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[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 ε33 T > 10 000 with a moderate electromechanical coupling factor k33 ∼ 0.79, leading to a high clamped dielectric permittivity ε33 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 N33 of ∼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 ∼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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[111]-oriented PIN-PMN-PT crystals with ultrahigh dielectric permittivity and high frequency constant for high-frequency transducer applications

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The electromechanical properties of [111]-oriented 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 were investigated for potential high frequency ultrasonic transducers. The domain-engineered tetragonal crystals exhibit an ultrahigh free dielectric permittivity $\varepsilon_{33}{}^{T} > 10\,000$ 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. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4961202]

I. INTRODUCTION

Ultrasonic imaging has recently taken an explosive growth for safe, economic, and high quality healthcare, which is very appealing for medical applications because of its non-ionizing and non-invasive characteristics. Piezoelectric materials, which transform the electrical stimuli to ultrasonic waves, are critical elements for ultrasonic imaging transducers.[1] The mainstay piezoelectric materials are the perovskite ferroelectrics, such as polycrystalline lead zirconate titanate (PZT) ceramics,[2] $Pb(Mg_{1/3}Nb_{2/3})O_3$-$PbTiO_3$ ceramics, and relaxor-PT single crystals [where PT is $PbTiO_3$ and relaxor includes $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Zn_{1/3}Nb_{2/3})O_3$, $Pb(In_{1/2}\ Nb_{1/2}O_3)$, etc.].[3]

In recent years, due to the continuous growth in demand of clinical applications (e.g., dermatologic skin and ophthalmic imaging[4–7]), ultrasonic arrays are expanding to higher frequency range, i.e., $\geq$20 MHz, which provide images with submillimeter-scale resolution. For achieving higher operational frequency of arrays, piezoelectric elements are required to work at smaller dimension/thickness. With decreasing the size of piezoelectric elements, however, some new issues appear, i.e., high crosstalk, low signal-to-noise ratio, and the difficulty of electrical impedance matching,[7] due to the decreased capacitance and increased impedance of piezoelectric elements. It should be noted that the decreased capacitance is not only related to the reduced dimension of elements (the area and the thickness of the pillars need to keep the aspect ratio for longitudinal vibration mode) but also associated with the ferroelectric material itself. The dielectric permittivity has been reported to be reduced with decreasing the thickness of both PZT ceramics and PMN-PT crystals due to the scaling effect.[8] To address the issues above from a material viewpoint, piezoelectric elements with significantly higher dielectric permittivities (electrically "soft") and higher frequency constants (elastically "stiff") are essential. For a piezoelectric element with fixed aspect ratio ($\sigma = w/t$, where w and t are width and thickness, respectively), its capacitance can be expressed by

$$C = \varepsilon \cdot w^2/t = \varepsilon \cdot t \cdot \sigma^2, \tag{1}$$

where C and ε are the capacitance and dielectric permittivity of piezoelectric element, respectively. According to Eq. (1), higher dielectric permittivities can directly enhance the capacitance of piezoelectric elements; meanwhile, higher frequency constants can make piezoelectric elements work at larger thickness for a certain frequency, as well leading to an enhanced capacitance. Previous investigations, however, have shown that electrically "soft" and elastically "stiff" can only be achieved at the expense of each other in polycrystalline PZT ceramics.[2,9] For example, PZT5H ceramics possess relatively high dielectric permittivities ($\varepsilon_{33}{}^{T} \sim 3400$) but low frequency constants ($N_{33} \sim 1800$ Hz m), while PZT8 ceramics possess low dielectric permittivities ($\varepsilon_{33}{}^{T} \sim 1050$) but high frequency constants ($N_{33} \sim 1930$ Hz m); thus, it is difficult to simultaneously achieve electrically "soft" and elastically "stiff" characters in PZT-based ferroelectric ceramics.

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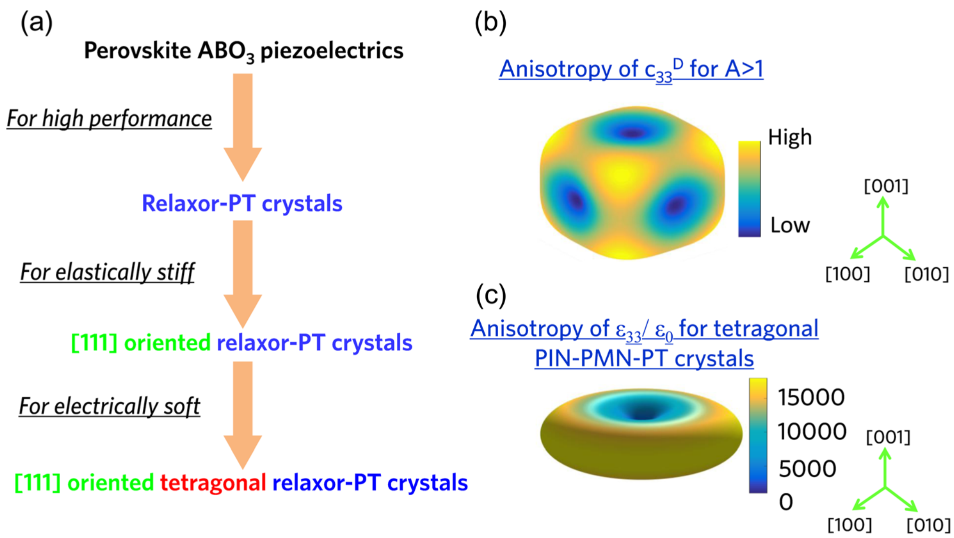

FIG. 1. (a) Flow chart of crystal selection process to achieve both elastically stiff and electrically soft in perovskite ferroelectrics; (b) the schematic anisotropy of c_{33}^D for the perovskite crystals; and (c) the anisotropy of dielectric permittivity $\varepsilon_{33}^T/\varepsilon_0$ for the tetragonal PIN-PMN-PT crystals with [001] poled single domain state.

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 ABO_3 perovskite structure, being insensitive to the ferroelectric phase.[10] 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 $[A = 2c_{44}/(c_{11}–c_{12})]$[11] is larger than 1, as given in Table I.[10,12–14] 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 ε_{33} generally exists along the nonpolar direction, as shown in Fig. 1(c), owing to the high contribution of "polarization rotation" in relaxor-PT systems.[15,16] 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.[17]

TABLE I. Elastic properties for ABO_3 perovskite ferroelectrics. The data are from Refs. 10 and 12–14.

	c_{11}^D (10^{10} N/m^2)	c_{12}^D (10^{10} N/m^2)	c_{44}^D (10^{10} N/m^2)	$A = 2c_{44}^D/(c_{11}^D–c_{12}^D)$
$BaTiO_3$[10]	24.8	15.7	9.1	2.0
$SrTiO_3$[10]	31.69	10.26	12.26	1.14
$PbTiO_3$[12]	17.46	7.93	11.11	2.33
PZN-4.5%PT[13]	12.8	10.4	6.7	5.6
PZN-7.0%PT[14]	11.37	10.37	6.8	13.6

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 3 m. Samples were cut with three orientations of $[1\bar{1}0]$, $[11\bar{2}]$, 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.[18] 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

TABLE II. The electromechanical properties of longitudinal mode for [111]-poled tetragonal PIN-PMN-PT crystals. 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.

	$\varepsilon_{33}^T/\varepsilon_0$	Loss factor	$\varepsilon_{33}^S/\varepsilon_0$	d_{33} (pC/N)	k_{33}	Q_m	c_{33}^D (10^{10} N/m^2)	$N_{33}=f_{a,33}l$ (m Hz)	$N_t=f_{a,t}l$ (m Hz)
[111] T crystal >0.5 mm thickness	11 000	0.7%	2800	1050	79%	150	19.76	2350	2640
[111] T crystal 0.1 mm thickness	10 000	0.8%	2600	1050	/	/	/	/	2650
[001] R crystal	5600	0.5%	800	1800	91%	100	9.05	1700	2000
Soft PZT (PZT5H)	3400	2%	1470	590	75%	65	14.7	1800	2000
Hard PZT (PZT8)	1015	0.5%	580	219	62%	1000	16.1	1930	2100

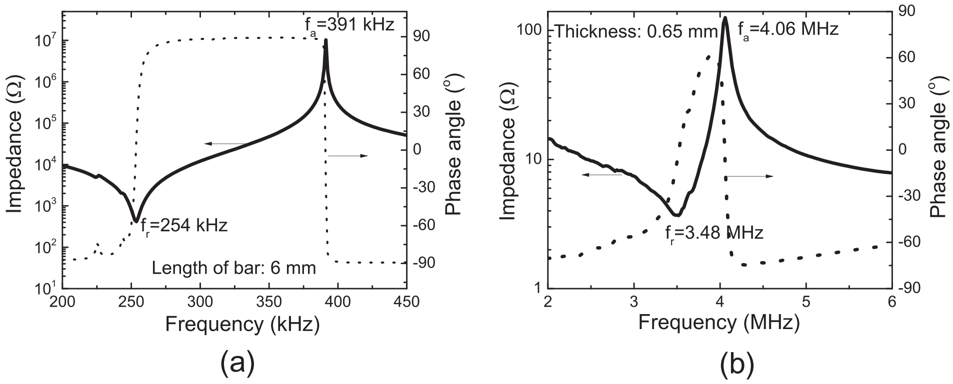

FIG. 2. Impedance and phase spectrum of the [111]-poled PIN-PMN-PT tetragonal crystals for (a) k_{33} and (b) k_t modes.

tetragonal PIN-PMN-PT crystals. It can be seen that the dielectric permittivity ε_{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 ε_{11}^T of single domain state is significantly higher in tetragonal crystals (15 000–20 000) than that in rhombohedral crystals (6000–8000).[19] 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 ε_{33} is mainly associated with their respective transverse dielectric permittivity of single domain state. Of particular significance is that the clamped dielectric permittivity ε_{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.

Fig. 2 shows the impedance spectra of k_{33}- and k_t-modes for the [111]-poled tetragonal crystals. The electromechanical coupling factors k_{33} and k_t were found to be 79% and 64%, respectively, while the frequency constants N_{33} and N_t were found to be 2350 Hz m and 2640 Hz m, respectively, being significantly larger than those of the [001]-poled rhombohedral crystals, as listed in Table II. The high frequency constant of the [111]-poled tetragonal crystals infers that a larger element dimension is allowed for a specific operational frequency, based on the equation of $N=f\cdot t$ (where t is the thickness of piezoelectric element), which will facilitate the fabrication process of ultrasonic arrays. Meanwhile, as shown in Eq. (1), a larger element dimension will result in a higher capacitance of piezoelectric elements, which can further enhance signal-to-noise ratio.

For the [001]-poled rhombohedral crystals, as reported in previous literatures,[8] an obvious decrease of electromechanical properties appears when the operational frequency is higher than 10 MHz (i.e., the thickness of an [001]-poled rhombohedral PMN-PT crystal is less than 0.15 mm). Thus, scaling effects were also investigated for the [111]-poled tetragonal crystals. As shown in Table II and Fig. 3, the dielectric permittivity of 0.1 mm-thickness sample was found to be on the order of 10 000, and the E-field-induced strains

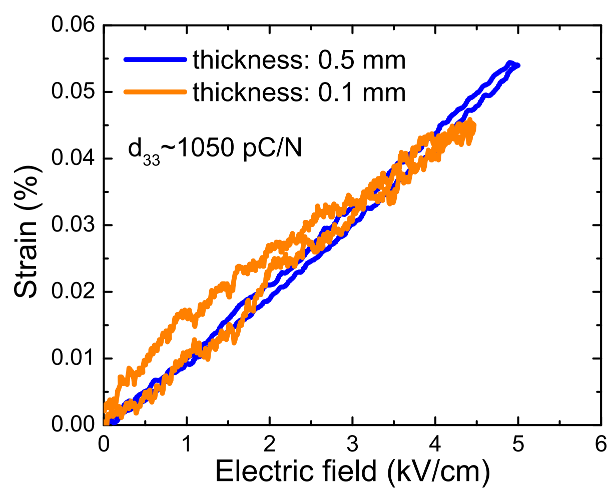

FIG. 3. Electric-field-induced strains for the [111]-poled PIN-PMN-PT tetragonal crystals with thicknesses of 0.5 mm and 0.1 mm.

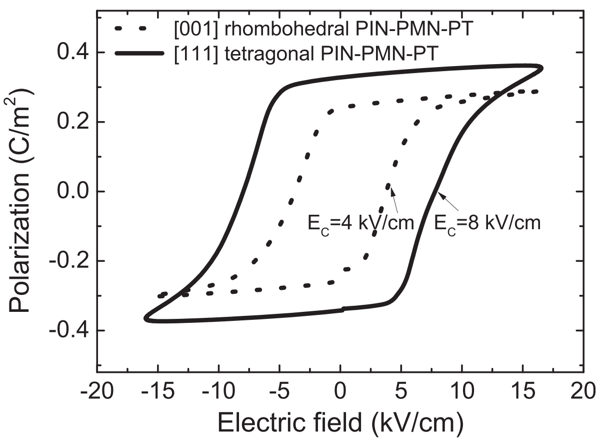

FIG. 4. Polarization-electric field hysteresis loops for [001]-oriented rhombohedral and [111]-oriented tetragonal PIN-PMN-PT crystals.

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 ε_{33}^T, 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.[19,20] As analyzed by phenomenological theory,[19,20] 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 °C).[21] With increasing temperature, therefore, the tetragonal PIN-PMN-PT crystal moves away from the

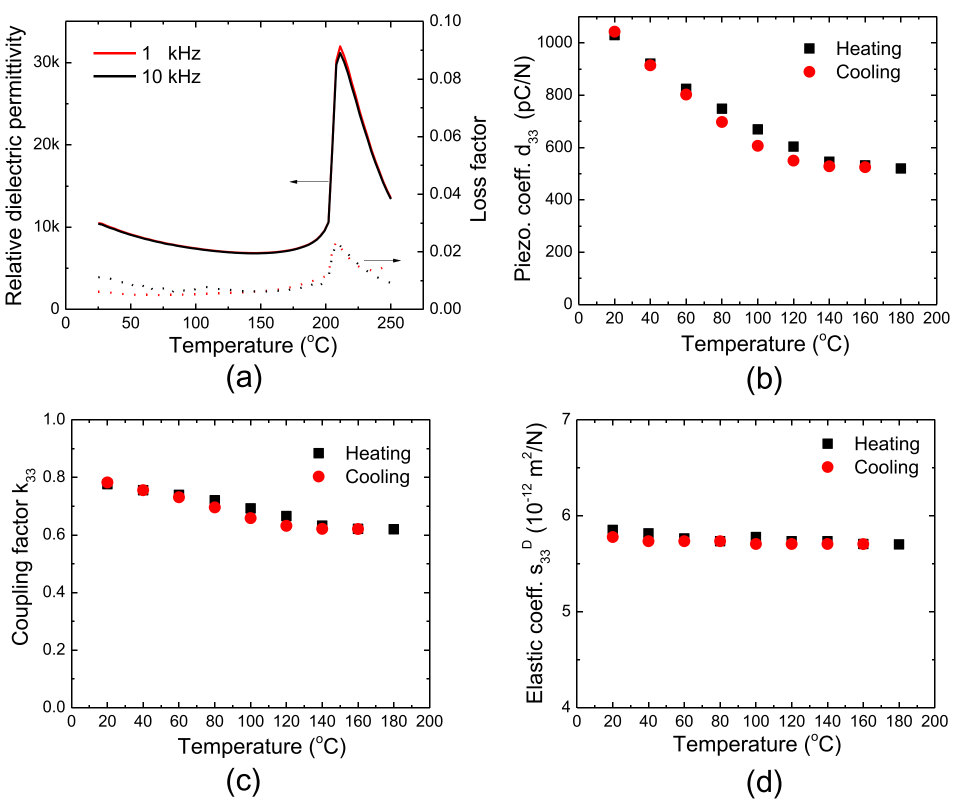

FIG. 5. Temperature dependence of the (a) dielectric permittivity ε_{33}^T, (b) piezoelectric coefficient d_{33}, (c) electromechanical coupling factor k_{33}, and (d) elastic constant s_{33}^D for the [111]-poled PIN-PMN-PT tetragonal crystals. In (b)–(d), samples were kept at each temperature for 15 min prior to measurement.

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 (>10 000), clamped dielectric permittivity (~2800), and high frequency constant (~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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