resolution X-ray diffraction analysis under various electrical and thermal conditions. Application of a bias field along [001] can shift down the Rhombohedral-Tetragonal structural phase transition, so that the morphotropic phase boundary is shifted by the bias field. We have quantified this shift under 1 kV dc bias along [001]. A transition between the normal ferroelectric and relaxor states was indicated by the appearance of a frequency dispersion shoulder slightly below \(T_C\), and an abrupt disappearance of the frequency dispersion at a lower temperature. This relaxor-ferroelectric transition was found to be thermally driven in the compositions with PbTiO\(_3\) (PT) contents from 31 to 33%. While for the composition with 29% PT content, a bias field can help to produce this transition.

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I. INTRODUCTION

In recent years, \((1-x)\)Pb\((\text{Mg}_{1/3}\text{Nb}_{2/3})\)O\(_3\)-xPbTiO\(_3\) (PMN-PT) single crystal system has attracted a lot of attention.\(^1\)–\(^15\) The rhombohedral symmetry single crystals with compositions near the morphotropic phase boundary (MPB) can produce multidomain structures that have piezoelectric constant \(d_{33}>2400\) pC/N, and the electromechanical coupling coefficient \(k_{33}>90\%\), when they are poled along [001] of cubic coordinates.\(^1\)–\(^4\) Such large piezoelectric constant and electromechanical coupling coefficient may bring a revolutionary change in term of sensitivity, bandwidth, and power for ultrasonic transducers and piezoelectric actuators.

At room temperature, the MPB of \((1-x)\)Pb\((\text{Mg}_{1/3}\text{Nb}_{2/3})\)O\(_3\)-xPbTiO\(_3\) system is at about \(x=0.34\). For compositions with \(x\geq0.35\), the crystal structure is tetragonal 4\(mm\), while for those with \(x\leq0.33\), the crystal symmetry is rhombohedral 3\(m\). Reported data showed that the PMN-PT single crystals with compositions near the MPB on the rhombohedral side give rise to these superior piezoelectric properties after poling along [001] of the prototype cubic perovskite structure.\(^1\)–\(^4\) It is known that composition, crystallographic orientation, electrical field, and temperature all have strong influence on the phase transition and effective materials properties of PMN-PT single crystals.\(^1\)–\(^7\) Several investigations have been conducted on these issues but only limited to one particular composition.\(^8\)–\(^10\) It is known that crystals with compositions near the MPB are subject to large fluctuations due to the Pb loss during growth and the sensitivity of properties to compositional change.\(^5\) Most of the reported MPB data were obtained in PMN-PT ceramics, which may not be applicable to single crystals due to the fact that many properties are highly correlated to the crystallographic orientation. For example, different orientation single crystals can exhibit significantly different field induced phase transitions.\(^8\)–\(^9\)

Since superior piezoelectric properties exist in [001] oriented PMN-PT single crystals with compositions near the MPB on the rhombohedral side, it is important to systematically study them in depth in order to gain better physical understanding. In the present work, we use the dielectric property change as a measure to systematically study the phase transition behavior in a series of [001] oriented PMN-PT single crystals with compositions near MPB (on the rhombohedral side), focusing on the effects of field bias.

II. EXPERIMENT

The PMN-PT single crystals, grown by a modified Bridgman technique, are provided by the Shanghai Institute of Ceramics. The crystals were oriented, cut and polished into a plate shape with three pairs of mutually perpendicular surfaces. The dimensions of the plates range from 2–4 mm on each side and 0.4–0.7 mm in thickness. The surfaces with the largest area have the orientation of [001], and the other two pairs of surfaces have the orientation of [010] and [100], respectively. All labeling of orientations in this article refers to the pseudocubic axes. The orientations of the surfaces were determined using a Laue camera with the accuracy of 0.5\(^\circ\). Gold or transparent conductive ITO (indium tin oxide) films were deposited onto the [001] polished surfaces to form electrodes.

The measurements of dielectric permittivity vs. temperature were performed using a HP4284A LCR meter with a Delta Design 9023 temperature chamber. The temperature was measured using a Cu-CuNi thermocouple and a Keithley 740 system scanning thermometer. The thermocouple was mounted inside a hole in an aluminum plate, which supports the sample. Measurements were performed under six conditions: (a) zero field cooling (ZFC), (b) zero field heating after zero field cooling (ZFZFC), (c) field heating after zero field cooling (FH-ZFC), (d) field cooling (FC), (e) zero field heating after field cooling (ZFH-FC), and (f) field heating after field cooling (FH-FC). The rate of temperature change is 2°C/min for all measurements. The LCR meter was protected by a blocking circuit (HP 16065A) when a high dc bias was used.
After ZFC (i.e., depoled) or FC (i.e., poled), the sample was mounted onto the sample holder of a two-circle x-ray diffractometer (Siemens D500) with temperature control system. The sample was heated from room temperature to 200 °C at 2 °C/min. During heating, the sample was kept at each designated temperature for 10 min to allow x-ray diffraction scanning of the 002 peak of the PMN-33%PT single crystals. In order to obtain high accuracy, the diffraction parameters were set as follows: aperture slits at 0.3°, detector slits at 0.018°, step size at 0.005°, and time constant to be 4 sec.

III. RESULTS AND DISCUSSIONS

A. Dielectric and phase transition behaviors in PMN-33% PT single crystals

Figure 1 shows the temperature dependence of the complex permittivity of [001] oriented PMN-33%PT single crystal during ZFC (1), ZFH-ZFC (2), and FH-ZFC (3) (the dc bias for FH is 1 kV/cm). The insets are enlargements of the low-temperature parts.

After ZFC (i.e., depoled) or FC (i.e., poled), the sample was mounted onto the sample holder of a two-circle x-ray diffractometer (Siemens D500) with temperature control system. The sample was heated from room temperature to 200 °C at 2 °C/min. During heating, the sample was kept at each designated temperature for 10 min to allow x-ray diffraction scanning of the (002) peak of the PMN-33%PT single crystals. In order to obtain high accuracy, the diffraction parameters were set as follows: aperture slits at 0.3°, detector slits at 0.018°, step size at 0.005°, and time constant to be 4 sec.

The lower-temperature peak is related to a structural phase transition (details will be discussed below).

The lower-temperature peaks exhibit significant temperature hysteresis, manifesting a first-order phase transition characteristic. Comparing FH-ZFC with ZFH-ZFC, it can be found that upon the application of a dc bias, the temperature of the lower-temperature peak decreases while the higher-temperature peak becomes much higher and sharper and also shifts slightly to higher temperature. Upon ZFC, the curve of ε’ vs temperature has a shoulder region just below T_C, in which ε’ shows frequency dispersion. Below this shoulder region, the frequency dispersion abruptly disappears. However, the shoulder region becomes very narrow in the ZFH-ZFC curve and completely disappears in the FH-ZFC curve. As expected, the curves of ε” vs temperature in Fig. 1(b) show the same feature as the ε’ vs temperature curve, i.e., two peaks and temperature hysteresis. A shoulder region occurs just below T_C with frequency dispersion in the ZFC case.

Figure 2 shows the temperature dependence of the dielectric constant of [001] oriented PMN-33%PT single crystal during FC (1), ZFH-FC (2), and FH-FC (3), with a dc bias of 1 kV/cm. and 90 °C [see the inset in Fig. 1(a)]. The higher-temperature peak occurs at around 150 °C, which is strong and sharp. It represents the phase transition between ferroelectric (FE) and paraelectric (PE) phases. The Curie temperature (T_C) of the PMN-33%PT single crystal is 150 °C, in good agreement with those reported by others,11–13 which provides a confirmation for the composition of the crystal. The XRD analysis showed that the lower-temperature peak is also related to a structural phase transition (details will be discussed below). The lower-temperature peaks exhibit significant temperature hysteresis, manifesting a first-order phase transition characteristic. Comparing FH-ZFC with ZFH-ZFC, it can be found that upon the application of a dc bias, the temperature of the lower-temperature peak decreases while the higher-temperature peak becomes much higher and sharper and also shifts slightly to higher temperature. Upon ZFC, the curve of ε’ vs temperature has a shoulder region just below T_C, in which ε’ shows frequency dispersion. Below this shoulder region, the frequency dispersion abruptly disappears. However, the shoulder region becomes very narrow in the ZFH-ZFC curve and completely disappears in the FH-ZFC curve. As expected, the curves of ε” vs temperature in Fig. 1(b) show the same feature as the ε’ vs temperature curve, i.e., two peaks and temperature hysteresis. A shoulder region occurs just below T_C with frequency dispersion in the ZFC case.
performed on the samples during ZFH-ZFC and ZFH-FC. The results are shown in Fig. 3. In the ZFH-ZFC case [Fig. 3(a)], the x-ray diffraction from (002) formed one peak below 80 °C. This peak splits into two peaks at a temperature below 100 °C. The separation of the two peaks becomes smaller and smaller from 100 °C to 140 °C and merges into one peak again at a temperature near 150 °C. There is only one peak for temperature above 160 °C. Cross referencing the XRD analyses with the dielectric results in Fig. 1, it becomes clear that the two dielectric peaks in Fig. 1 arise from two structural phase transitions occurred at ~72 and ~150 °C in the ZFH-ZFC case. After FC, the sample is in a depoled multidomain state. In this state, x-ray diffraction from (002) forms one peak for rhombohedral symmetry, two peaks for tetragonal symmetry, and three peaks for orthorhombic, monoclinic, or triclinic symmetry. Therefore, according to the present XRD results, the PMN-33%PT single crystal should be in a rhombohedral phase from room temperature to ~85 °C and in the tetragonal phase from ~85 to ~150 °C during ZFH-ZFC. The lattice parameters were calculated from the XRD peaks and shown in Fig. 4. These lattice parameters at different temperatures are very close to those obtained by high resolution x-ray diffractions on PMN-PT ceramic samples reported by Noblanc et al.\textsuperscript{13} and Noheda et al.\textsuperscript{14}

In the ZFH-FC case [Fig. 3(b)], the position of the XRD peak from (002) has abrupt changes from 60 to 80 °C and from 140 to 160 °C, indicating the occurrence of two structure phase transitions. Considering both the XRD results and the fact that there are two dielectric peaks at ~72 and ~150 °C in Fig. 2, one can conclude that two structure phase transitions indeed occurred at ~72 and ~150 °C in the ZFH-FC case. After FC, the sample is in a [001] poled state. A [001] poled R or T phase could form only one (002) XRD peak. However, more than one peak can exist for the [001] poled orthorhombic, monoclinic or triclinic phases. Therefore, the sample should be either in \textit{R} or \textit{T} phase below 150 °C. Comparing these results with those for the ZFH-ZFC case, it is concluded that during ZFH-FC, the sample is in a \textit{R} phase between room temperature and 72 °C, a \textit{T} phase between 72 and 150 °C, and finally becomes a cubic phase above 150 °C.

Further investigation was performed to see the effect of different dc biases on the temperature dependence of the dielectric constant of [001] poled PMN-33%PT single crystal, and the results are shown in Fig. 5. It can be seen that a bias

![Fig. 3. X-ray diffraction scans of the (002) peak at different temperatures for [001] oriented PMN-33%PT single crystal during (a) ZFH-ZFC and (b) ZFH-FC.](image)

![Fig. 4. Lattice parameters of the PMN-33%PT single crystal at different temperatures calculated from the XRD results in Fig. 3(a).](image)

![Fig. 5. Temperature dependence of the dielectric constant of [001] oriented PMN-33%PT single crystal during ZFC and FC at 1 kHz with different dc bias field. The inset is an enlargement of the low-temperature part.](image)
of 0.05 kV/cm has no observable influence to the dielectric constant. However, when the bias increases to 0.25 kV/cm, the lower-temperature dielectric constant peak for the $R$-$T$ transition becomes much higher and sharper, and the transition temperature is significantly lowered. With further increasing dc bias, the transition temperature and the height of the dielectric peak decrease further. On the other hand, with the increase of dc bias, the higher-temperature peak for the tetragonal-cubic transition becomes higher and sharper. The shoulder region below $T_C$ becomes much narrower at a bias of 0.25 kV/cm, and disappears totally when the bias is greater than 1 kV/cm.

**B. Dielectric and phase transition behaviors in different composition single crystals**

Figure 6 shows the temperature dependence of the dielectric constant during ZFC and ZFH-ZFC for different compositions of [001] oriented PMN-PT single crystals. The insets are enlargements of the low-temperature parts.

![FIG. 6. Temperature dependence of the dielectric constant at 1 kHz during (a) ZFC and (b) ZFH-ZFC for different compositions of [001] oriented PMN-PT single crystals. The insets are enlargements of the low-temperature parts.](image)

![FIG. 7. Temperature dependence of the dielectric constant at different frequencies for [001] oriented PMN-29%PT single crystal during ZFC.](image)

![FIG. 8. Temperature dependence of the dielectric constant at 1 kHz during FC with a dc bias of 1 kV/cm for different compositions of [001] oriented PMN-PT single crystals. The inset is an enlargement of the low-temperature part.](image)

each one shows two peaks and one wide shoulder region just below $T_C$ during ZFC, but the absence or existence of a very narrow shoulder region during ZFH-ZFC. On the other hand, the dielectric behavior of PMN-29%PT is significantly different from the others. It has no shoulder region below $T_C$ and the lower-temperature peak cannot be found. One possibility is that the very weak lower-temperature peak is merged into the very broader higher-temperature peak since it moves up to higher temperature with decreasing PT content. Furthermore, the dielectric constants at different frequencies in Fig. 7 for PMN-29%PT show the extension of the frequency dispersion from $T_C$ down to room temperature.

The dc bias effect on the temperature dependence of the dielectric constant for different compositions are shown in Fig. 8. Again, the three compositions of PMN-33%PT, PMN-32%PT, and PMN-31%PT exhibit similar features during FC, i.e., application of the dc bias during cooling resulted in the elimination of the shoulder region just below $T_C$ and an increase in the strength of the lower-temperature peak. As a
general trend, the lower-temperature peak decreases but the Curie temperature increases with the increase of PT content. Several important changes occurred in the PMN-29%PT sample during FC. The dc bias induced formations of a shoulder region just below $T_C$ and a strong lower-temperature dielectric peak. Figure 9 shows that strong frequency dispersion exists in the shoulder region then abruptly disappears below this region in the PMN-29%PT sample.

One important phenomenon in the observed dielectric temperature spectra is the existence of a dielectric peak below $T_C$. The XRD analysis indicated that this peak arises from a $R-T$ phase transition in the PMN-33%PT sample. Considering the similarity of this dielectric peak in all compositions investigated (Fig. 8), one can conclude that the corresponding peaks in other compositions are also related to $R-T$ phase transition. A series of $R-T$ phase transition temperatures was obtained from the dielectric peaks during ZFC and FC, and therefore, the MPB for [001] oriented PMN-PT single crystal system was determined both under zero field and 1 kV dc bias conditions. The partial phase diagram for [001] oriented PMN-PT single crystal, including MPB and the Curie temperatures determined from the dielectric measurements, are shown in Fig. 10. The data obtained by other researchers$^{11,15}$ were also shown in Fig. 10 for comparison. The MPB separating the rhombohedral and tetragonal phases in PMN-PT solid solutions was first reported in ceramic materials by Ouchi.$^{16}$ Due to the Pb loss during ceramic sintering, the MPB was never reported before, which is important to know since the temperature of the MPB has been explained as a field induced transition from a relaxor phase to a long-range polar order.$^{8}$

These samples was cut into several small pieces and also ground into different thickness. The homogeneity of the composition in each sample was checked by measuring the Curie temperature of different pieces cut from the same large sample. The results showed that the fluctuation in Curie temperature is less than $\pm 2\,^\circ\text{C}$, proving the excellent homogeneity in the composition, which ensures the accuracy of our measurements.

We have also investigated the electrical field effect on the MPB in [001] oriented PMN-PT single crystals. It can be seen in Fig. 10 that the determined MPB under zero field in the present work is in good agreement with the one obtained from dielectric measurements on ceramic materials by Choiet al.$^{11,12}$ It also matched well with the one determined from high resolution x-ray diffractions on ceramic materials by Noheda et al.$^{14}$ although they found the existence of a monoclinic phase in between rhombohedral and tetragonal phases near MPB. The MPB shift under electrical field has never been reported before, which is important to know since most applications of these single crystals are concerned with the properties of [001] oriented single crystals under electrical field. It was found that the MPB curve was lowered by a dc bias along [001] since the temperature of $R-T$ phase transition deuces with increasing dc bias (Figs. 5 and 8). In Fig. 10, one can also see that the phase boundary between tetragonal and cubic phases determined in the present work is in excellent agreement with the one obtained from dielectric measurements of ceramic materials by Noblanc et al.$^{13}$

Another important phenomenon observed in our dielectric studies is the existence of a frequency dispersion shoulder region just below $T_C$ and an abrupt disappearance of frequency dispersion below this region. Comparing Fig. 9 with Fig. 7, it is clear that this phenomenon shown in Fig. 9 for PMN-29%PT sample is due to the application of a dc bias. In Ref. 7, this phenomenon has been explained as a field induced transition from a relaxor phase to a long-range polar order.
phase, i.e., from microdomain to macrodomain states. However, during zero field cooling, a similar phenomenon occurred in the samples of PMN-31% PT, PMN-32%PT, and PMN-33%PT [Figs. 1(a) and 6(a)]. We noticed that during ZFC, the composition with lower PT content (<31%), such as PMN-29%PT in Fig. 7, shows a typical relaxor behavior with frequency dispersion from $T_C$ down to room temperature, while the composition with higher PT content (>33%), such as PMN-34%PT in Fig. 3 of Ref. 10, shows a normal ferroelectric behavior below $T_C$. In the PMN-xPT system, the ferroelectric nature enhances with increasing $x$, while the relaxor feature gradually diminishes toward the MPB. The compositions investigated in the present work are in the vicinity of the MPB, therefore, during ZFC, microdomains exist below $T_C$ in a certain temperature region (i.e., the shoulder region) and then transform into macrodomains with further decreasing temperature.

IV. SUMMARY AND CONCLUSIONS

The Rhombohedral-Tetragonal phase transition below Curie temperature was indicated by dielectric temperature spectrum and high resolution x-ray diffraction analysis in [001] oriented $(1-x)$Pb(Mg$_{1/3}$Nb$_{2/3}$)O$_3$-xPbTiO$_3$ single crystals with $x =$ 29, 31, 32, and 33%. The effect of electrical field on this phase transition was investigated. It was found that this phase transition temperature decreases with increasing PT content and/or dc bias. As a result, the determined MPB in [001] oriented PMN-PT single crystal system curved to the low PT content and was suppressed to lower temperature by a dc bias. A transition between a relaxor and a normal ferroelectric was indicated by the appearance of a frequency dispersion shoulder region just below $T_C$ and an abrupt disappearance of frequency dispersion below this region in the dielectric temperature spectra. This transition can be spontaneous, thermally driven in the compositions with PT contents from 31 to 33% and also can be induced by applying a dc bias in the composition with relatively lower PT content, such as PMN-29%PT. In other words, crystals with compositions near the MPB on the rhombohedral side have mixed behaviors of relaxor and normal ferroelectric, which is very sensitive to both applied electrical field and temperature.

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