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Study of electric-field-induced phase transitions in [111] oriented $0.955Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.045PbTiO_3$ single crystals

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Abstract

We report the presence of a field-induced intermediate ferroelectric phase in pre-poled [111] oriented $0.955Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.045PbTiO_3$ (PZN–4.5%PT) single crystals, based on the dielectric, differential scanning calorimetry and pyroelectric measurements. It was found that this phase exists in a very narrow interval of 4.3 °C between the ferroelectric rhombohedral and tetragonal phases. This may be explained as an electric-field-induced orthorhombic phase based on previous investigations on the PZN–8%PT single crystals. An electric-field-induced phase diagram of <111> oriented PZN–PT has been redrawn based on this study.

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1. Introduction

Piezoelectric materials, which interconvert the mechanical and electrical energies are widely used in many industrial, military and civilian applications, such as medical ultrasonic transducers, sonar system and telecommunication. Single-crystal relaxor ferroelectrics with very large piezoelectric strains have been developed recently in the lead zinc niobate–lead titanate (PZN–PT) system, at PT concentrations between 4% and 9% [1,2]. It has been demonstrated [3,4] that the superior piezoelectric properties of PZN–PT crystals within these concentrations are closely correlated with the morphotropic phase boundary (MPB), similar to the case of lead zirconate titanate (PZT) piezoceramics, although the maximum piezoelectric coefficient occurs just before the MPB in the PZN–PT system and within the MPB in the PZT case.

The phase stability of the PZT ceramics and the PZN–PT crystals is complicated. Investigations on PZT ceramics have shown the presence of a ferroelectric monoclinic FE_m phase over a very narrow composition range near the MPB between ferroelectric rhombohedral and tetragonal phases [5,6]. It was proposed that the polar direction in this phase lies in the <hhk> type planes, which may act as a bridge between the tetragonal <001> and rhombohedral <111> polarization directions. This “bridging” effect is suggested to be responsible for the enhanced electromechanical properties in PZT near the MPB. Recently, experimental evidence by high-energy X-ray diffraction also shows the presence of a ferroelectric orthorhombic FE_o phase in between FE_r and FE_t phases in PZN–PT crystal system near the MPB composition [7,8].

A few studies have been carried out to determine the stability range of each of the “morphortropic” phases in PZN–PT crystals. Priya et al. [9] reported the presence of an intermediate FE_o phase in between the FE_r and FE_t phases in poled <111> 0.92PZN–0.08PT (PZN–8%PT) single crystals through dielectric and pyroelectric measurement. Lu et al. [10] found similar results in poled PZN–8%PT and 0.9PZN–0.1PT (PZN–10%PT) crystals based on the optic and dielectric data acquired under different electric conditions and temperatures, while FE_o phase was not found in

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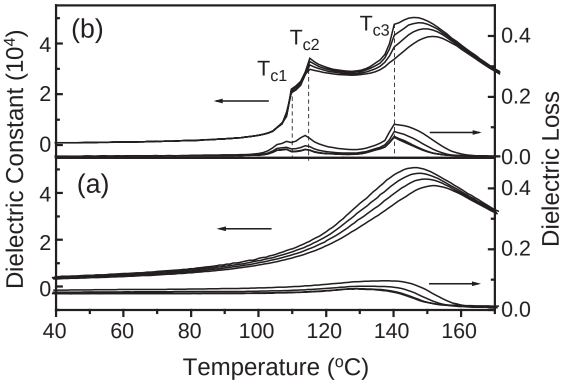

Fig. 1. Dielectric constant and loss as a function of temperature of (a) unpoled and (b) poled under 0.6 kV/cm <111> oriented PZN–4.5%PT crystals.

the 0.955PZN–0.045PT (PZN–4.5%PT) for all the orientations in their study. Forrester et al. [11] have also reported that there are only two electrical-field-induced phase transitions from FE_r to FE_t and then to cubic in poled <111> PZN–4.5%PT crystals by means of single-crystal neutron diffraction. These results seems to be in disagreement with the first-principles calculations in this material by Fu and Cohen [12], which predicted the rotation of the polarization between the rhombohedral and tetragonal phases via a third phase. In the present study, we found clear evidence showing the presence of the intermediate phase in between the FE_r and FE_t phases in poled <111> PZN–4.5%PT single crystals through dielectric, differential scanning calorimetry (DSC) and pyroelectric measurements, although it exists in a very narrow temperature region.

2. Experiment

The electric-field-induced phase transitions were studied by the following three methods: dielectric, DSC, and pyroelectric measurements. The measurements were performed on the same [111] oriented PZN–4.5%PT single crystals grown by the high temperature flux method. The crystals were cut into a plate shape with the orientations of [111], $[\bar{1}10]$ and $[\bar{1}\bar{1}2]$, respectively. The sample dimensions are 4 × 4 × 1 mm with the larger surface to be the [111] face. The [111] and $[\bar{1}\bar{1}\bar{1}]$ faces were polished and electroded with gold. First, the sample was cooled under a 0.6 kV/cm electric field from a temperature above 200 °C to room temperature, then different measurements were performed on heating from room temperature up without bias. The dielectric and pyroelectric responses were measured using a HP4284A LCR meter and a Kethley 6517A meter, respectively. The temperature was controlled by a computer assisted Delta 9023 oven at a rate of 3 °C/min and measured using a platinum resistance thermocouple and a Keithley 740 system scanning thermometer. The thermocouple was mounted inside an aluminum plate, which supports the sample. DSC was performed using a Perkin-Elmer DSC7 tester in the temperature increasing mode with a scan rate of 3 °C/min.

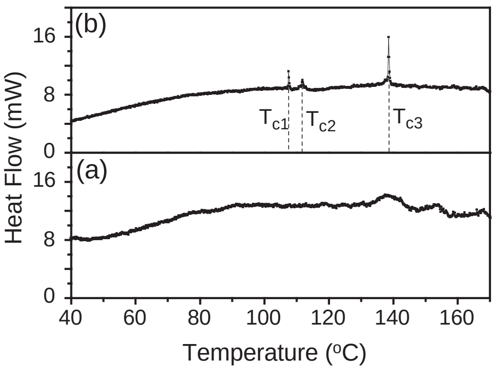

Fig. 2. DSC data as a function of temperature corresponding to Fig. 1.

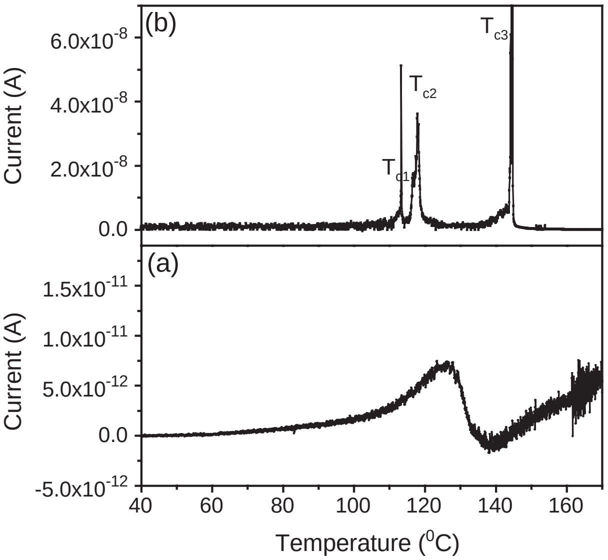

Fig. 3. Pyroelectric current as a function of temperature corresponding to Fig. 1.

3. Results and discussions

In a recent study [13], we have reported the dielectric anomalies in [111] oriented PZN–4.5%PT single crystals under different electrical and thermal conditions based on the dielectric measurements, and found three dielectric anomalies during zero-field heating the poled sample from room temperature up to 200 °C. Fig. 1(a) and (b) shows the dielectric constant and loss as a function of temperature for the unpoled and poled sample, respectively. Compared with the unpoled case, three dielectric anomalies were

Table 1
The field-induced phase transition temperatures measured by three different methods

Unit: °C	T_{c1}	T_{c2}	T_{c3}	(T_{c2}-T_{c1})	(T_{c3}-T_{c2})
Dielectric constant and loss	109.6	113.9	140.3	4.3	26.4
DSC measurement	107.4	111.5	138.0	4.1	26.5
Pyroelectric current	113.1	117.6	144.2	4.5	26.6

induced in the poled sample as shown in Fig. 1(b), which were assumed to be associated with FE_r–FE_o, FE_o–FE_t, and FE_t–cubic phase transitions [13], similar to the analysis in the [111] oriented PZN–8%PT single crystals [9]. However, since T_{c1} is very close to T_{c2}, and the transition at T_{c1} is only a kink instead of a peak in the figure, the phase transition at T_{c1} is inconclusive based on the dielectric data alone. Thus, we performed DSC and pyroelectric measurements to further confirm these three field-induced phase transitions.

DSC monitors heat effects associated with phase transitions in solids as a function of temperature. The intensity of the heat flow is plotted in Fig. 2 as a function of temperature for both unpoled and poled samples. Upon heating the sample, three endothermic peaks occur in the poled one, confirming the existence of three electric-field induced phase transitions. Fig. 3(a) and (b) shows the pyroelectric measurements for the unpoled and poled crystals, respectively. Again three field-induced peaks are obviously present in the poled sample. The positions of these three temperature peaks obtained by the above three measurements are summarized in Table 1. On average, T_{c1}, T_{c2} and T_{c3} are centered near 110, 114 and 141 °C, respectively. However the temperature peaks of T_{c1}, T_{c2} and T_{c3} are slightly different when the test method is changed, which is ascribed to the slight difference in the transition temperature to the different mechanism of each measurement. However, the intervals between these three peaks obtained by the three measurements are almost the same (4.3 ± 0.2 °C for $T_{c2}-T_{c1}$ and 26.5 ± 0.1 °C for $T_{c3}-T_{c2}$), as presented in Table 1. From the results in Figs. 1-3, one can conclude that an intermediate phase exists between the rhombohedral and tetragonal phases in a very narrow temperature interval of 4.3 °C for the PZN–4.5%PT crystal. Because we cannot determine the crystal symmetry of this intermediate phase from the above measurements and the high temperature XRD system doe not have enough resolution, we use the information from Refs. [9,10], which is a similar investigation on [111] oriented PZN–8%PT, to identify this intermediate phase to be orthorhombic. One reason that this phase was not identified in previous neutron and optical investigations [10,11] is the narrow temperature interval for this FE_o phase in the PZN–4.5%PT, unlike the situation in PZN–8%PT.

As demonstrated above, dielectric, DSC and pyroelectric measurements provide key information to confirm the observation of a field-induced orthorhombic phase in PZN–4.5%PT single crystals. At room temperature, the poled [111] oriented crystal has rhombohedral symmetry, with a unique polar axis along <111>. At about 110 °C, a transition to FE_o phase occurs, which has a unique polar axis along <110>. As pointed out by Priya et al. [9] that the existence of an intermediate transitional region between FE_r and FE_o having the symmetry of the monoclinic point group is essential, in order to accommodate the strain generated by the deformation of the crystal from 3 m to 4 mm symmetries. Our results are also consistent with the phenomenological prediction of Amin et al. [14] that an orthorhombic ferroelectric phase was always present as a metastable state in PZT. On the rhombohedral side of the MPB, it was higher in free energy than the rhombohedral phase, but lower than the tetragonal ones. We believe that this is similar to the case of PZN–4.5%PT, a ferroelectric orthorhombic ferroelectric phase, that is very close in free energy to the rhombohedral one, can exist in PZN–4.5%PT, but the temperature interval for this phase is very narrow.

The above results allow us to comment on the electric-field-induced phase diagram of <111> oriented PZN–PT. Base on our new data, we have modified the phase diagram of Lu et al. [10] to give a new phase diagram as shown in Fig. 4. The data points represent the peak positions of the dielectric loss at different compositions. Note the data for pure PZN is taken from Ref. [15]. Our new data are shown at $x = 4.5$, which extend the region of the FE_o phase although the modification to the diagram of Lu et al. is fairly minor.

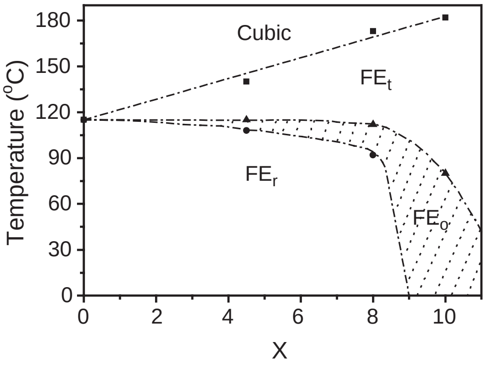

Fig. 4. The phase diagram for <111> oriented PZN–PT (X is the mol% of PT) with the transition temperatures. The data at $X = 4.5$ were determined in this work. The data at $X = 0$ is taken from Ref. [15] and the data at $X = 8$ and 10 were taken from Ref. [10]. The dashed and solid lines are suggested phase boundaries.

4. Conclusions

Based on the dielectric, DSC and pyroelectric measurements, one can clearly see three electric-field-induced phase transitions in pre-poled [111] oriented PZN–4.5%PT single crystals, which we describe them as the structural phase transitions from FE_r to FE_o, from FE_o to FE_t, and from FE_t to cubic, respectively. The intermediate phase, which we believe to be the orthorhombic FE_o phase, similar to the report of Refs. [9,10] for PZN–8%PT, exists in a very narrow temperature interval of 4.3 °C between the ferroelectric rhombohedral and tetragonal phases. Based on this new information, we have modified the electric-field-induced phase diagram of <111> oriented PZN–PT system as shown in Fig. 4.

Acknowledgments

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