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Poling field versus piezoelectric property for $[001]_c$ oriented $91\%Pb(Zn_{1/3}Nb_{2/3})O_3–9\%PbTiO_3$ single crystals

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Abstract Electromechanical property measurements and microstructure observations using optical microscopy were performed on a $[001]_c$ oriented k_{33} resonator made of $91\%Pb(Zn_{1/3}Nb_{2/3})O_3–9\%PbTiO_3$ single crystal, which was polarized under different electric fields. At room temperature, when the poling field is 1100 V/mm, the electromechanical coupling factor k_{33} is 0.90 and piezoelectric coefficient d_{33} is 1665 pC/N. Such superior electromechanical properties could be attributed to the formation of monoclinic multi-domain structure, which transforms to tetragonal phase at 46 °C. While at a higher poling field of 1200 V/mm, the crystal becomes single-domain tetragonal state and its k_{33} and d_{33} are only about 0.69 and 850 pC/N, respectively. The critical poling field to transform the monoclinic phase to the tetragonal phase is found to be $\sim$1120 V/mm.

Introduction

As one of the most promising next-generation piezoelectric materials for high-sensitivity small size sensors, transducers and actuators, relaxor-based ferroelectric single crystals $(1\text{-}x)Pb(Zn_{1/3}Nb_{2/3})O_3–xPbTiO_3$ (PZN–xPT) have been under extensive investigations for their extraordinary high piezoelectric behaviors [1–3]. Due to special structural stability, the crystal with composition near the morphotropic phase boundary (MPB, $x \approx 9\%$) exhibit unique physical properties.

There are numerous reports on unpolarized PZN–9%PT single crystals. Uesu et al. [4] observed both orthorhombic and tetragonal phases in unpoled PZN–9%PT single crystal at room temperature. Kiat et al. [5] found monoclinic and tetragonal phases in unpoled PZN–9%PT powder after being annealed at 800 °C for 1 h. There were also some investigations about the coexistence of rhombohedral and tetragonal phases in PZN–9%PT single crystals [6–8]. However, up to date, there were little reports on poling influence to the properties of PZN–9%PT single crystals. In general, the macroscopic properties of domain engineered $(1\text{-}x)Pb(Zn_{1/3}Nb_{2/3})O_3–xPbTiO_3$ single crystals are strongly related to their domain structures. The aim of the present work is to experimentally establish a relationship between the macroscopic properties and domain structures of $[001]_c$ poled PZN–9%PT single crystals.

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Experimental procedure

PZN–9%PT single crystals used in this work were supplied by the Microfine Materials Technologies P/L (Singapore). The sample was oriented, cut and polished into a k_{33} resonator with the dimensions of 1 mm//$[100]^L \times 1$ mm//$[010]^W \times 6$ mm//$[001]^T$. Thin layer gold electrodes were sputtered on both ends (1×1 mm). The bar sample was poled progressively in silicone oil at room temperature from 100 to 1400 V/mm. Before each repoling at different poling field, the sample was heat treated at 400 °C for 3 h to release the internal stresses and completely depole the sample. After each poling step, the dielectric permittivity ε_{33}^T at 1 kHz, the electromechanical coupling factors k_{33} and elastic compliance coefficient s_{33}^E were determined by the resonance and antiresonance frequencies measured by an impedance analyzer (Agilent 4294A). The piezoelectric constant d_{33} was measured by a Berlincourt-type d_{33} meter.

Results and discussions

The measured properties of $[001]_c$ oriented PZN–9%PT single crystal as a function of the poling field are given in Fig. 1. If the poling field is less than 600 V/mm, the corresponding piezoelectric coefficient d_{33} is less than 400 pC/N. When the poling field is increased to 700 V/mm, d_{33} increases to 1380 pC/N and the coefficients s_{33}^E, k_{33}, and ε_{33}^T are 133 × 10^{-12} m^2/N, 0.87 and 2090ε_0, respectively. When the poling field is further increased to 1110 V/mm, d_{33} s_{33}^E, ε_{33}^T, and k_{33} reach 1670 pC/N, 136 × 10^{-12} m^2/N, 2807ε_0 and 0.90, respectively. But when the poling field is increased to 1120 V/mm, all the electromechanical properties start to decrease abruptly. When the field level reached 1200 V/mm, the elastic compliance coefficient s_{33}^E becomes 120 × 10^{-12} m^2/N, and the dielectric permittivity ε_{33}^T (1426ε_0), electromechanical coupling factors k_{33} (0.69), and piezoelectric constant d_{33} (849 pC/N) of the sample become much smaller than the corresponding

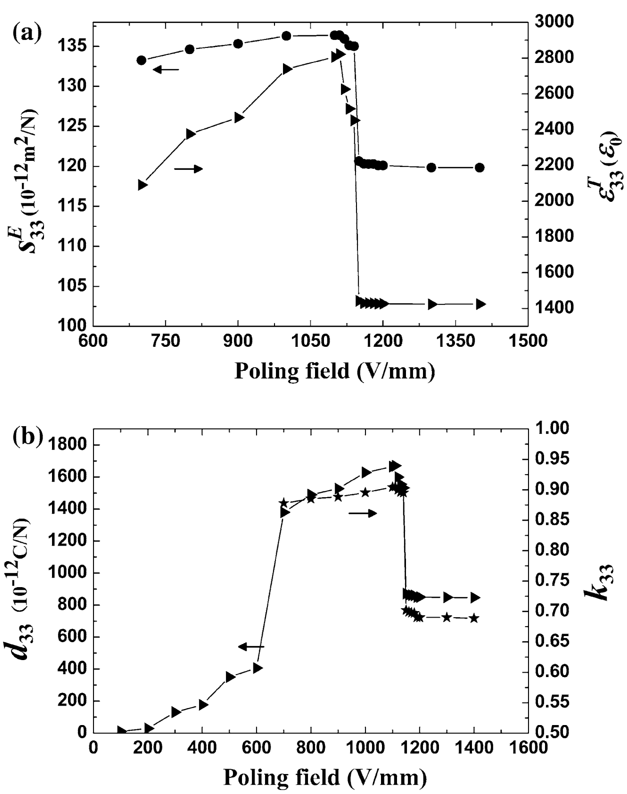

Fig. 1 Dielectric permittivity ε_{33}^T, elastic compliance s_{33}^E, electromechanical coupling factor k_{33}, and piezoelectric coefficient d_{33} of PZN–9%PT single crystal as functions of poling field

values of the sample poled under a field of 1100 V/mm ($\varepsilon_{33}^T = 2807\varepsilon_0$, $k_{33} = 0.90$, and $d_{33} = 1665$ pC/N, respectively). Therefore, the critical poling field for this sample is 1120 V/mm.

In order to explain this phenomenon, we have carried out a detailed study on the electromechanical property and domain structures of PZN–9%PT single crystal poled under 1100 and 1200 V/mm. Upon heating the sample from room temperature with a heating/cooling stage (Linkam TEMS600), the dielectric permittivity ε_{33}^T at 1 kHz, electromechanical coupling factors k_{33} and elastic compliance coefficient s_{33}^E were measured by the resonance technique using an impedance analyzer and the piezoelectric constant d_{33} was calculated from the following equation:

$$d_{33} = k_{33}\sqrt{\varepsilon_{33}^T s_{33}^E}. \quad (1)$$

Ferroelectric domain configurations were observed by polarized light microscopy (ZEISS AXIOSKOP40). To be consistent for all measurements, the same k_{33} resonator was used for all studies, including measurements of dielectric, piezoelectric, elastic compliance coefficients, and optical microscopy studies of domain structures.

Figure 2 shows the temperature dependence of ε_{33}^T, s_{33}^E, k_{33}, and d_{33} for the bar-shaped sample poled under a field of 1100 V/mm. During heating, all electromechanical properties exhibit two peaks at about 46 and 177 °C. The lower temperature abnormality at 46 °C corresponds to the phase transition from monoclinic to the tetragonal phase, while the peak at 177 °C indicates tetragonal to cubic paraelectric phase transition (T_c). The maximum values of ε_{33}^T (50614ε_0) and d_{33} (4209 pC/N) appear at $T_c \sim 177$ °C.

Monoclinic phase M_B-type and M_A-type with space group C_m, and M_C-type with space group P_m were observed in these type of piezo crystals [9–11]. For the case of PZN–9%PT poled along $[001]_c$, the M_B phase can be excluded, which was observed in $[110]_c$ oriented sample under electric bias [5]. Domain structure observation were performed on the PZN–9%PT single crystal after being poled under a field of 1100 V/mm at room temperature. We found that there were no complete extinctions observed on the three pairs of surfaces in any direction under crossed polarizers due to the overlapping of different domains and the reflection of light from dense domain walls [12]. When the polarizer is along <001>, the sample becomes darker than when the crossed polarizers are in any other directions. This indicates that the domain structure belongs to the M_C-type monoclinic phase [13].

Figure 3 shows domain configurations at room temperature on (100), (010), and (001) surfaces under crossed polarizers. The domain configurations on (100) shown in Fig. 3a and on (010) shown in Fig. 3b are similar, exhibit mutually perpendicular dark stripes. When focusing on the

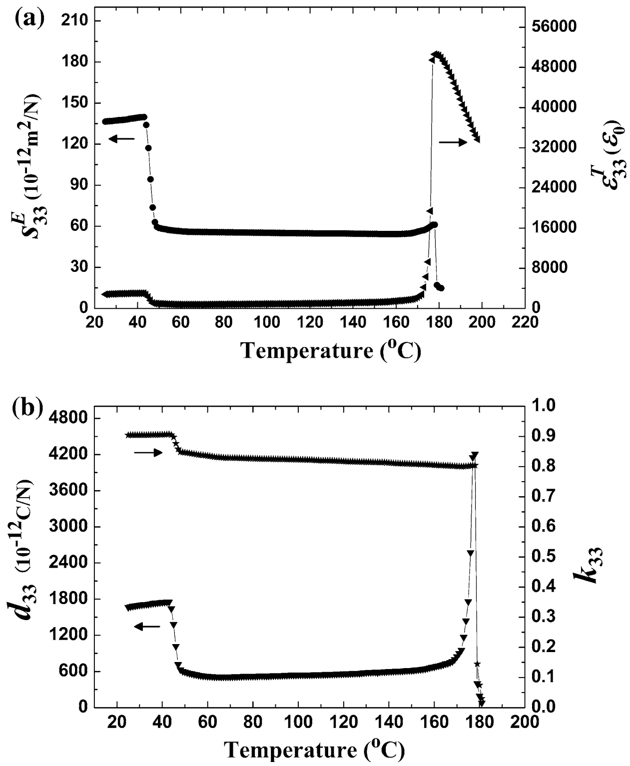

Fig. 2 Temperature dependence of dielectric permittivity ε_{33}^{T}, elastic compliance s_{33}^{E}, electromechanical coupling factor k_{33}, and piezoelectric coefficient d_{33} of the sample poled under a field of 1100 V/mm

same area but different depth along $[100]_c$ or $[010]_c$, the dark stripes will shift but retaining their directions along <011> or <101>, which indicates that the domain walls are not perfectly perpendicular to the surfaces but are slightly inclined. Therefore, the different incline angles make the domain walls appear to have different thickness [12]. Crossing domain structure can be observed on the (001) surface, as shown in Fig. 3c.

When the poling field is along $[001]_c$, four different polarization orientations remained for the M_C phase, which are denoted by PI, PII, PIII, and PIV as shown in Fig. 4a. According to the polarization orientation in the M_C phase provided by Devonshire theory [14] as well as domain configurations observed in PZN–9%PT single crystal shown in Fig. 3, typical domain patterns are depicted in Fig. 4b. All domain walls in Fig. 4b are permissible by the mechanical compatibility argument in ferroelectric crystals with M_C monoclinic symmetry [12]. From the observation and analysis above, it can be concluded that M_C phase exists in $[001]_c$ oriented PZN–9%PT crystal when it is poled under a field level of 1100 V/mm at room temperature.

It should be noted that the domain structures described here are different from that reported in Ref. [15] for the poled PZN–9%PT crystals. The authors of Ref. [15] observed broad, straight domains separated by the walls along $[010]_c$, which may belong to monoclinic C_m space group [12]. However, $[001]_c$ electric field could not induce monoclinic M_A and M_B phases in PZN–9%PT single crystal [16], so the crystal used in Ref. [15] might have PT content lower than 9%.

For the PZN–9%PT single crystal sample poled under an electric field of 1200 V/mm, the dielectric permittivity ε_{33}^{T}, elastic compliance coefficient s_{33}^{E}, electromechanical coupling factors k_{33} and piezoelectric coefficient d_{33} vs. temperature curves are shown in Fig. 5. Only one peak appears at $T_c \sim 177$ °C in each curve, which corresponds to the tetragonal to cubic phase transition. This means that the sample poled under an electric field of 1200 V/mm is in tetragonal phase at room temperature.

At room temperature, when the microscope is focused on the (001) surface of the sample poled under the field of 1200 V/mm, the crystal appears in complete extinction under crossed polarizers. By focusing the microscope on (100) and (010) surfaces of the k_{33} vibrator, complete extinction only occurs when the direction of one of the polarizers is along $[001]_c$. These phenomena indicate that the crystal poled under the field of 1200 V/mm is in single-domain tetragonal state with the polarization vector along $[001]_c$ at room temperature.

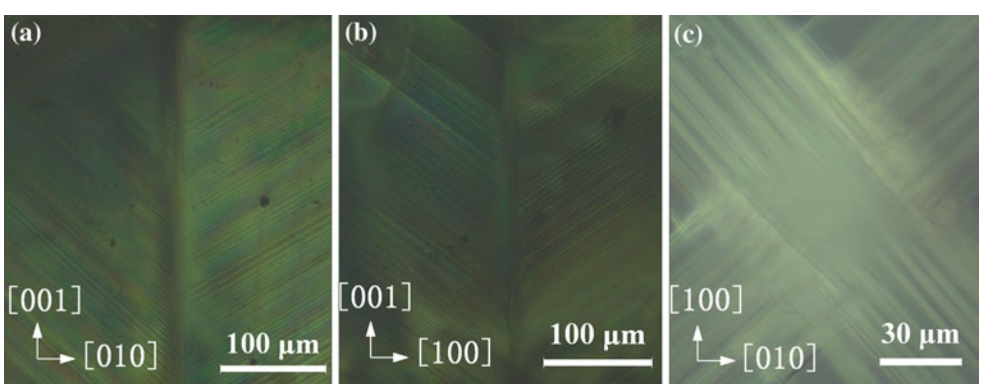

Fig. 3 Domain structures at room temperature on **a** (100), **b** (010), and **c** (001) surfaces of a k_{33} resonator made of PZN–9%PT single crystal

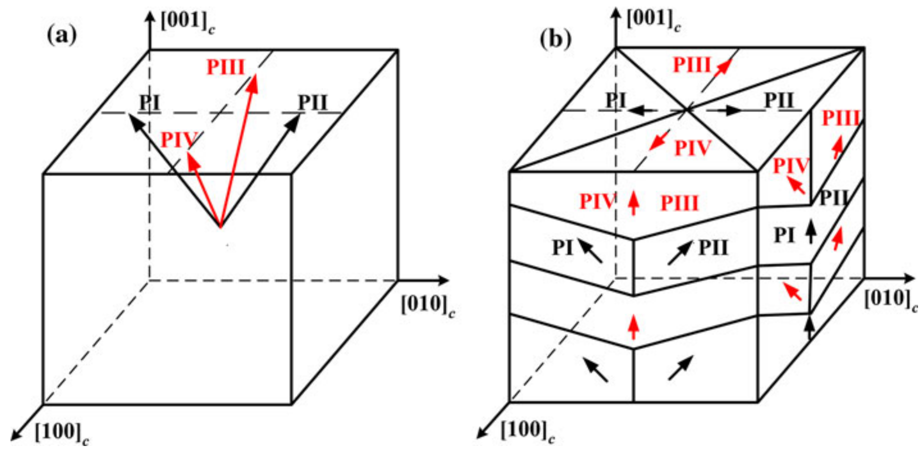

Fig. 4 **a** Four different polarization orientations in $[001]_c$ poled PZN–9%PT single crystal. **b** Illustration of domain patterns formed in a $[001]_c$ poled PZN–9%PT single crystal

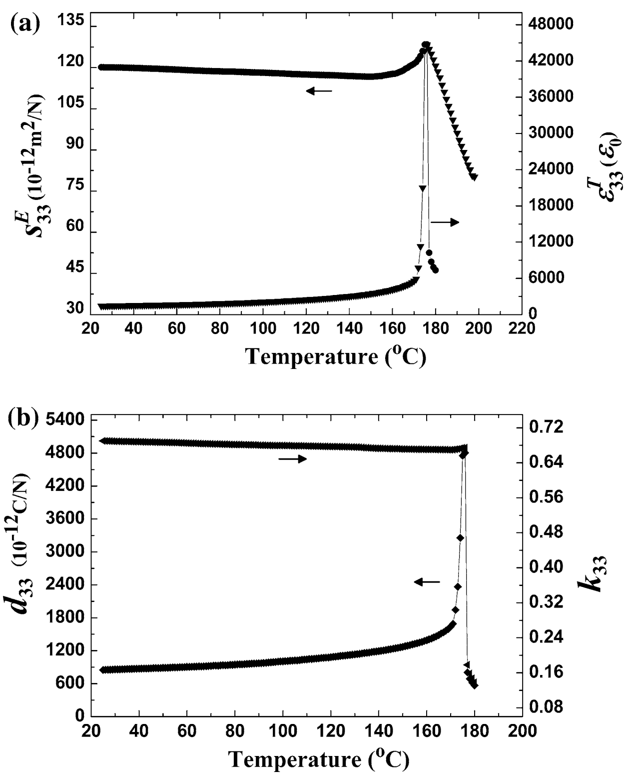

Fig. 5 Temperature dependence of dielectric permittivity ε^T_{33}, elastic compliance s^E_{33} electromechanical coupling factor k_{33}, and piezoelectric coefficient d_{33} of the sample poled under a field of 1200 V/mm

Moreover, it is clear that 1110 V/mm is the optimum poling field for the PZN–9%PT single crystal, which produces monoclinic multi-domain structures (Fig. 3) and gives the best electromechanical properties. If the field increases further, some monoclinic domains will be switched to the tetragonal phase, resulting in the degradation of crystal performance. This can be verified by the decrease of electromechanical property values of the crystal when the poling field is increased beyond 1120 V/mm, as shown in Fig. 1. When the field is larger than 1150 V/mm, all four differently polarized domains will be completely switched to the field direction $[001]_c$ and the crystal becomes single-domain tetragonal phase. This field induced phase transition leads to the drastic degradation of the electromechanical properties.

Summary and conclusions

In summary, electromechanical property measurements and optical microscopy observations of domain microstructures were performed on a $[001]_c$ oriented k_{33} resonator made of 91%Pb($Zn_{1/3}Nb_{2/3}$)O_3–9%$PbTiO_3$ single crystal under different poling electric fields, and as a function of temperature. The optimum poling field for PZN–9%PT single crystal is determined to be 1110 V/mm, which produced M_C-type monoclinic multi-domain structures, the electromechanical coupling factor k_{33} reaches 0.90 and the piezoelectric coefficient d_{33} is 1670 pC/N. Upon heating, the M_C phase transformed into tetragonal phase at about 46 °C, then to cubic phase at $T_c \sim 177$ °C. At room temperature, the critical poling field value was found to be 1120 V/mm, beyond which some domains will be switched to tetragonal phase so that the macroscopic electromechanical properties will degrade. When the poling field is beyond 1150 V/mm, all domains will be completely switched to the field direction $[001]_c$ so that the crystal becomes single-domain tetragonal phase, resulting a drastic decrease of the piezoelectric coefficient d_{33} ($\sim$850 pC/N) and dielectric permittivity ε^T_{33} ($\sim 1400\varepsilon_0$) at room temperature. Upon heating, these single-domain resonators underwent only one phase transition from tetragonal to cubic phase at $T_c \sim 177$ °C.

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References

1. Park SE, Shrout TR (1997) J Appl Phys 82:1804
2. Kuwara J, Uchino K, Nomura S (1981) Ferroelectrics 37:579
3. Kuwata J, Uchino K, Nomura S (1982) Jpn J Appl Phys 21:1298
4. Uesu Y, Matsuda M, Yamada Y, Fujishiro K, Cox DE, Noheda B, Shirane G (2002) J Phys Soc Jpn 71:960
5. Kiat M, Uese Y, Dkhil B, Matsuda M, Malibert C, Calvarin G (2002) Phys Rev B 65:064106
6. Uesu Y, Yamada Y, Fujishiro K, Tazawa H, Enokido S, Kiat JM, Dikhil B (1998) Ferroelectrics 217:319
7. Zhang L, Dong M, Ye ZG (2000) Mater Sci Eng B 78:96
8. Singh G, Bhaumik I, Ganesamoorthy S, Karnal AK, Tiwari VS (2007) Cryst Ref Technol 42:378
9. Cao H, Bai FM, Wang NG, Li JF, Viehland D, Xu GY, Shirane G (2005) Phys Rev B 72:064104
10. Ye ZG, Noheda B, Dong M, Cox D, Shirane G (2001) Phys Rev B 64:184114
11. Noheda B, Cox DE, Shirane G, Gao J, Ye ZG (2002) Phys Rev B 66:054104
12. Bokov AA, Ye ZG (2004) J Appl Phys 95:6347
13. Bao P, Yan F, Liu XM, Zhu JS, Shen HM, Wang YN, Luo HS (2006) Appl Phys Lett 88:092905
14. Vanderbilt D, Cohen MH (2001) Phys Rev B 63:094108
15. Renault AE, Dammak H, Calvarin G, Thi MP, Gaucher P (2002) Jpn J Appl Phys 41:3846
16. Noheda B, Zhong Z, Cox DE, Shirane G, Park SE, Rehrig P (2002) Phys Rev B 65:224101