[111]-oriented PIN-PMN-PT crystals with ultrahigh dielectric permittivity and high frequency constant for high-frequency transducer applications

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Abstract
The electromechanical properties of [111]-oriented tetragonal Pb(In1/2Nb1/2O3)-Pb(Mg1/3Nb2/3O3)-PbTiO3 (PIN-PMN-PT) crystals were investigated for potential high frequency ultrasonic transducers. The domain-engineered tetragonal crystals exhibit an ultrahigh free dielectric permittivity $\varepsilon_{33}^T > 10000$ with a moderate electromechanical coupling factor $k_{33} \sim 0.79$, leading to a high clamped dielectric permittivity $\varepsilon_{33}^S$ of 2800, significantly higher than those of the rhombohedral relaxor-PT crystals and high-K (dielectric permittivity) piezoelectric ceramics. Of particular significance is that the [111]-oriented tetragonal crystals were found to possess high elastic stiffness, with frequency constant $N_{33}$ of $\sim 2400$ Hz m, allowing relatively easy fabrication of high-frequency transducers. In addition, no scaling effect of piezoelectric and dielectric properties was observed down to thickness of 0.1 mm, corresponding to an operational frequency of $\sim 24$ MHz. These advantages of [111]-oriented tetragonal PIN-PMN-PT crystals will benefit high-frequency ultrasonic array transducers, allowing for high sensitivity, broad bandwidth, and reduced noise/crosstalk.

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The objective of this work is to explore the relaxor-PT crystals with both high dielectric permittivity and frequency constant for potential use in the high-frequency ultrasonic transducers, by utilizing crystal anisotropy. The [111]-oriented tetragonal relaxor-PT crystals were selected as the candidate piezoelectrics. The underlying reason for selecting this type of crystals is presented in the following and schematically shown in Fig. 1. For perovskite crystals, the elastic anisotropy is dominated by the ABO3 perovskite structure, being insensitive to the ferroelectric phase. First, perovskite crystals, in general, possess the highest elastic stiffness constant $c_{33}^{D}$ along the pseudo-cubic (111) body diagonals, since the anisotropy factor $A = 2c_{44}^{D}(c_{11}-c_{12})^{1/2}$ is larger than 1, as given in Table I. Therefore, perovskite crystals oriented along the [111] direction are selected to achieve a high frequency constant $N_{33}$. Second, the special ferroelectric phase for [111]-oriented crystals, in which high dielectric permittivities present, must be identified. For relaxor-PT crystals, the anisotropy of the dielectric permittivity is associated with the ferroelectric phase. A high dielectric permittivity $c_{33}^{D}$ generally exists along the nonpolar direction, as shown in Fig. 1(c), owing to the high contribution of “polarization rotation” in relaxor-PT systems. From this point of view, either orthorhombic or tetragonal crystals are potential candidates, since their polar vectors are not along [111] directions, but (110) and (100) directions, respectively. In this work, tetragonal Pb(In$_{1/2}$Nb$_{1/2}$O$_{3}$)-Pb(Mg$_{1/3}$Nb$_{2/3}$O$_{3}$)-PbTiO$_{3}$ (PIN-PMN-PT) crystals are finally selected, since the temperature usage range can be up to 200°C for the tetragonal PIN-PMN-PT crystals (no ferroelectric phase transition between room temperature and Curie temperature), while the orthorhombic counterparts can only be used below 80°C due to the existence of orthorhombic-tetragonal phase transition between room temperature and Curie temperature.

### II. EXPERIMENTS

A PIN-PMN-PT single crystal with nominal composition of xPIN-(1-x-y)PMN-yPT, where x = 0.25–0.35 and y = 0.30–0.34, was grown using the modified Bridgman technique. The tetragonal crystal, located on the top of the as-grown crystal, was oriented by real-time Laue x-ray and poled along [111] direction. The macroscopic symmetry of [111]-poled tetragonal crystals is 3m. Samples were cut with three orientations of [110], [112], and [111]. Longitudinal rods (1.5 × 1.5 × 6 mm) for $k_{33}$, the thickness plate (5 × 5 × 0.65 mm) for $k_{t}$, and the rectangular samples (5 × 7 × 8 mm) for ultrasonic measurements were prepared. Vacuum sputtered gold was applied to the polished surface as the electrodes for all the samples. The [111]-oriented samples were poled using a dc electric field of 2 kV/mm at 120°C. The impedance spectra for the various vibration modes were determined using an HP4194A impedance analyzer. The dielectric permittivity, piezoelectric coefficients, and electromechanical coupling factors were determined following the IEEE Standard on Piezoelectricity. A 15 MHz longitudinal wave transducer (Ultran laboratories, Inc.) was used for the pulse-echo measurements to determine $c_{33}^{D}$. The electric-field-induced strain was determined using a linear variable differential transducer driven by a lock-in amplifier (Stanford research system, model SR830). The temperature dependence of the dielectric permittivity was determined using an LCR meter HP4284A being connected to a computer-controlled temperature chamber. The temperature-dependent electromechanical properties were obtained from an impedance analyzer HP4194A connected to a temperature chamber.

### III. RESULTS AND DISCUSSION

Table II shows the dielectric and piezoelectric properties of both 33-mode and thickness-mode for the [111]-poled...
tetragonal PIN-PMN-PT crystals. It can be seen that the dielectric permittivity $\varepsilon_{33}^T$ of the [111]-poled tetragonal crystal is two times the value of the [001]-poled rhombohedral one. This is due to the fact that the transverse dielectric permittivity $\varepsilon_{11}^T$ of single domain state is significantly higher in tetragonal crystals (15 000–20 000) than that in rhombohedral crystals (6000–8000). For domain-engineered relaxor-PT crystals (i.e., crystals poled along nonpolar direction, such as [111]-oriented tetragonal and [001]-oriented rhombohedral crystals), the longitudinal dielectric permittivity $\varepsilon_{33}$ is mainly associated with their respective transverse dielectric permittivity of single domain state. Of particular significance is that the clamped dielectric permittivity $\varepsilon_{33}^S$ was found to be 2800 for the [111]-poled tetragonal crystal, which is three times higher than that of the [001]-poled rhombohedral counterpart (~800) and two times higher than that of commercial PZT5H ceramics (~1470). The elastic stiffness constant $c_{33}^D$ of the [111]-oriented tetragonal crystal is also double the value of the [001]-oriented rhombohedral crystal and 35% higher than that of PZT5H ceramics, being related to the nature of the perovskite structure, in which {111} is the stiffest orientation. As expected, the [111]-poled tetragonal crystals are the electrically “soft” (high permittivity) and elastically “stiff” (high elastic constant $c_{33}^D$) piezoelectric materials in contrast to various piezoelectric counterparts, as listed in Table II.

The electromechanical properties of longitudinal mode for [111]-poled tetragonal PIN-PMN-PT crystals are given for comparison. The related properties of [001]-poled rhombohedral PIN-PMN-PT crystals, soft and hard PZT ceramics are given for comparison. The data for PZT ceramics are from Ref. 2.

<table>
<thead>
<tr>
<th>Thickness</th>
<th>$\varepsilon_{33}^T/\varepsilon_0$</th>
<th>Loss factor</th>
<th>$\varepsilon_{33}^S/\varepsilon_0$</th>
<th>$d_{33}$ (pC/N)</th>
<th>$k_{33}$</th>
<th>$Q_m$</th>
<th>$c_{33}^D$ ($10^{10}$ N/m²)</th>
<th>$N_{33} = f_{a,33}^s$ (m Hz)</th>
<th>$N_t = f_{a,t}^s$ (m Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[111] T crystal &gt;0.5 mm thickness</td>
<td>11 000</td>
<td>0.7%</td>
<td>2800</td>
<td>1050</td>
<td>150</td>
<td>97.6</td>
<td>19.76</td>
<td>2350</td>
<td>2640</td>
</tr>
<tr>
<td>[111] T crystal 0.1 mm thickness</td>
<td>10 000</td>
<td>0.8%</td>
<td>2600</td>
<td>1050</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
<td>/</td>
</tr>
<tr>
<td>[001] R crystal</td>
<td>5600</td>
<td>0.5%</td>
<td>800</td>
<td>1800</td>
<td>91%</td>
<td>100</td>
<td>9.05</td>
<td>1700</td>
<td>2000</td>
</tr>
<tr>
<td>Soft PZT (PZT5H)</td>
<td>3400</td>
<td>2%</td>
<td>1470</td>
<td>590</td>
<td>17%</td>
<td>65</td>
<td>14.7</td>
<td>1800</td>
<td>2000</td>
</tr>
<tr>
<td>Hard PZT (PZT8)</td>
<td>1015</td>
<td>0.5%</td>
<td>580</td>
<td>219</td>
<td>62%</td>
<td>1000</td>
<td>16.1</td>
<td>1930</td>
<td>2100</td>
</tr>
</tbody>
</table>

FIG. 2. Impedance and phase spectrum of the [111]-poled PIN-PMN-PT tetragonal crystals for (a) $k_{33}$ and (b) $k_t$ modes.

FIG. 3. Electric-field-induced strains for the [111]-poled PIN-PMN-PT tetragonal crystals with thicknesses of 0.5 mm and 0.1 mm.
were almost the same for the 0.5 mm- and 0.1 mm-thickness samples. These results indicate that the [111]-poled tetragonal crystals can be used above the frequency of 20 MHz without degradation of the piezoelectric and dielectric properties.

In order to check the allowable drive electric field for [111]-oriented tetragonal PIN-PMN-PT crystals, the polarization-electric field hysteresis loops were measured. It can be seen from Fig. 4 that [111]-oriented tetragonal crystals exhibit much higher coercive field (8 kV/cm) when compared to their rhombohedral counterparts (4 kV/cm), indicating that tetragonal crystals can be used at relatively higher electric field. The high coercive field of tetragonal PIN-PMN-PT crystals can be attributed to the strong tetragonality due to the high ratio of PbTiO$_3$ end-member.

The temperature dependence of the dielectric permittivity $\varepsilon_{33}$, piezoelectric coefficient $d_{33}$, elastic constant $s_{33}^{-D}$, and electromechanical coupling factor $k_{33}$ is shown in Fig. 5. It can be seen from Fig. 5(a) that the Curie temperature of the [111]-poled tetragonal crystal is around 215°C, prior to which no other phase transition occurs above room temperature, demonstrating that the usage temperature range of the [111]-poled tetragonal PIN-PMN-PT crystals is much broader than that of the [001]-poled rhombohedral counterparts, which are limited by the rhombohedral to tetragonal phase transition around 80–120°C. As shown in Figs. 5(b)–5(d), the elastic constants, piezoelectric coefficients, and electromechanical coupling factors of the [111]-poled tetragonal crystals are recoverable as the temperature goes back to room temperature with minimal thermal hysteresis. This indicates that the reductions of these properties at high temperature are not associated with the temperature-induced depolarization, which is important for practical applications.

To better understand the temperature-dependent properties, one should know that the high longitudinal dielectric and piezoelectric response of the [111]-poled tetragonal relaxor-PT crystals mainly come from the transverse dielectric and shear piezoelectric responses of the single domain state, respectively. As analyzed by phenomenological theory, the transverse dielectric permittivity and shear piezoelectric coefficient of single domain perovskite ferroelectric crystals will decrease with temperature deviating from a polymorphic phase transition. As previously reported, there was a tetragonal-orthorhombic phase transition for tetragonal PIN-PMN-PT crystal below room temperature ($-50$ to $-30^\circ$C). With increasing temperature, therefore, the tetragonal PIN-PMN-PT crystal moves away from the...
tetragonal-orthorhombic phase transition point, leading to the decreased permittivity and piezoelectric coefficient. The elastic compliance $s_{33}^{D}$, however, was found to maintain the same value with respect to the temperature, due to the fact that the elastic constant under constant electric displacement is insensitive to the phase transition, revealing that the operational frequency remains constant as a function of temperature.

IV. CONCLUSION

In summary, the [111]-oriented tetragonal PIN-PMN-PT crystals were investigated for potential applications in high-frequency ultrasonic transducers. Compared to the state-of-the-art [001]-oriented rhombohedral counterparts and commercial PZT5H ceramics, the [111]-oriented tetragonal crystals simultaneously exhibit the ultrahigh free dielectric permittivity ($>10^{4}$), clamped dielectric permittivity ($\sim$2800), and high frequency constant ($\sim$2400 Hz m). These features demonstrate that the [111]-oriented tetragonal crystals, as piezoelectric elements for ultrasonic arrays, can be operated with a higher capacitance and a larger physical dimension, which will benefit the electrical impedance matching and enhance the signal-to-noise ratio for high frequency ultrasonic arrays. Furthermore, the depoling temperature of the tetragonal PIN-PMN-PT crystals is much higher when compared to the rhombohedral counterparts, since there is not any phase transition between room temperature and Curie temperature, which will facilitate the “dice and fill” process for piezoelectric arrays fabrication.

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