HTML ABSTRACT + LINKS

Abnormal phase transitions for tetragonal $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ single crystals at low temperature

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Dielectric spectroscopy and ultrasonic sound velocity were investigated for tetragonal PMN-*x*PT single crystals over a wide range of temperature. In addition to the expected phase transition from the tetragonal ferroelectric phase to the cubic paraelectric phase at a high temperature, an abnormal ferroelectric phase transition below room temperature is observed. The low-temperature phase transition shows a relaxor behavior though tetragonal PMN-*x*PT single crystal is considered to be typical normal ferroelectrics. By comparing the dielectric constants of poled and depoled conditions and by analyzing $[BO_6]$ oxygen-octahedra units of perovskite structure, it is suggested that the low-temperature phase transition in poled tetragonal PMN-*x*PT single crystal could be tetragonal to rhombohedral ferroelectric phase transition. © *2004 American Institute of Physics*.
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I. INTRODUCTION

The complex perovskite $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$ (PMN-*x*PT) single crystals are well-known ferroelectrics. The solid solutions have a morphotropic phase boundary (MPB) near $x\sim0.33$ to 0.35,[1] dividing the rhombohedral phase and the tetragonal one. For compositions with $x\geqslant0.35$, the compounds have a tetragonal structure with symmetry of $P4mm$, for those with $x\leqslant0.33$, the crystal symmetry is rhombohedral $R3m$. Normal ferroelectric behavior increases as a function of *x*, whereas relaxor behavior decreases.[2] PMN-*x*PT single crystals have come into prominence in the past few years due to their very high piezoelectric coefficients ($d_{33}>2500$ pC/N), extremely large piezoelectric strains (>1.7%), and extrahigh electromechanical coupling factor in the longitudinal bar mode ($k_{33}\sim94\%$).[3–6] Such excellent properties point to a potential revolution in an electromechanical transduction for a broad range of applications. Recent studies show that the materials with tetragonal structure exhibit excellent optical properties,[7,8] especially the electro-optic properties.[9,10] The result shows that tetragonal PMN-*x*PT single crystals are also promising candidates for optical devices.[8]

Recently, an intensive theoretical and experimental research has been undertaken in order to understand the origin of these enhanced dielectric and piezoelectric properties. Fu and Cohen pointed out that a large piezoelectric response could be driven by a polarization rotation induced by an external electric field.[11] At almost the same time, Noheda *et al.* revealed the existence of a monoclinic phase between the previously established tetragonal (FE_T) and rhombohedral (FE_R) regions in $PbZr_{0.52}Ti_{0.48}O_3$, which further supports the concept of polarization rotation.[12,13] Subsequently, similar experiments were carried out on PMN-*x*PT single crystals, and it was found that monoclinic (FE_M) orthorhombic and (FE_O) phases can also be induced in a narrow range of compositions with an appropriate poling history.[14] Based on the dielectric constants obtained on a poled ⟨001⟩-oriented PMN-0.3PT single crystal, Viehland *et al.* suggested that the transition from a normal ferroelectric state (macrodomains) to a relaxor state (microdomains) with an increasing temperature is responsible for the secondary transformation near 90 °C.[15] For a poled ⟨001⟩-oriented PMN-0.33PT single crystal, Lu *et al.* also found an additional ferroelectric phase transition (FE-FE) at 80 °C using dielectric constant measurements. However, they were uncertain whether this phase change corresponds to a FE_O-FE_T or a FE_R-FE_O transition.[16] From the dielectric constant measurements, the secondary phase transition below T_m (the temperature of the permittivity maximum) has been found for PMN-*x*PT single crystals by many groups.[17–21] But all the investigations are limited to compositions near the MPB, and there is no report on tetragonal PMN-*x*PT single crystals.

The aim of this work is to investiagate tetragonal PMN-*x*PT single crystals over a wide range of temperature using dielectric spectroscopy. In addition to a phase transition at T_m, an abnormal ferrolectric phase transition below room temperature is observed in all the main crystallo-

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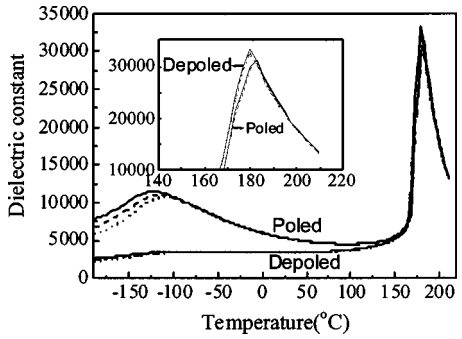

FIG. 1. Temperature dependence of dielectric constants of ⟨110⟩-oriented PMN-0.38PT single crystal (solid line: 100 Hz; dashed line: 1 kHz; dotted line: 10 kHz).

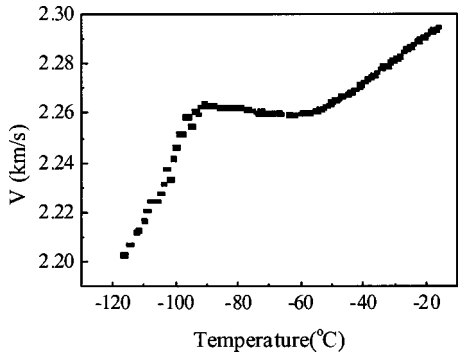

FIG. 2. Temperature dependence of longitudinal ultrasonic sound velocity of ⟨110⟩-oriented PMN-0.38PT single crystal.

graphic directions ⟨001⟩, ⟨110⟩, and ⟨111⟩. The phase transition has been supported by an ultrasonic sound velocity measurement.

II. EXPERIMENTAL PROCEDURE

Large-size and high-quality PMN-*x*PT single crystals were grown directly from melt by the modified Bridgman technique.[22,23] The crystals were oriented and cut along three main crystallographic directions ⟨001⟩, ⟨110⟩, and ⟨111⟩ by an x-ray diffractometer. Rectangular-shaped specimens ($6\times6\times1$ mm^3) were prepared for property measurements.

Silver paste was painted and sintered at 580 °C for 30 min. Then, the samples were poled with an electric field of 10 kV/cm for 15 min at 160 °C in a silicone oil and then slowly cooled to room temperature with the half of the applied electric field.

In this work, dielectric spectroscopy was measured using a HP4194A impedance analyzer in the temperature range from −180 to 200 °C. The sample was placed inside a liquid-nitrogen bath cryostat (Oxford DN1704-type). The temperature of the sample was stabilized by a digital temperature controller (Oxford ITC 601-type). The longitudinal ultrasonic sound velocity was measured using the AUW-100 Advanced Ultrasonic Workstation with a 10-MHz $LiNbO_3$ transducer.

III. RESULTS AND DISCUSSION

Figure 1 shows the dielectric constants versus temperature curve of the ⟨110⟩-oriented PMN-*x*PT single crystal. The dielectric constant exhibits a sharp change at 180 °C, so the PT content in the sample is about 0.38, which is deduced from the equation, $T_m=5x$-10 (where T_m is the temperature in Celsius scale and x is the PT content).[7] PMN-0.38PT single crystal is known to possess the tetragonal structure at room temperature and shows a normal ferroelectric behavior. The sharp change corresponds to the phase transition from the tetragonal ferroelectric phase (FE_T) to the cubic paraelectric phase (PE_C), and the dielectric constants exhibit very little frequency dispersion at this range, as shown in the inset of Fig. 1. All the properties agree well with the previous reports.[24,25]

The most remarkable result of our dielectric measurements is the second dielectric peak at about −120 °C, also shown in Fig. 1, which has not been observed for the tetragonal PMN-*x*PT single crystal so far. Furthermore, as we know, PMN−0.38PT single crystal is considered to be typical normal ferroelectrics, while the dielectric constants near the second peak are frequency-dependent. It shows that this peak possesses relaxor behavior and demonstrates a "micro- to macrodomain" transition, similar to that previously reported PMN-*x*PT single crystals in the MPB region.[15] After the first heating measurement to 220 °C, the sample wad depoled. We also measured the dielectric spectroscopy for the deploed sample and found that the peak near −120 °C disappeared, which indicates that the abnormal dielectric peak only exists in the poled sample. From the theory of polarization rotation,[11] the dipoles will rotate along different paths under different poling directions. When the poling was done, the polar direction is expected to incline close to the electric field in each domain, possibly resulting in an increased tetragonal lattice distortion. However, the distortion doesn't result in the structure transformation at room temperature because there is no additional dielectric peak from room temperature to T_m. Decreasing the temperature may result in the collapse of the distortion and induce another phase transition at a low temperature.

The low-temperature phase transition has been supported by ultrasonic measurement. Figure 2 shows the temperature dependence of the longitudinal ultrasonic sound velocity propagated along the ⟨110⟩ direction for the PMN-0.38PT single crystal. With a decreasing temperature from 27 °C, the sound velocity softens smoothly and reaches a local minimum at about −60 °C, and then follows a slight stiffening with further cooling of the temperature. The broad softening of the sound velocity reflects that the acoustic phonon damps over a wide temperature range. As is known, the compositional fluctuations-induced random electric fields can suppress the development of a long-range ferroelectric order and give rise to order-parameter fluctuations in a wide temperature range.[26] The coupling between the elastic strain and the fluctuating order parameters, hence, leads to the smooth softening of the sound velocity in a wide temperature range from 27 to −30 °C. Similar acoustic anomalies have also been observed in $PbMg_{1/3}Nb_{2/3}O_3$ (PMN)[27,28] and $PbMg_{1/3}Ta_{2/3}O_3$ (PMT)[29] by the measurements of micro-Brillouin scattering. In contrast to the smooth softening of the sound velocity at high temperatures, the sound velocity

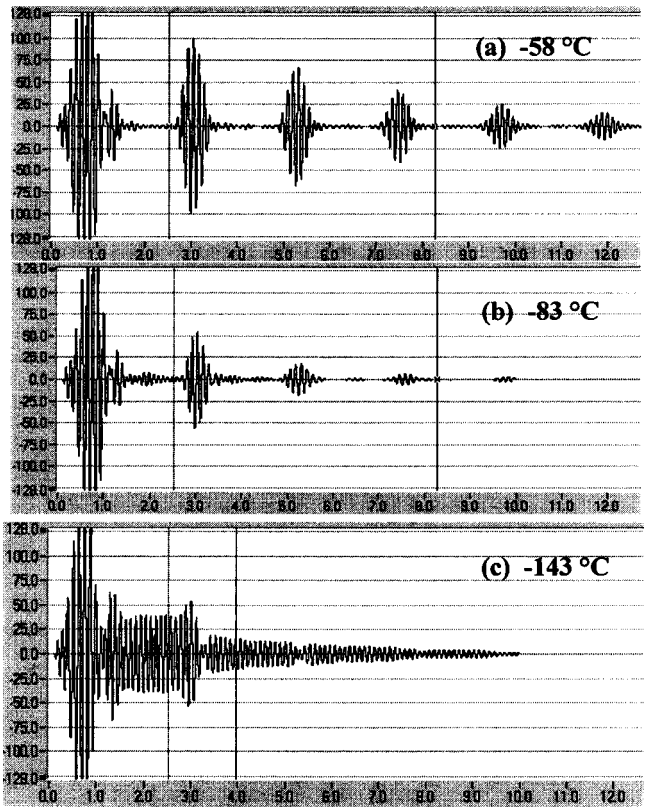

FIG. 3. Pulse-echo patterns at (a) −58 °C, (b) −83 °C, and (c) −143 °C.

shows a drastic softening with a decreasing temperature from −90 to −120 °C, which has not yet been observed in similar PMN and PMT single crystals. Due to the increasing large attenuation with the decreasing temperature, the ultrasonic echo signal disappears completely below −120 °C (see Fig. 3), which possibly resulted from the scattering of another phase below −120 °C. We note that with an increasing temperature from a low temperature (77 K) to room temperature, the ultrasonic echo signal appears again at about −120 °C, which may correspond to a reverse structural phase transition. The large ultrasonic attenuation below −120 °C makes it impossible to measure the sound velocity below −120 °C. We want to stress that such a large attenuation, together with a large softening of the sound velocity below −90 °C, strongly implies a structural phase transition associated with the dielectric constants anomaly. Similar large softening of the sound velocity has been observed near the structural phase-transition points in $Ba_{1-x}Sr_xTiO_3$.[30]

From the dielectric measurements, we observed an abnormal relaxor peak at about −120 °C for normal ferroelectric PMN-0.38PT single crystal. The peak was confirmed to be corresponding with a phase transition by ultrasonic sound velocity measurement. We know that the lattice distortions and the angles in different phases for the PMN-*x*PT single crystal differ only slightly, so they are very different to be detected,[31] especially at such a low temperature. However, it is estimated that the low-temperature phase couldn't be the orthorhombic phase, which has been observed in PMN-*x*PT single crystals with rhombohedral structure or in the MPB region.[16–20] It is generally accepted that for PMN-*x*PT single, crystals, the dielectric constant shows the minimum value

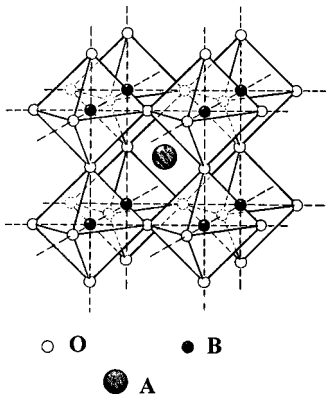

FIG. 4. Schematic diagram of ABO_3 perovskite structure composed of $[BO_6]$ oxygen octahedra by their vertexes ($A:Pb^{2+}; B:Mg^{2+}, Nb^{5+}$, or Ti^{4+}).

when the crystals are poled along the spontaneous polarization direction. For example, the dielectric constants at room temperature for tetragonal PMN-0.38PT single crystal are about 780, 6972, and 9784, respectively, for the samples poled along ⟨001⟩, ⟨110⟩, and ⟨111⟩ directions.[25] The dielectric constant of the spontaneous polarization direction ⟨001⟩ shows the minimum value. As shown in Fig. 1, the dielectric constants for the ⟨110⟩-poled sample around the low-temperature phase-transition region are much larger than those of the depoled condition. Such evidence may be believed that the ⟨110⟩ direction is not the polarization direction. That is to say, the phase that appeared near −120 °C cannot be an orthorhombic phase.

The structure of PMN-*x*PT single crystals can be regarded as the one made of $[BO_6]$ ($[TiO_6]$, $[NbO_6]$, and $[MgO_6]$) coordination polyhedra linked by their vertexes. Figure 4 shows the schematic diagram of the perovskite structure composed of $[BO_6]$ oxygen octahedra. Ferroelectric PMN crystals have rhombohedral phase and its T_m is about −10 °C, ferroelectic PT crystals have tetragonal phase and its T_m is about 490 °C. It is in favor of the rhombohedral phase by adding PMN in the PMN-*x*PT solid solutions or decreasing temperature. Therefore, it is reasonable to think that the polarization in $[TiO_6]$ octahedra appears dominant along the ⟨001⟩ direction, it's dominant along ⟨111⟩ in $[NbO_6]$ or $[MgO_6]$ octahedra. In tetragonal single crystals, $[NbO_6]$ and $[MgO_6]$ octahedra are forced to distort along the ⟨001⟩ direction in the pressing of $[TiO_6]$ octahedral. When decreasing temperature or adding PMN, $[NbO_6]$ and $[MgO_6]$ octahedra slip the leash of $[TiO_6]$ octahedra, and simultaneously make $[TiO_6]$ octahedra distort along ⟨111⟩, resulting in the FE_T-FE_R ferroelectric phase transition. The FE_T-FE_R phase transition has been found in the other compositions. For example, the FE_T-FE_R phase-transition temperature T_{RT} is about 89, 78, and 66 °C, respectively, for PMN-0.256PT, PMN-0.296PT, and PMN-0.324PT.[17] One can draw the conclusion that the T_{RT} decreases with an increasing PT concentration. The T_{RT} of our sample, PMN-0.38PT, is about −120 °C, which is consistent with the trend. Combined with its dielectric properties and ultrasonic sound velocity results, it is assume that the phase below −120 °C in the poled

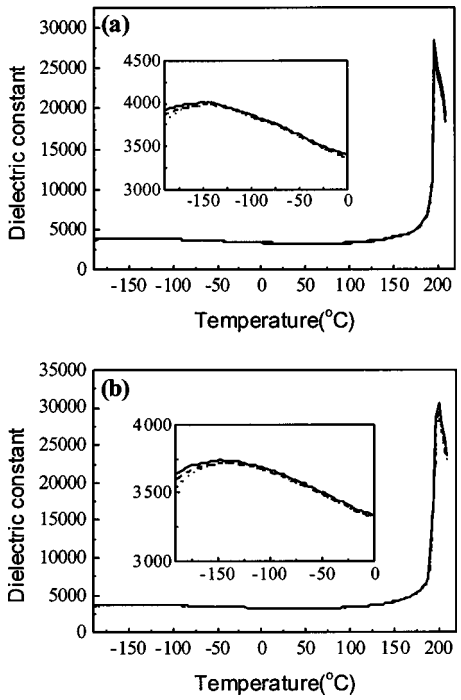

FIG. 5. Temperature dependence of dielectric constants of poled (a) ⟨001⟩ and (b) ⟨111⟩-oriented PMN-*x*PT single crystals (solid line: 100 Hz; dashed line: 1 kHz; dotted line: 10 kHz).

PMN-0.38PT single crystal could be the ferroelectric rhombohedral phase and the peak could be the FE_T-FE_R phase transition.

We note that the similar peaks also appear in the ⟨001⟩ and ⟨111⟩ direction of poled tetragonal PMN-*x*PT single crystals. Figure 5 shows the temperature dependence of dielectric constants of poled ⟨001⟩ and ⟨111⟩-oriented PMN-*x*PT single crystals. They both have a sharp change and T_m is about 196 °C for the ⟨001⟩ direction and 199 °C for ⟨111⟩ one, indicating that the PT content for them is about 0.412 and 0.418, respectively. So they are both in tetragonal phase. As shown in the inset of Fig. 5, they also have an additional frequency-dependent peak at about −145 °C, as observed for the ⟨110⟩ direction. But they are much "evener" compared with the peak of the ⟨110⟩ direction. We should also mention here that accurate structure measurements for the low-temperature phases, such as high-resolution powder x-ray diffraction measurements, must be carried out to find out the nature of the phase. The authentic experimental evidences are still under investigation and more details will be discussed in later work.

IV. CONCLUSION

Dielectric spectroscopy and ultrasonic sound velocity were investigated for tetragonal PMN-*x*PT single crystals over a wide range of temperature. In addition to the expected phase transition from the tetragonal ferroelectric phase to the cubic paraelectric phase at T_m, an abnormal ferroelectric phase transition below room temperature is observed. Furthermore, the low-temperature phase transition shows relaxor behavior though tetragonal PMN-*x*PT single crystal is regarded as typical normal ferroelectrics. By comparing the dielectric constants of the poled and depoled conditions and by analyzing $[BO_6]$ oxygen-octahedra units of perovskite structure, it is suggested that the low-temperature phase transition in poled tetragonal PMN-*x*PT single crystal could be tetragonal to rhombohedral ferroelectric phase transition.

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