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Direct observation of dynamic property of domain configuration in ferroelectric $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ single crystals with synchrotron topography

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In situ observation of the ferroelectric phase transition in $Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZNT91/9) single crystals has been carried out by white-beam synchrotron radiation X-ray topography. Sequent phase transitions are confirmed by the dynamic behavior of the domain configuration in the PZNT crystal upon heating, which exhibits good agreement with dielectric measurement of the same sample. Such ferroelectric transitions exhibit a first-order-transition character observed by the dynamic property of the domain structure combined with dielectric measurement. Abnormal fluctuation of domain walls is observed around temperatures for which phase transitions occur, which cannot be interpreted by the nature of the ferroelectric phase transition. Such interesting phenomena are supposed to be related to nucleation and growth of domains and lattice distortion induced by thermal stress. An interpretation is put forward regarding the influence of temperature on the domain-wall energy and the potential barrier surmounted for domain reversal combined with a thermal stress-induced domain effect. This experiment furnishes an understanding of the nature of a first-order ferroelectric phase transition with some diffused character.

1 Introduction

$(1-x)Pb(Zn_{1/3}Nb_{2/3})O_3 - xPbTiO_3$ (PZNT) single crystals with composition near the morphotropic phase boundary (MPB, 8–10.5 mol% of $PbTiO_3$) have attracted much attention nowadays due to their exceptionally high dielectric constant, large piezoelectric constant and electromechanical coupling factor [1, 2]. Such excellent performance makes the piezocrystals promising candidates for next-generation electromechanical transducer materials (such as in ultrasonic medical diagnostic equipment and undersea sonar applications) [3, 4]. Compared with the conventional $Pb(Zr,Ti)O_3$ (PZT) ceramic system, PZNT is relatively easy to prepare in single-crystal form over the whole composition range by a fluxing method [1, 5, 6]. Much work has been undertaken on PZNT crystal growth and physical performance, which affords abundant information on the growth mechanism and furnishes an understanding of the nature of the ferroelectric phase transition [5–7]. Lately, our research group has developed a novel modified Bridgman method to grow PZNT single crystals, which ensures the reproducible fabrication of large PZNT single crystals with high quality in pure perovskite structure [7].

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$Pb[(Zn_{1/3}Nb_{2/3})_{0.91}Ti_{0.09}]O_3$ (PZNT91/9) is a ferroelectric of complex perovskite structure, which undergoes sequent ferroelectric phase transitions upon heating, and vice versa [1, 5, 6]. During crystal growth, when the furnace temperature cooled through the Curie temperature (T_C, around 175 ± 10 °C for a PZNT crystal with the MPB composition), PZNT piezocrystals underwent a phase transition from paraelectric (PE) cubic phase to ferroelectric (FE) tetragonal and/or rhombohedral phase, depending on composition, i.e. $P4/m\bar{3}2/m \rightarrow P4mm$ and/or $\rightarrow R3m$ [8], which is a first-order ferroelectric transition with some diffused character. After the phase transition, orientational domains occurred in the FE (low-temperature) phase. According to Dudnik and Shuvalov's work, the number of orientation states in the FE phase equals $h_p/h_f = 48/8 = 6$ or $h_p/h_f = 48/6 = 8$, where h_p is the order of the space group $P4/m\bar{3}2/m$ of the prototype phase (high-temperature phase) and h_f the order of P4mm or R3m of the low-symmetry phase (low-temperature phase) [8, 9]. During the phase transition 40 or 42 symmetry elements are lost. Any of the lost elements can characterize the boundary, but they generate different orientations or positions of the boundary in PZNT crystals. That is to say, there are six different kinds of orientational domains and 15 kinds of boundaries (twin boundaries) between them in tetragonal FE phase, or eight orientational domains and 28 twin boundaries in rhombohedral FE phase [10].

A ferroelectric phase transition is a crystallographic transition occurring due to the low-symmetry lattice deviating slightly from the high-symmetry one, which leads to the formation of a domain structure with differently oriented spontaneous polarization. Since the domain structure as well as the composition fluctuation resulting from segregation during crystal growth influence the crystal electrical property greatly, they have absorbed considerable research effort [11–13]. However, no in situ observation of this transition has been carried out by a synchrotron radiation topography method. Compared with conventional domain-observing methods, such as polarized light and transmission electron microscopy, white-beam X-ray diffraction topography uses an efficient imaging method – a synchrotron-radiation (SR) source with characters of extremely strong intensity and natural high collimation, which offers a convenient method to map domain patterns to show the spontaneous polarization state and to observe domain dynamic behavior during variation of the sample environment in real time [10, 14, 15]. In this paper, we apply this technique to study the dynamic behavior of domain configuration across the rhombohedral and/or tetragonal–cubic FE and/or FE-PE phase transition in PZNT91/9 crystals and to discuss the possible mechanism of domain evolution as well. This investigation can furnish direct and abundant information on the dynamic behavior of domains and the nature of the ferroelectric phase transition. We believe that the dynamic property is associated with the intrinsic nature of the first-order ferroelectric phase transition with some diffused character.

2 Material and methods

PZNT91/9 single crystals used in the experiment were grown from PbO flux by a modified Bridgman method using an allomeric seed technique [7]. Crystal orientation was determined by a Laue-diffraction method. A few crystal plates were cut normal to the pseudocubic ⟨001⟩ direction and well polished to about 70 μm in thickness. Topographic observation was performed using a transmission X-ray topography technique at the 4W1A beam line of the Synchrotron Topography Station of Beijing Synchrotron Radiation Laboratory (BSRL) when the storage ring of the Beijing Electron–Positron Collider (BEPC) was run in the dedicated synchrotron-radiation mode at an energy of 2.2 GeV with an electron current varied between 110 and 40 mA. The specimens were heated in a cylindrical furnace with coiled heating elements arranged axially around the sample space. The furnace temperature was measured by a thermocouple mounted below the sample using a Eurotherm 815/818 temperature controller and the temperature scale was calibrated by an iodine-standard thermometer. The accuracy of the temperature in the furnace was estimated to be within 1.5 °C and the temperature stability was regulated to ±0.1 °C.

3 Results and discussion

Although lead and niobium are highly absorbing elements, we still obtain clear topographs with high resolution due to the high intensity of the SR source. Many reflection spots are obtained simultaneously in one Laue topograph when the incident SR white beam is normal to the PZNT (001) plane. Each Laue

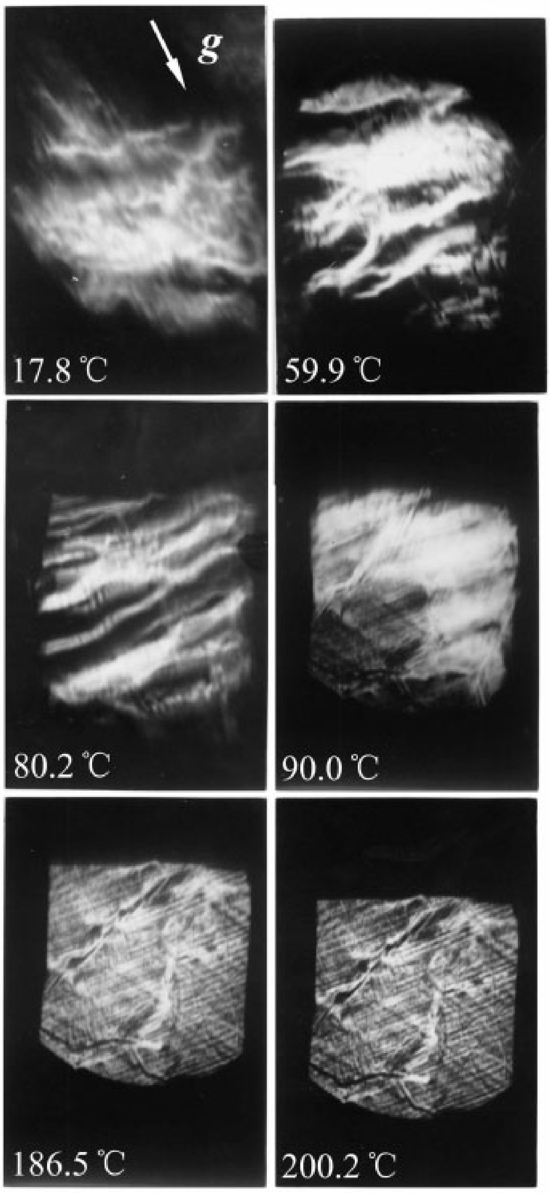

Fig. 1 Evolution of domain configuration shown by synchrotron-radiation X-ray topography of a PZNT91/9 (001) plane crystal upon heating. The distance between the film and the specimen is 154.6 mm. The storage ring was run in a dedicated mode at an energy of 2.2 GeV with the electron current varied between 110 and 40 mA.

spot was a projection of the irradiated area of the specimen along the diffracted beam onto films. Due to the existence of many kinds of orientational domains and twin boundaries discussed above, the synchrotron topographs shown on the films can display the dynamic property of the domain configuration in the PZNT91/9 crystals with increasing temperature.

Domain evolution of a PZNT (001) plate during the heating process is shown in Fig. 1. Successive changes of domain configuration with the increase of temperature indicate the occurrence of ferroelectric phase transitions, which agree well with dielectric measurement. No contrast stripe presents in the 17.8 °C topograph since the crystal crystallizes in rhombohedral FE phase, where no macro domain forms and the whole symmetry of the crystal can be regarded as cubic due to the random orientation of spontaneous polarization. Wide alternate bright–black contrast stripes appear at the left-hand part of the 59.9 °C topograph, whereas the other part shows no apparent change. Combined with dielectric measurement (an abnormal shoulder present around this temperature in the dielectric response), such a change of domain structure is supposed to be related to the rhombohedral FE–tetragonal FE phase transition [1, 2, 5–7].

With the further increase of temperature, these domain-contrast stripes progressively pervade the whole reflection spot from bottom to top due to the spatial temperature gradient existing in the sample, which is illustrated in the 80.2 °C topograph. The dielectric character also indicates that the sample changes wholly into a tetragonal FE state. An unusual variation of domain contrast appears in the 90.0 °C topograph – regular dense black–bright stripes appear at the left corner part accompanied with a decrease of contrast of the other part, which is presumed to be correlated with further nucleation of domains, domain growth and lattice distortion induced by thermal stress.

Dielectric measurement shows a FE–PE phase transition at around 180 °C, which indicates that the crystal will change into a homogeneous PE state and the ferroelectric domain structure will disappear at an elevated temperature due to the thermal hysteresis character of the first-order transition [16]. However,

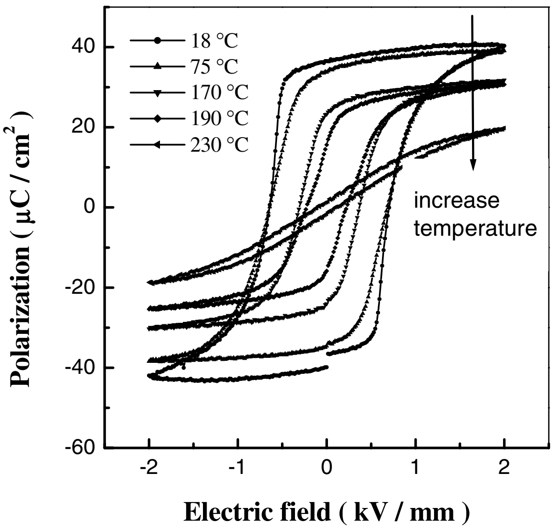

Fig. 2 Temperature dependence of the polarization induced by electric field of a flux Bridgman PZNT91/9 (001) plane crystal.

the SR topographs exhibit an abnormal phenomenon. In the 186.5 °C topograph two sets of dense regular domain-contrast stripes cross each other at a small angle and occupy the whole spot. Although ferroelectric measurement confirms that spontaneous polarization can be retained at temperatures higher than the Curie temperature, indicating micro FE state regions distributed in the PE state matrix (Fig. 2), it cannot explain the appearance of such a dense domain contrast. When increasing the temperature further, the contrast of the domain stripes enhances and the domain stripes become wider. Such an abnormal phenomenon is regarded as being related to lattice distortion induced by thermal stress, which is further confirmed since the margin of the reflection spots becomes clear gradually with the increase of the temperature.

The ferroelectric phase transition in the PZNT91/9 crystal is of first order with some diffused character, which can be explained using a phenomenological Landau-type expansion of the free energy in terms of the ferroelectric order parameter P [17, 18]

$$G = G_0 + \alpha_0(T - T_0)\,\eta^2 + \beta\eta^4 + \Lambda\,. \tag{1}$$

The change of the energy of a domain wall E_w during the ferroelectric phase transition is just the difference between the Landau–Ginzburg energy and the Landau energy, displayed in the following form:

$$E_w = \int [G(x) - G]\,dx = \int \{\alpha_0(T - T_0)\,[\eta^2(x) - \eta^2] + \beta[\eta^4(x) - \eta^4] + \Lambda + K[d\eta(x)/dx]^2\}\,dx\,. \tag{2}$$

The abnormal domain fluctuation shown in the 90.0 °C topograph can be interpreted from the temperature dependence of the domain-wall energy and the potential barrier surmounted for the reversal of domains. Such a dependence influences the probability of domain-wall annihilation J_a and creation J_c, in the present case, which can be expressed in the following forms, respectively [19]:

$$J_a = A \exp\,[-(\Delta G_p V - E_w S)/kT] \tag{3}$$

and

$$J_c = C \exp\,[-(\Delta G_p V + E_w S)/kT]\,, \tag{4}$$

where ΔG_p is the potential barrier that must be surmounted for the domain reversal per volume of the domain, E_w is the energy of the domain wall per area of domain wall and V and S are the volume of the domain and the interface area of the domain wall, respectively. For the sake of simplification, we suppose that V and S are approximately constant and the coefficients A and C are temperature independent. Since the decrease of the potential barrier ΔG_p is drastically faster than that of the domain-wall energy E_w with the increase of temperature, the domain configuration disappears finally at an elevated temperature.

However, domain walls can be readily introduced in PZNT crystal by thermal stress, which exerts a great influence on the ferroelectric when the rising temperature approaches the Curie point. Then the energies ΔG_p and E_w become vanishingly small, i.e. the creation of domain walls will become easy. Such a complex domain configuration is observed on the white-beam topographs with strong contrast as domain walls.

4 Conclusions

In situ observation of the ferroelectric phase transitions in PZNT91/9 single crystals has been performed by synchrotron-radiation X-ray topography. Successive changes of domain contrast with the increase of temperature are observed in the synchrotron topographs, which agree well with the dielectric measurement, indicating that the sequent phase transitions are of first order. Abnormal fluctuation of domain walls appears in the 90.0 °C topograph and the topographs around the Curie temperature, which can be interpreted as further nucleation of domains, domain growth and lattice distortion induced by thermal stress. Such interesting phenomena are considered to be relevant to the nature of a first-order ferroelectric phase transition with some diffused character.

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