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Letter

Phase transition characteristics of the relaxor-based 0.24PIN–0.51PMN–0.25PT single crystals

Yuhui Wan, Zhenrong Li *, Zhuo Xu, Shiji Fan, Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, China

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ABSTRACT

Phase transition characteristics of relaxor-based 0.24PIN–0.51PMN–0.25PT single crystal were investigated through combination of dielectric and piezoelectric properties measurement, hysteresis loop measurements and domain morphology observation with increasing temperature. The phase transition from rhombohedral phase to relaxor cubic phase occurs near 120 °C. The poled crystals exhibit dielectric properties of normal ferroelectrics below 120 °C with frequency independence and show no piezoelectricity over 120 °C with disappearance of resonance and anti-resonance peaks in the impedance spectrum. The poled crystals show clearer domain morphology than that of unpoled crystals. Square hysteresis loop feature was found to transform to double loop like feature under the temperature of about 10 °C lower than 120 °C. The double like hysteresis loop disappears and the hysteresis loop is nearly linear above dielectric maximum temperature ~150 °C. The more evident dielectric dispersion phenomenon and finer domains with width 1–3 μm are presented in 0.24PIN–0.51PMN–0.25PT crystal, compared to 0.76PMN–0.24PT single crystal.

1. Introduction

Lead-based relaxor ferroelectric crystal $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$–$xPbTiO_3$ ((1−*x*)PMN–*x*PT) with compositions near morphotropic phase boundary (MPB, $0.30 < x < 0.35$) between rhombohedral (R) and tetragonal (T) phases have been extensively investigated due to their superior electromechanical coupling factors ($k_{33} > 90\%$) and high piezoelectric coefficients ($d_{33} > 2000$ pC/N) [1–3]. Owing to the inevitable compositional segregation in the crystal growth process, the concentration of the cation Ti was found to be low near the bottom of the crystal boule and gradually increase along the growth direction [4]. Relaxor characteristics were observed for $x < 0.3$ in (1−*x*)PMN–*x*PT through dielectric investigation and the degree of relaxor characteristics decreases with increasing *x* [5]. The PMN–PT can transform from the typical relaxor ferroelectrics to normal ferroelectrics with increasing of PT content [6].

Perovskite $Pb(In_{1/2}Nb_{1/2})O_3$ (PIN) is a typical relaxor ferroelectric material with R symmetry in the disordered state, where the niobium cation (Nb^{5+}) and indium cation (In^{3+}) are randomly arranged on the B sites, and undergoes a diffuse phase transition. PIN can exhibit a transition from the disordered state to the ordered state (antiferroelectric with orthorhombic symmetry) by long-time thermal annealing and undergoes a sharp transition [7,8]. The incorporation of PIN in PMN–PT crystal results in an increase of rhombohedral to tetragonal phase transition temperature and coercive field (E_c) comparing with PMN–PT crystal in addition to maintaining the excellent piezoelectric and dielectric properties, making them promising candidates for medical ultrasonic imaging probes, sonar transducers and actuators [9,10]. As reported for PMN–PT crystals, the compositions of PIN–PMN–PT boule along the growth direction are varied due to the segregation of titanium, with lower PT content at the bottom part of the crystals and higher PT content near the top of the crystal boule [11,12]. Recently, many researchers have focused on the properties and domain in PIN–PMN–PN single crystals [13–16]. The dielectric permittivity at the Curie temperature of PMN–PT near MPB was found to be very sharp with discontinuous change while that of PIN–PMN–PT is broad and diffused [13,14]. The phase transition behaviors might be different between binary and ternary systems. Xu et al. [15] investigated the domain dynamics and phase transitions under polarizing microscopy while heating and cooling R and T phase PIN–PMN–PT crystal. It was found the T phase PIN–PMN–PT crystal exhibits first-order T-to-C (Cubic) phase transition of normal ferroelectrics whereas the R phase PIN–PMN–PT shows diffusive R-to-T and T-to-C phase transitions of relaxor ferroelectrics. Kim et al. [16] compared the phase transition behaviors of unpoled and [001]-poled R phase PIN–PMN–PT crystal ($T_{RT} \sim 126$ °C, $T_C \sim 183$ °C) by Brillouin light scattering and dielectric spectroscopes. A typical characterization in relaxors with diffused elastic anomaly and substantial dielectric dispersion was

* Corresponding author. Tel.: +86 29 82668679; fax: +86 29 82668794.
E-mail address: zhrli@mail.xjtu.edu.cn (Z. Li).

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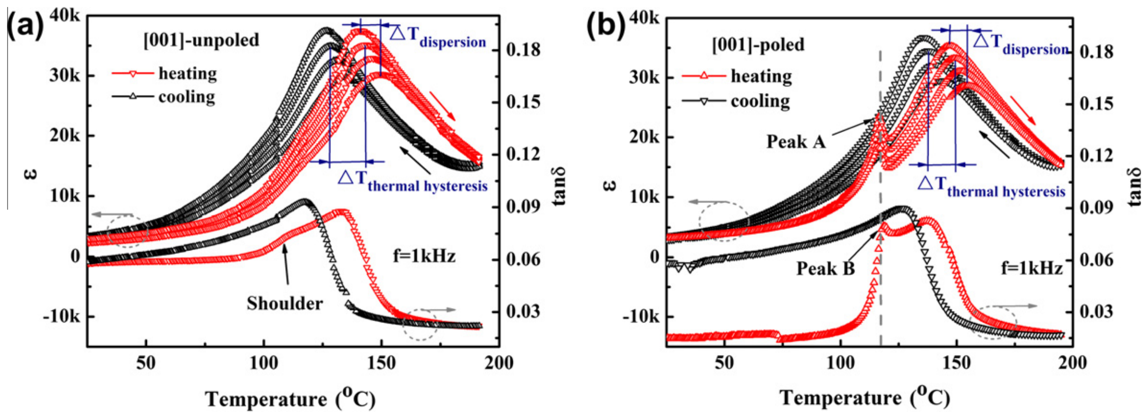

Fig. 1. Dielectric constant (ε) at different frequencies (0.1, 1, 10, 100 kHz) and dielectric loss ($\tan\delta$) at 1 kHz for the (a) unpoled and (b) poled samples, measured on cooling and heating process.

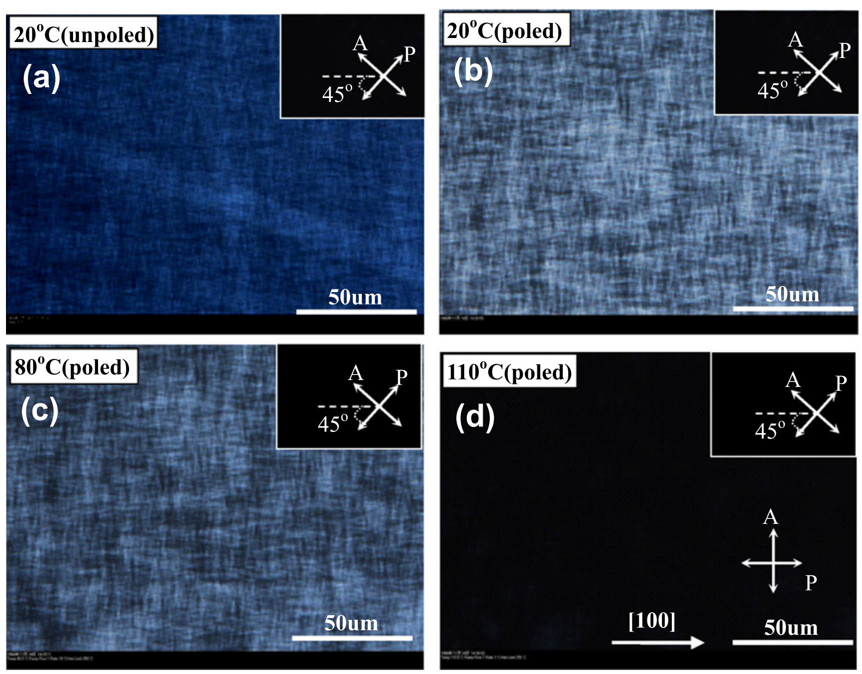

Fig. 2. Domain morphology of 0.24PIN–0.51PMN–0.25PT single crystal (a) in unpoled state at 20 °C, and in poled state at different temperature: (b) 20 °C, (c) 80 °C, (d) 110 °C.

found in the unpoled crystal. For poled crystal, the R-to-T and T-to-C phase transition were discovered and the latter remained diffused with dielectric dispersion due to local random fields inherent in relaxors.

In PIN–PMN–PT system, compared with PMN–PT system, the phase transition characteristics are more complicated. The studies on the behavior of PIN–PMN–PT with different compositions will help to understand the phase diagram of PIN–PMN–PT. In this paper, the phase transition behavior of the 0.24PIN–0.51PMN–0.25PT single crystal was investigated in detail based on the measurement of dielectric and piezoelectric properties, *P–E* hysteresis loops, and the observation of the domain morphology at different temperatures. The behavior of phase transition of the PIN–PMN–PT single crystal was discussed.

2. Experimental

PIN–PMN–PT single crystals were grown using a modified Bridgman method [12]. Composition of the crystal was analyzed by an electron probe X-ray microanalyzer (EPMA, JEOL JXA-8230 superprobe) to be 0.24PIN–0.51PMN–0.25PT. [001]-Oriented single crystals of size of $5 \times 5 \times 0.8$ mm^3 were chosen for dielectric and hysteresis loops (*P–E*) measurement. The crystal bars with size of $1.0 \times 1.0 \times 3.0$ mm^3 were chosen for piezoelectric constant d_{33} measurements. Silver pastes on 5.0×5.0 mm^2 and 1.0×1.0 mm^2 faces of the samples were fired at 600 °C for 10 min, respectively. The samples were poled at 10 kV/cm dc field at room temperature for 5 min in silicon oil. Dielectric measurements were performed at frequencies of 0.1, 1, 10 and 100 kHz, respectively, in the range of room temperature to 190 °C at a heating/cooling rate of 2 °C/min, by using an automated system where a computer was employed to control a Delta temperature box and an HP4284A LCR meter. *P–E* loops were measured using TF ANALYZER 2000 with frequency of 0.5 Hz at fixed temperature in the range of 20–150 °C. Piezoelectric constants d_{33} was calculated through the resonance and anti-resonance frequencies in the range of room temperature to 150 °C using an HP 4294A impedance-phase gain analyzer with a Delta temperature box. Domain morphology observation was performed in the range of 20–160 °C by using a polarizing light microscope (PLM, Olympus BX51) with LINKAM heating-cooling stage. The sample were unpoled and poled [001]-oriented crystals with 80 μm in thickness and optical surface finish for PLM observation.

3. Results and discussion

Fig. 1 shows the dielectric permittivity (ε) and loss ($\tan\delta$) as function of temperature for unpoled and poled [001]-oriented 0.24PIN–0.51PMN–0.25PT single crystal on heating and cooling