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Electric-field-induced strain and piezoelectric properties of a high Curie temperature $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--PbTiO}_3$ single crystal

Yiping Guo^{*}, Haosu Luo, Tianhou He,
Xiaoming Pan, Zhiwen Yin

*State Key Laboratory of High Performance Ceramics and Superfine Microstructure,
Shanghai Institute of Ceramics, Chinese Academy of Sciences,
215 Chengbei Road, Jiading, Shanghai 201800, China*

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Abstract

The temperature dependence of dielectric and piezoelectric properties, electric-field-induced strains of 0.66 $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--}0.34 \text{PbTiO}_3$ single crystals, which were grown directly from melt by using the modified Bridgman technique with the allomeric $\text{Pb}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3\text{--PbTiO}_3$ seed crystals, were determined as a function of crystallographic orientation with respect to the prototypic (cubic) axes. Ultrahigh piezoelectric response ($d_{33} \sim 2000 \text{ pC/N}$, $k_{33} \sim 94\%$) and strain levels up to 0.8%, comparable to rhombohedral $(1-x)\text{Pb}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3\text{--}x\text{PbTiO}_3$ and $(1-x)\text{Pb}(\text{Zn}_{2/3}\text{Nb}_{1/3})\text{O}_3\text{--}x\text{PbTiO}_3$ single crystals, were observed for the $\langle 001 \rangle$ -oriented crystals. Strain levels up to 0.47% and piezoelectric constant $d_{33} \sim 1600 \text{ pC/N}$ could be achieved being related to an electric-field-induced rhombohedral–orthorhombic phase transition for the $\langle 110 \rangle$ -oriented crystals. In addition, high electromechanical coefficients k_{33} ($\sim 88\%$) can be achieved even heating to 110°C . High T_C ($\sim 200^\circ\text{C}$), large electromechanical coefficients k_{33} ($\sim 94\%$) and low dielectric loss factor ($\sim 1\%$), along with large strain make the crystals promising candidates for a wide range of electromechanical transducers.

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1. Introduction

Recently, there is considerable interest in single crystals of solid solutions of lead-based complex perovskite $\text{Pb}(\text{B}_1, \text{B}_2)\text{O}_3$ ($\text{B}_1 = \text{Mg, Zn, Ni, Fe, Sc, In}$; $\text{B}_2 = \text{Nb, Ta, W}$) relaxor ferroelectrics and

^{*} Corresponding author. Tel.: +86-21-3998-6059; fax: +86-21-5992-7184.

E-mail address: ggyp@sina.com (Y. Guo).

the normal ferroelectric PbTiO_3 (PT) system near the morphotropic phase boundaries (MPBs), for their potential application in ultrasonic transducers, nondestructive testing (NDT) and high strain actuators [1–3]. Much of this interest has been centered on $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PMNT) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PZNT) single crystals exhibit superior piezoelectric properties by utilizing domain engineering [3–8]. For example, $0.67\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--}0.33\text{PbTiO}_3$ (PMNT 67/33) single crystals exhibit ultrahigh piezoelectric response ($d_{33} \sim 2000$ pC/N, $k_{33} \sim 92\%$) when poled in the $\langle 0\ 0\ 1 \rangle$ direction instead of the polar $\langle 1\ 1\ 1 \rangle$ direction [9]. These values are much larger than that of $d_{33} \sim 700$ pC/N and $k_{33} < 80\%$ of conventional $\text{Pb}(\text{Zr,Ti})\text{O}_3$ (PZT) ceramics [10,11]. One of the disadvantages of PMNT and PZNT single crystals near the MPBs are their relatively low rhombohedral–tetragonal phase transition temperature ($T_{\text{R-T}}$) of 65–80 and 80–100 °C, respectively, which comes with the expense of more temperature dependent properties, and less polarization stability, i.e. aging and loss of piezoelectric activity. The system of $(1-x)\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3\text{--}x\text{PbTiO}_3$ (PINT) near MPB ($x = 0.37$) has been reported to possess a high Curie temperature (>250 °C) [12–15].

In this study, the temperature dependence of the dielectric and piezoelectric properties, electric-field-induced strains of PINT 66/34 single crystals, which were grown directly from the melt by using the modified Bridgman technique with the allomeric PMNT seed crystals, were investigated as function of crystallographic orientation. The temperature dependence electromechanical coefficient in the longitudinal bar mode, k_{33} , was also presented.

2. Experimental procedure

Single crystals of PINT 66/34 (start composition) near the MPB were grown directly from the melt by using the modified Bridgman technique, in which $\langle 1\ 1\ 1 \rangle$ -oriented allomeric PMNT 71/29 seed crystals were used. The crystals were light yellow in color with perovskite structure. The larger dielectric constant at room temperature, good perovskite phase thermal stability, and lower T_{C} (~ 200 °C) than that of previously reports [12,13] was attributed to the diffuseness of the magnesium ion into the PINT single crystal during crystal growth, as confirmed by X-ray fluorescence analysis in the previous work [16]. The as-grown crystals were oriented using an X-ray diffractometer.

For dielectric characterization, the crystals with thickness 0.5 mm were polished with Al_2O_3 powders, silver paste was painted on the crystal surfaces and fired at 550 °C for 30 min. The specimens were immersed in silicon oil and poled by field cooling (15 kV/cm) at 150 °C. Capacitance properties were measured using a computer controlled HP4192A LCR meter from room temperature to 300 °C between 100 Hz and 10 kHz. For determination of electromechanical coupling factor k_{33} , a longitudinal bar of 6 mm \times 6 mm \times 1 mm was used. The electromechanical coupling coefficient k_{33} and piezoelectric constant d_{33} was calculated from resonant–antiresonant frequency method using a HP4192A analyzer. The d_{33} was also measured using a quasi-static meter of Berlincourt type at about 55 Hz to compare the calculated values. High-field measurements included polarization and strain hysteresis using a modified Sawyer–Tower circuit and linear variable differential transducer (LVDT). The maximum electric field of 20 kV/cm was applied using an amplified bipolar waveform at 0.1 Hz. During testing the samples were submerged in silicon oil, to prevent arcing.

3. Results and discussion

3.1. Dielectric and piezoelectric properties

Fig. 1a and c shows the temperature dependences of the relative dielectric permittivity ϵ_r and dielectric loss factor ($tg\delta$) of poled PINT 66/34 single crystals for different crystallographic orientations.

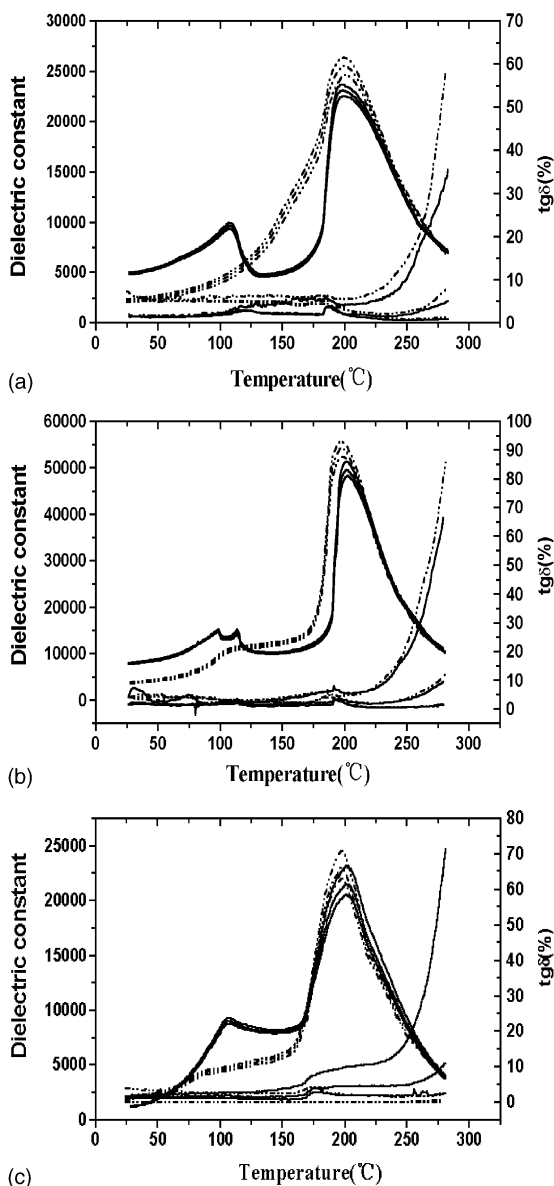


Fig. 1. Dielectric constant and dielectric loss factor as a function of temperature at 10^2 , 10^3 , and 10^4 Hz with heating (solid line) and reheating (dotted line) process: (a) $\langle 001 \rangle$; (b) $\langle 110 \rangle$; and (c) $\langle 111 \rangle$.

It was found that the dielectric permittivity ϵ_r shows a weaker frequency-dependent behavior than that of unpoled samples. The small peak of the $\langle 111 \rangle$ and $\langle 001 \rangle$ -oriented crystals should be connected to the rhombohedral–tetragonal phase transition (Fig. 1a and c). Two small peaks were observed for the $\langle 110 \rangle$ -oriented crystals (Fig. 1b), perhaps an electric-field-induced rhombohedral–orthorhombic phase transition occurred, which has also been confirmed in PMNT and PZNT single crystals [17–19]. The first small peak (Fig. 1b) should indicate a transition from ferroelectric rhombohedral (FE_r) to orthorhombic ferroelectric (FE_o) state, and the second small peak should indicate a transition from the FE_o to tetragonal ferroelectric (FE_t) state. Furthermore, an interesting feature is the change of the dielectric loss factor ($tg\delta$) of the PINT crystals. The loss factor increased as the temperature is above the peak near 185 °C, especially in the low frequencies. This peak is the result of Debye-type relaxation of the defect dipoles [20], subsequent increase in the loss factor should be connected to the dipole conduction effects result from the formation of oxygen vacancies as well as lead vacancies, which arise from the sublimation of In_2O_3 and evaporation of lead during the preparation PINT crystals. This behavior was also found in the $Pb[(Zn_{1/3}Nb_{2/3})_{0.5}(Zr_{0.47}Ti_{0.53})_{0.5}]O_3$ specimens after thermal annealing in argon and nitrogen atmosphere [21].

Table 1 presents dielectric properties and piezoelectric constant (d_{33}) at room temperature as a function of crystallographic orientation. PINT 66/34 crystals oriented along $\langle 001 \rangle$ exhibited piezoelectric

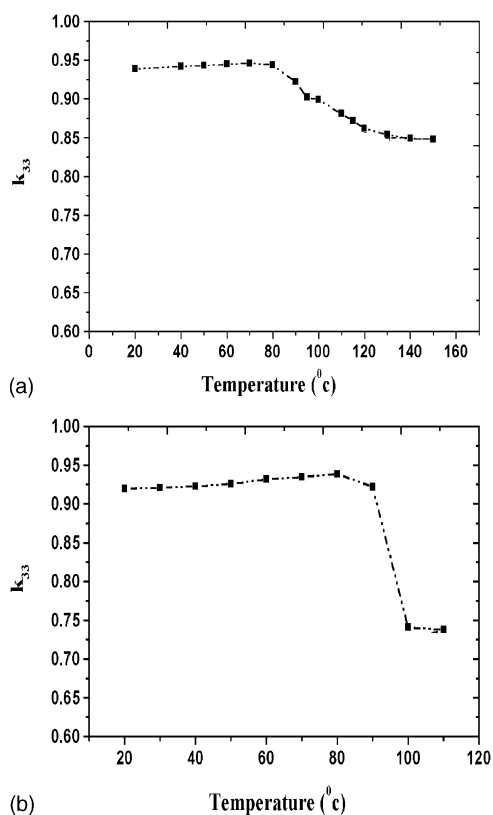


Fig. 2. Electromechanical coupling coefficient k_{33} as a function of temperature: (a) for $\langle 001 \rangle$ -oriented PINT 66/34 single crystal and (b) for $\langle 001 \rangle$ -oriented PMNT 68/32 single crystal.

Table 1

Dielectric properties (1 kHz) and piezoelectric constant (d_{33}), of PINT crystal at room temperature, as a function of crystallographic orientation

Crystal orientation	d_{33} (pC/N)	Dielectric constant	Loss $tg\delta$ (%)
$\langle 001 \rangle$	2100	4100	1.2
$\langle 110 \rangle$	1600	7800	1.0
$\langle 111 \rangle$	87	1050	1.6

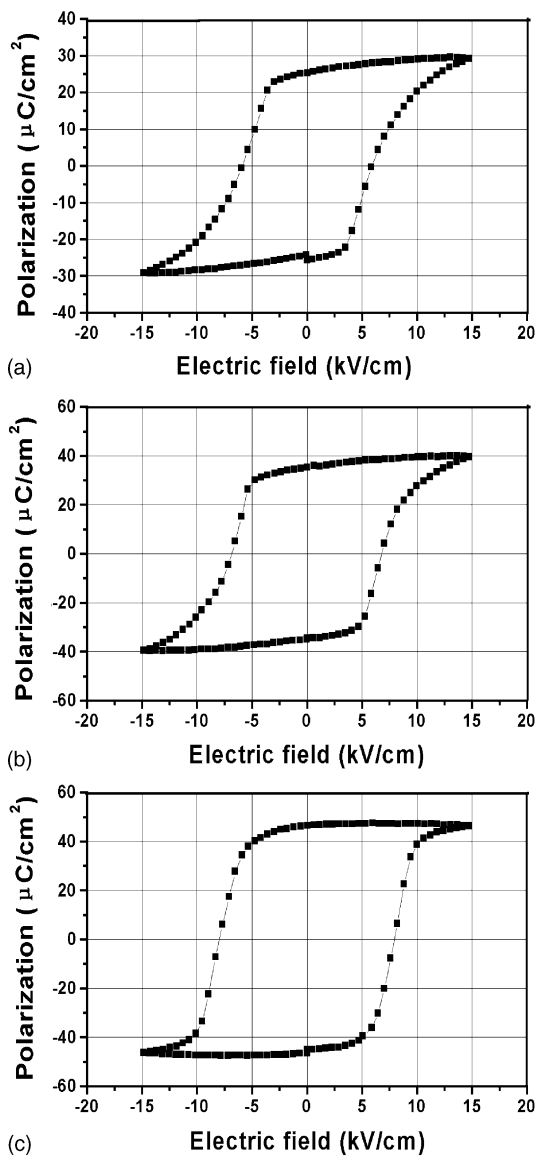


Fig. 3. Polarization vs. E -field curves for different crystallographic orientation PINT 66/34 crystals: (a) $\langle 001 \rangle$; (b) $\langle 110 \rangle$; and (c) $\langle 111 \rangle$.

constant (d_{33}) as high as 2100 pC/N. Crystals oriented $\langle 110 \rangle$ exhibited values of $d_{33} \sim 1600$ pC/N. However, crystals oriented along their polar direction $\langle 111 \rangle$, exhibited value of $d_{33} \sim 87$ pC/N, significantly inferior to those oriented along $\langle 001 \rangle$ and $\langle 110 \rangle$, which has also been found in rhombohedral PZNT and PMNT single crystals [9].

Fig. 2a and b show the electromechanical coupling coefficients k_{33} as a function temperature for PINT 66/34 and PMNT 68/32 crystals, respectively. In the heating process, for $T < 110$ °C, the value of k_{33} can be seen to be relatively temperature independent for $\langle 001 \rangle$ -oriented PINT 66/34 single crystals, with a value between 0.88 and 0.94 (Fig. 2a). But for a $\langle 001 \rangle$ -oriented PMNT 68/32 single crystal, we can see from Fig. 2b that the value of k_{33} decreases rapidly to 0.73 across 85 °C. Judging

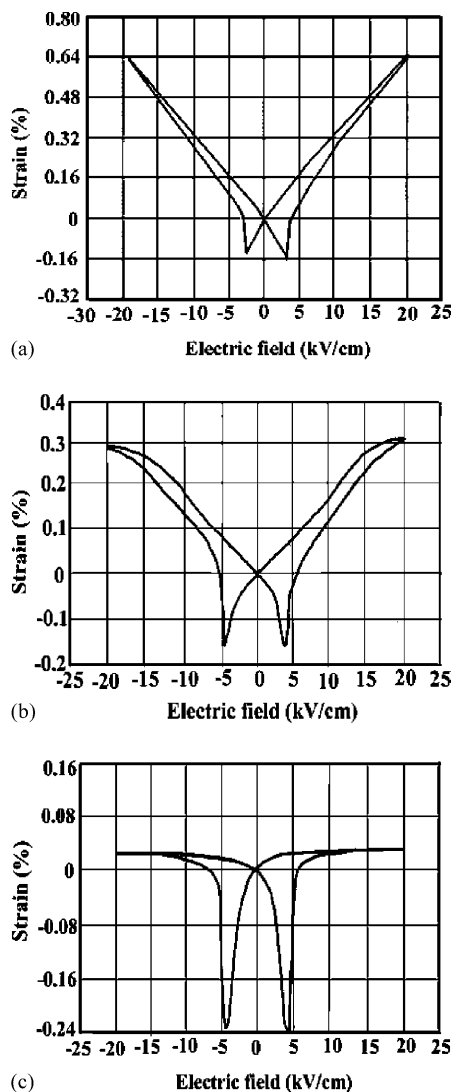


Fig. 4. Strain vs. electric-field curves for different crystallographic orientation PINT 66/34 crystals under bipolar electric field below 20 kV/cm with 0.1 Hz frequency at room temperature: (a) $\langle 001 \rangle$; (b) $\langle 110 \rangle$; and (c) $\langle 111 \rangle$.

from the large k_{33} and the weaker temperature dependence of k_{33} , the PINT single crystals are promising candidates for application to medical imaging, NDT, and actuators.

3.2. Electric-field-induced polarization and strain

The P – E hysteresis loops for $\langle 1\ 1\ 1 \rangle$, $\langle 1\ 1\ 0 \rangle$, and $\langle 0\ 0\ 1 \rangle$ -oriented PINT crystals are shown in Fig. 3a–c, respectively. Domain switching by bipolar field occurs at higher coercive field (E_c) than that of PMNT single crystals. It was also found that the value of E_c (~ 8 kV/cm) for the $\langle 1\ 1\ 1 \rangle$ -oriented crystals is larger than that of $\langle 1\ 1\ 0 \rangle$ -oriented crystals (~ 7 kV/cm) and $\langle 0\ 0\ 1 \rangle$ -oriented crystals (~ 6 kV/cm). The results demonstrate that domain switching under electric field would cause larger elastic energy in $\langle 1\ 1\ 1 \rangle$ -oriented crystals than that of $\langle 1\ 1\ 0 \rangle$ and $\langle 0\ 0\ 1 \rangle$ -oriented crystals. Remnant polarization ($P_r \sim 26$ $\mu\text{C}/\text{cm}^2$) of $\langle 0\ 0\ 1 \rangle$ -oriented rhombohedral crystal is $1/\sqrt{2}$ ($P_r \sim 37$ $\mu\text{C}/\text{cm}^2$) of $\langle 1\ 1\ 0 \rangle$ -oriented crystal and $1/\sqrt{3}$ ($P_r \sim 45$ $\mu\text{C}/\text{cm}^2$) of $\langle 1\ 1\ 1 \rangle$ -oriented crystals. Therefore, domain switching at E_c is expected to be 71° domain switching.

Strain as a function of electric field for $\langle 1\ 1\ 1 \rangle$, $\langle 1\ 1\ 0 \rangle$, and $\langle 0\ 0\ 1 \rangle$ -oriented rhombohedral crystals are presented in Fig. 4. Strains as high as 0.8% were observed for $\langle 0\ 0\ 1 \rangle$ -oriented crystals (Fig. 4a), which is comparable to that of PMNT and PZNT single crystals. Fig. 4b shows the bipolar ε – E response of an $\langle 1\ 1\ 0 \rangle$ -oriented crystal. It clearly illustrates an electrically induced rhombohedral–orthorhombic phase transformation in the vicinity of 12 kV/cm. This result is consistent with that of temperature dependent dielectric constant measurements. This behavior has been observed in PMNT and PZNT single crystals [17–19]. Strain levels up to 0.47% could be achieved. Strain as function of E field for $\langle 1\ 1\ 1 \rangle$ -oriented crystal is presented in Fig. 4c. It was evident a single domain state could be achieved under a bias field of 20 kV/cm. Strain as low as 0.27% with large hysteresis was obtained. It should attribute to domain instability. On the basis of the above results, we believed the concept that engineered domain configuration is universal and can be applied to all perovskite type ferroelectric crystals.

4. Conclusions

The ferroelectric related properties of rhombohedral PINT 66/34 crystals (start composition), which were grown directly from melt by a modified Bridgman technique with the allomeric PMNT 71/29 seed crystals, were investigated as a function of crystallographic orientation. High T_C (~ 200 °C), ultrahigh piezoelectric constant $d_{33} \sim 2000$ pC/N, the large electromechanical coefficient ($k_{33} \sim 94\%$), and strain levels up to 0.8% were observed for the $\langle 0\ 0\ 1 \rangle$ -oriented crystals. Strain levels up to 0.47% and piezoelectric constant $d_{33} \sim 1600$ pC/N could be achieved being related to an electric-field-induced rhombohedral–orthorhombic phase transformation for the $\langle 1\ 1\ 0 \rangle$ -oriented crystals. The high T_C (corresponding to weaker dependent properties), superior piezoelectric properties indicate that PINT crystals are promising candidates for application to medical imaging, NDT and actuators.

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