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Phase Transitions and Domain Structures in Relaxor-based Ferroelectric $(PbZn_{1/3}Nb_{2/3}O_3)_{0.915}(PbTiO_3)_{0.085}$ Single Crystal

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Polarization-electric field (P-E) hysteresis loops and domain structures have been measured as a function of temperature in relaxor-based ferroelectric single crystal $(PbZn_{1/3}Nb_{2/3}O_3)_{0.915}(PbTiO_3)_{0.085}$ (PZN-8.5%PT). In order of increasing temperature, PZN-8.5%PT undergoes successive phase transitions: rhombohedral phase (below ~375 K) → coexistence of rhombohedral and tetragonal phases (between ~375 and ~390 K) → tetragonal phase (between ~390 and ~420 K) → coexistence of tetragonal and cubic phases (between ~420 and ~460 K) → cubic phase (above ~460 K). Phase coexistence suggests an inhomogeneous distribution of Ti^{4+} concentration in the PZN-8.5%PT crystal.

Keywords: relaxor-based ferroelectric; PZN-8.5%PT; phase transition; domain structure

INTRODUCTION

Relaxor ferroelectrics generally mean the complex perovskites with ABO_3-type unit cell and are crystals in which unlike-valence cations belonging to a given site (A or B) are present in the correct ratio for charge balance, but are situated randomly on these cation sites. These randomly different cation charges give rise to random fields, which tend to make the phase transitions "diffuse" instead of sharp as in normal ferroelectrics.[1] Lead zinc niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN), has a disordered complex structure in which the Zn^{2+} and Nb^{5+} cations exhibit short-range order on the B site. Near 410 K, the PZN crystal undergoes a diffuse phase transition (which is characterized by a broad frequency-dependent dielectric maximum) and

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has rhombohedral symmetry at room temperature with space group *R3m*.[2] The normal ferroelectric (FE) crystal $PbTiO_3$ (PT) has tetragonal symmetry with space group *P4mm* at room temperature and has a normal FE phase transition taking place at $T_c = 760$ K.[2]

The relaxor-based FE crystals $(PbZn_{1/3}Nb_{2/3}O_3)_{1-x}(PbTiO_3)_x$ (PZN-*x*PT) naturally have a morphotropic phase boundary (MPB) (for $\sim 5\% < x < \sim 14\%$) and exhibit successive phase transitions as temperature changes.[3] The spontaneous deformations of the tetragonal state appear along the equivalent $\langle 001 \rangle$ directions, giving six FE domain states and the optical axes (OA) oriented parallel to $\langle 001 \rangle$. In the low temperature region, the crystals exhibit a polar rhombohedral phase, which has eight equivalent FE domain states and the OA oriented along the $\langle 111 \rangle$ direction.

Several papers have reported the large piezoelectric constants ($d_{33} \sim 1500 \times 10^{-12}$ C/N) and electromechanical coupling parameters ($k_{33} \approx 92\%$) of PZN-*x*PT crystals.[4,5] Such high piezoelectric performance, which converts mechanical and electric energies, is crucial in medical imaging, telecommunication and ultrasonic devices and may revolutionize these applications.[5] Many works have been undertaken on the growth and characterization of relaxor-based ferroelectrics.[6–10] However, limited attention has been paid to fundamental issues in these crystals, such as phase transitions and domain structures. It is believed that phase coexistence and domain structure near the MPB play an important role in the high electro-mechanical coupling effect. Therefore, to provide better physical understanding, we carried out temperature-dependent measurements of P-E hysteresis loops and domain structures on a PZN-8.5%PT single crystal.

EXPERIMENTAL

The lead zinc niobate-lead titanate single crystal PZN-8.5%PT was cut perpendicular to the $\langle 001 \rangle_{cub}$ direction without electric poling. Here, direction "$\langle\rangle_{cub}$" refers to the pseudocubic axes. For measurement of P-E hysteresis loop, the applied electric field was along the $\langle 001 \rangle_{cub}$ direction. The measuring frequency of electric field is 47 Hz. A *Janis Model CCS-450* closed cycle refrigerator was used with a *Lakeshore Model 340* temperature controller.

Domain structures were studied by using a *Nikon Model E600POL* polarized light microscope. The sample was cut perpendicular to the $\langle 001 \rangle_{cub}$ direction and was finely polished. In order to minimize superposition of domains, the thickness of sample was about 40 μm. A *Linkam Model THMS600* heating/cooling stage mounted on the microscope was used for studying domain structures as a function of temperature. Domain structures were observed between crossed polarizer-analyzer along the $\langle 001 \rangle_{cub}$ direction. When observing the $\langle 001 \rangle_{cub}$-cut sample between crossed polarizers, the cross section of the optical indicatrix will exhibit extinction directions parallel to equivalent $\langle 110 \rangle_{cub}$ directions in the rhombohedral domain.[11] For the tetragonal domain, the extinction parallels to equivalent $\langle 100 \rangle_{cub}$ directions.[11]

RESULTS AND DISCUSSION

P-E hysteresis loops for several selected temperatures are shown in Fig. 1. At room temperature, the remanent polarization P_r of PZN-8.5%PT is about 24 $\mu C/cm^2$, and is about the same as the spontaneous polarization P_s defined

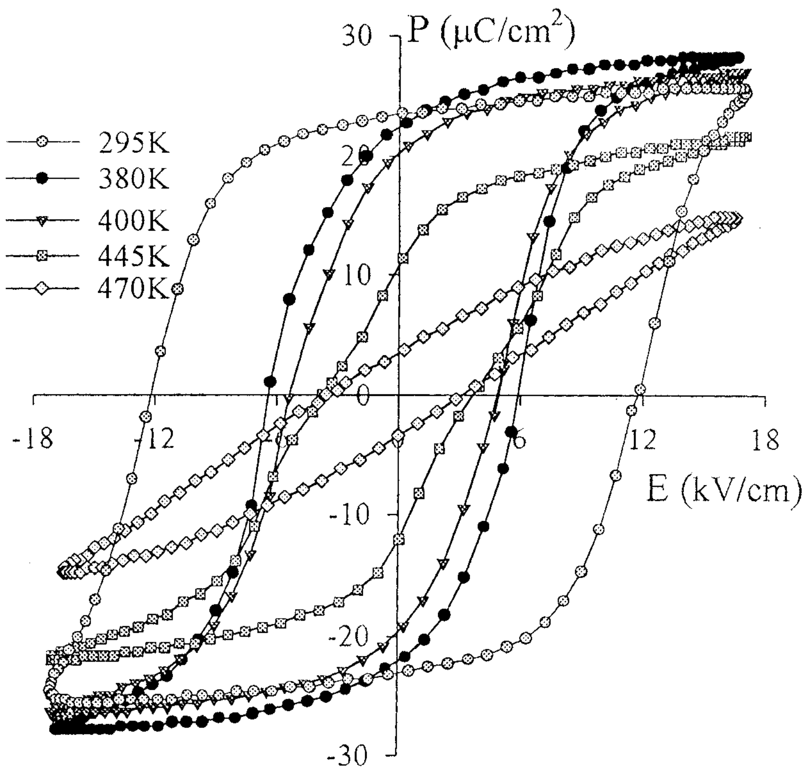

Figure 1. P-E hysteresis loops upon heating sequence.

as the intercept at zero field of the straight-line portion of the hysteresis loop. The temperature-dependent behaviors of P_r and dielectric permittivity ε are plotted in Fig. 2. The data of dielectric permittivity ε were taken from our previous result,[12] in which ε exhibits a broad frequency-dependent behavior with maximums located near 445 K. As shown in Fig. 2(i), remanent

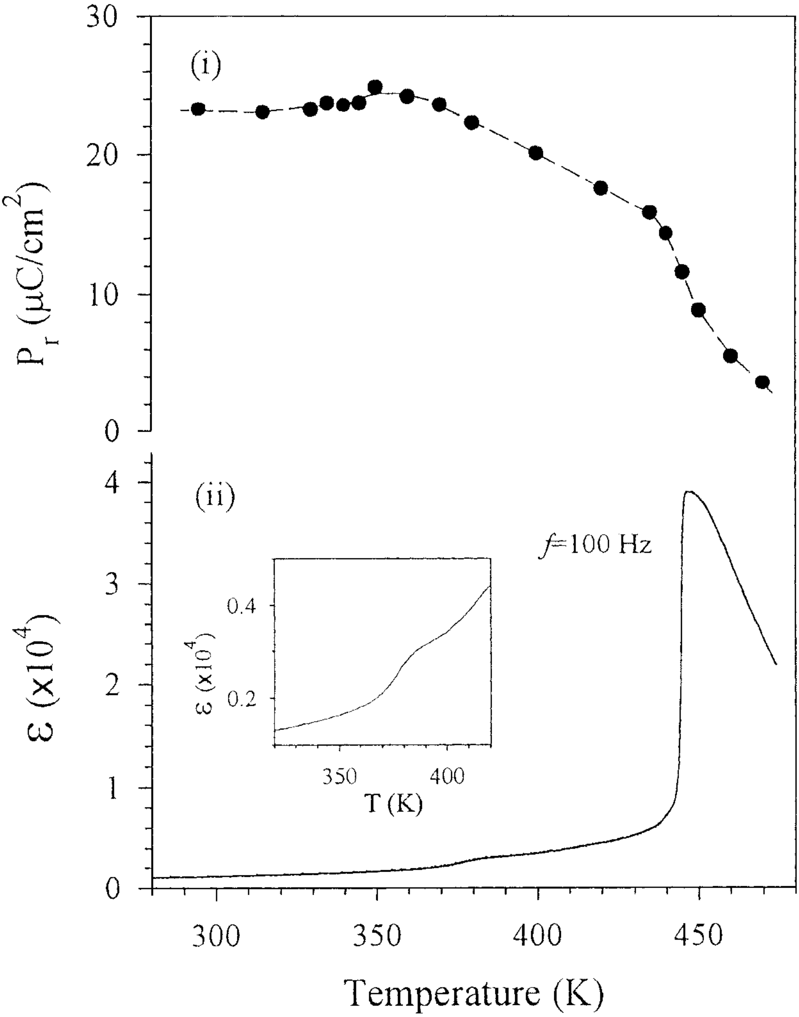

Figure 2. Temperature dependences of (i) remanent polarization P_r and (ii) dielectric permittivity ε. The dashed lines are guides for the eye.

polarization P_r shows a weak step-up anomaly near 350 K. Such an anomaly may relate to a field-induced phase transition. A gradual step-like dielectric anomaly [inset of Fig. 2(ii)] was also observed near 375 K. Compared with the prototypical relaxor PZN (whose ε_m is about 5×10^4),[2] the ε of PZN-8.5%PT shows a lower value of $\varepsilon_m \sim 2.6 \times 10^4$ (for $f = 10$ kHz). $T_m \sim 445$ K corresponding to the temperature giving maximum value ε_m, is higher than one of PZN due to PT content.

Temperature-dependent domain structures of PZN-8.5%PT are shown in Fig. 3 upon heating sequence. Fig. 3(a) shows complicated inference patterns at room temperature. These inhomogeneous inference patterns are probably caused mostly by clusters or micro-domains but partly by macro-domains with deviation of the extinction direction from normal crystallgraphic axes. In order to find out symmetries of domains, Fig. 3(b) shows domain structures after the crossed polarizer-analyzer was rotated 45°. Clearly, most area of domain patterns become dark (optical extinction). Since extinction direction of rhombohedral state is along the $\langle 001 \rangle_{cub}$ direction,[11] Fig. 3(b) reveals that PZN-8.5%PT possesses a rhombohedral phase at room temperature. As temperature increases, as shown in Fig. 3(f & g), near 377 K "bright" domain regions begin to show up and the crystal turns into fully optically transparent near 390 K. These phenomena indicate that PZN-8.5%PT undergoes a coexistence of rhombohedral and tetragonal phases between ~375 and ~390 K, and develops a tetragonal phase entirely above 390 K. It is believed that the gradual step-like dielectric anomaly near 375 K (Fig. 2) must correlate to the slow-moving establishment of the long-range FE tetragonal state.

Upon further heating, as seen in Fig. 3(h–j), dim domain regions begin to develop near 420 K and completely occupy the PZN-8.5%PT crystal near 460 K. Instead of an abrupt change, a step-like discontinuity in P_r (Fig. 2) was observed in the region of ~420–460 K. Thus, PZN-8.5%PT undergoes another coexistence of tetragonal and cubic phases between ~420 and ~460 K, and develops an optically isotropic cubic phase entirely above 460 K. Such wide-range phase coexistence certainly is responsible for the broad frequency-dependent dielectric maximums.[12] Similar phase coexistence of tetragonal and cubic states, was observed in the PMN-xPT system.[11]

Since the MPB depends sensitively on the relative Ti^{4+} occupancy on the B site, spatial phase coexistence suggests an inhomogeneous distribution of the Ti^{4+} concentration in the PZN-8.5%PT crystal. Such a fluctuation is believed to result from a quenched unequal occupation of the B site by the competitive ions Zn^{2+}, Nb^{5+} and Ti^{4+}. Similar spatial inhomogeneous distribution of the Ti^{4+} concentration, was also observed in the PMN-xPT system.[11]

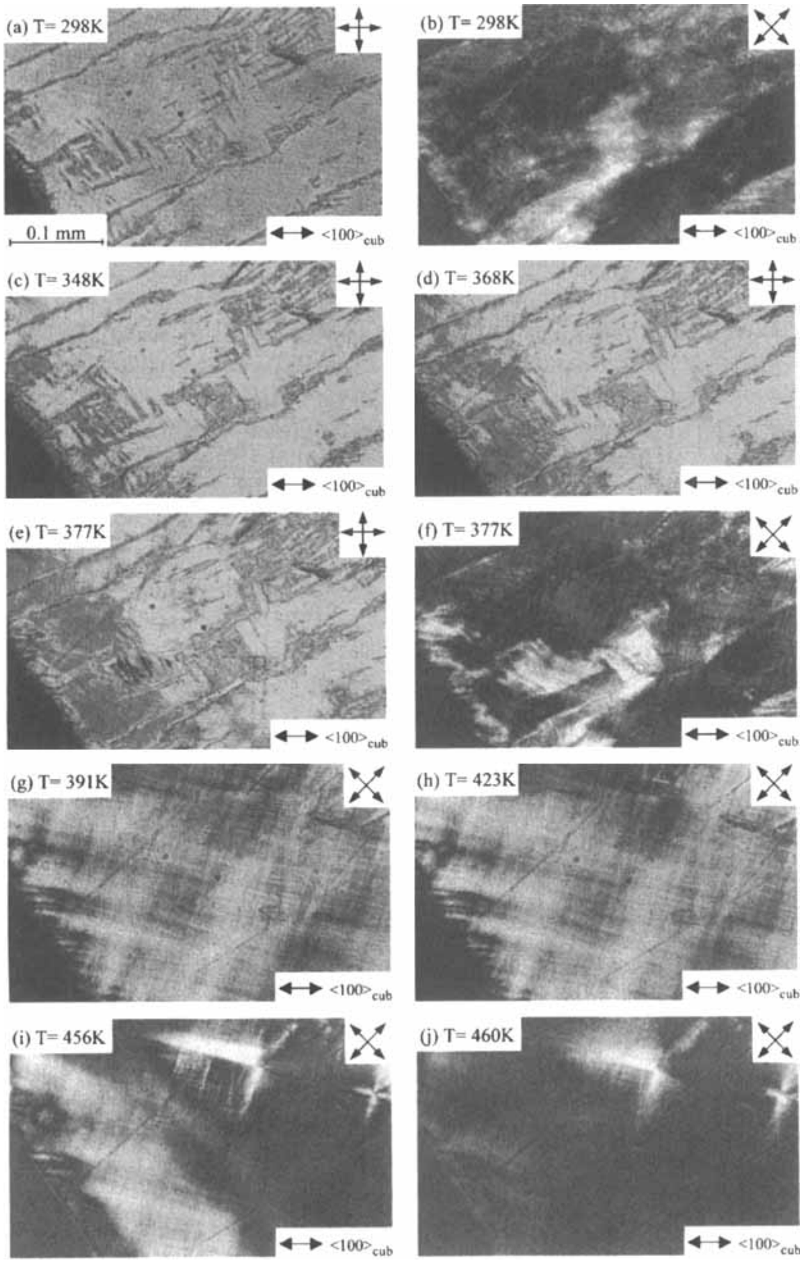

Figure 3. Domain structures observed on a $\langle 001 \rangle_{cub}$ oriented platelet upon heating sequence. (Color Plate I)

CONCLUSIONS

It was found that PZN-8.5%PT undergoes successive phase transitions as temperature changes. Below ~375 K, PZN-8.5%PT exhibits a rhombohedral (pseudocubic) FE phase. A coexistence of rhombohedral and tetragonal phases was observed in the region of ~375–390 K. Above ~390 K, the PZN-8.5%PT crystal goes entirely into the tetragonal phase. Upon further heating, PZN-8.5%PT goes into another coexistence of tetragonal and cubic phases between ~420 and ~460 K, and develops an isotropically cubic phase above 460 K. Spatial phase coexistence suggests an inhomogeneous distribution of Ti^{4+} concentration in the PZN-8.5%PT crystal.

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