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Metastable ferroelectric phase in lanthanum-doped lead zirconate titanate stannate antiferroelectric ceramics

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Abstract

Metastable ferroelectric phase induced by electric field in lanthanum-doped lead zirconate titanate stannate antiferroelectric ceramics near morphotropic phase boundary were studied as a function of electric field, temperature and hydrostatic pressure. Upon application of an electric field to the antiferroelectric ceramics, the rhombohedral FE phase can be induced from tetragonal AFE phase when the induced field was larger than the critical field $E_{\text{AEF-FE}}$, and the induced FE phase can remain metastable state when the electric field was removed. The metastable FE phase was unstable, which recovered to AFE phase again with the increasing of temperature at about 80 °C and the increase of hydrostatic pressure at 150 MPa, respectively. Large charge release from remanent polarization of metastable FE phase was accompanied with phase transition. The relationships of critical parameters of field-induced phase transition were also shown.

Keywords: A. Powder: Solid state reaction; C. Electrical properties; D. PZT; Metastable phase

1. Introduction

Antiferroelectric ceramics of lead zirconate stannate titanate (PZST) in Zr-rich region have been studied extensively in the past 40 years for many potential applications, such as large displacement transducer, high charge-storage capacitor, pyroelectric detector, and so on [1–4]. When the compositions of PZST are near the antiferroelectric (AFE) and ferroelectric (FE) morphotropic phase boundary (MPB), the free energy difference between AFE and FE phase is small [5]. As a result, it is easy to control the AFE-FE or FE-AFE phase transition of these ceramics by the external fields of electric-filed, stress or temperature [1], it is also easy to tailor the phase transition behaviors by modifying the composition [6,7]. Due to the differences of AFE and FE phases in the unit cell parameters, this phase transition is accompanied by a nonlinear change in physical properties, such as an abrupt jump in polarization and strain, or large charge release.

In this paper, metastable FE phase induced by electric field was studied as a function of temperature and pressure. The phase structure was shown with different conditions. The relationships of critical parameters of temperature-induced and pressure-induced phase transition were also given for potential applications.

2. Experimental procedure

The composition chosen for study was $(Pb_{0.98}La_{0.02})(Zr_{0.75}Sn_{0.15}Ti_{0.1})_{0.995}O_3$, which is in the region of AFE phase, near the morphotropic phase boundary (MPB) between AFE phase and FE phase [1]. It is well known that AFE phase is tetragonal structure, and FE phase is rhombohedral structure here.

Samples were prepared by conventional solid-state reaction using the reagent-grade raw materials. The raw materials were first mixed and pre-sintered at 900 °C for 2 h, and then sintered at 1250 °C in lead-rich environment in order to minimize lead volatilization. All samples were disks of 10 mm in diameter and 0.5 mm in thickness.

Electric field-induced polarization as a function of temperature was measured using a computer controlled Sawyer–Tower circuit. A Trek Model 609A dc amplifier supplied a high-voltage with 0.39 Hz sine wave. Pyroelectric current was measured from −10 to 200 °C with a HP 4140B pA meter by Byer-Roundy method. The total charge release forced

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by hydrostatic pressure was collected and recorded with Keithley 6517A electrometer.

3. Results and discussion

Fig. 1 shows the XRD patterns of antiferroelectric ceramics with different conditions at room temperature. Curve (a) shows the result of virgin sample. Obviously, tetragonal structure was observed, i.e., the virgin sample was AFE phase. Curve (b) shows the result after sample was poled. As shown, the structure of sample was changed to rhombohedral phase, i.e., the poled sample was FE phase. Curve (c) shows the result after poled sample was forced by hydrostatic pressure. We noted that the structure of this sample recovered to tetragonal AFE phase again.

It is well known that the remanent polarization of AFE phase is zero when the applied electric field is zero. Fig. 2 shows the polarization-electric field hysteresis loop with first cycle of virgin sample at room temperatures. Here, the $E_{\text{AFE-FE}}$ represents the forward switch field to induce AFE to FE phase transition, and the E_c represents the coercive field of FE phase. As shown, virgin sample was first induced from AFE to FE phase with a high switching field of $E_{\text{AFE-FE}}$, and then the remanent polarization P_r remained after electric field was removed, i.e., the induced FE phase remained by the form of metastable phase. Obviously, the forward switch field $E_{\text{AFE-FE}}$ of AFE phase was larger than the coercive field E_c of FE phase. Here, $E_{\text{AFE-FE}} = 2.1$ kV/mm, $E_c = 1$ kV/mm. Therefore, the virgin sample was intrinsic AFE phase for this composition, which was coincident with the XRD patterns shown in Fig. 1(a). After poled, the phase structure of virgin sample was changed to FE phase at room temperature. In the following, we will show that the metastable FE phase of poled sample is unstable, which will recover to AFE phase again at some conditions.

Fig. 3 shows the pyroelectric properties of poled sample, and insets show the polarization-electric field hysteresis loops of poled sample at different temperature. As shown, there was a strong current peak appeared at about 80 °C with the increase of temperature, which was caused by the charge release of remanent polarization from the metastable FE to AFE phase transition. The insets show the change of phase transition clearly. At room temperature, the poled sample showed a classical FE hysteresis loop with a low coercive field of E_c, P_r was about 27 μC/cm^2. At about 75 °C, the polarization-electric field hysteresis loops showed a tendency from FE to AFE phase transition. When temperature was above 80 °C, it was noted that the poled sample showed a classical double-hysteresis loop characteristic of AFE phase, not FE phase. The P_r was zero after the electric field was removed.

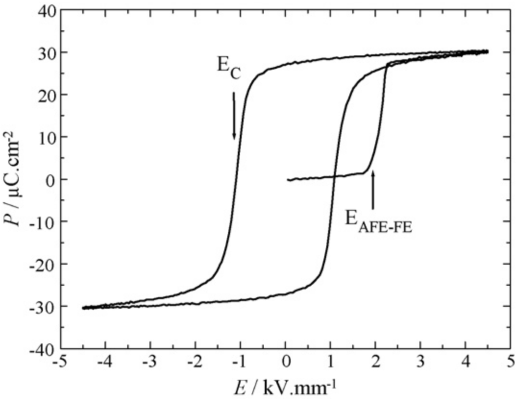

Fig. 2. Polarization-electric field hysteresis loops of virgin sample with first circle at room temperature.

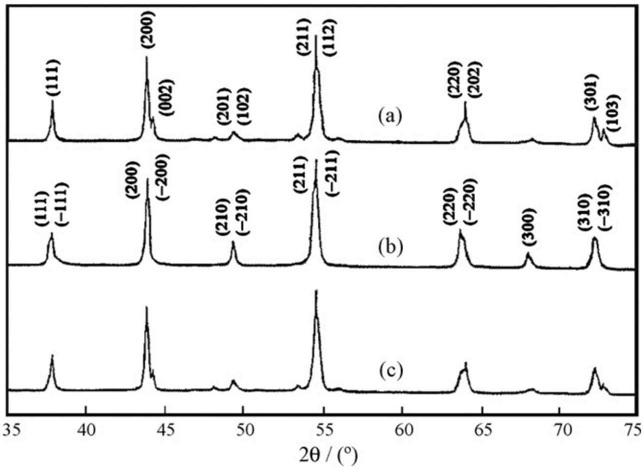

Fig. 1. XRD patterns with different conditions at room temperature (a: virgin, b: poled, c: pressured).

According the above results, therefore, it suggested that below a certain temperature, the induced metastable FE phase could remain, but it was unstable. As the increasing of temperature, the metastable FE phase recovered to AFE phase again at temperature of $T_{\text{FE-AEF}}$. For this composition, the $T_{\text{FE-AEF}}$ is about 80 °C. The $T_{\text{FE-AEF}}$ was observed to be dependent strongly on the composition, which increased linearly with the increase of Ti [6]. Later, we will show the $T_{\text{FE-AEF}}$ is also an important parameter of pressure-induced phase transition.

Fig. 4 shows the charge release of remanent polarization from metastable FE phase to AFE phase forced by hydrostatic pressure at room temperature. As shown, when the hydrostatic pressure was smaller than 100 MPa, the charge was released

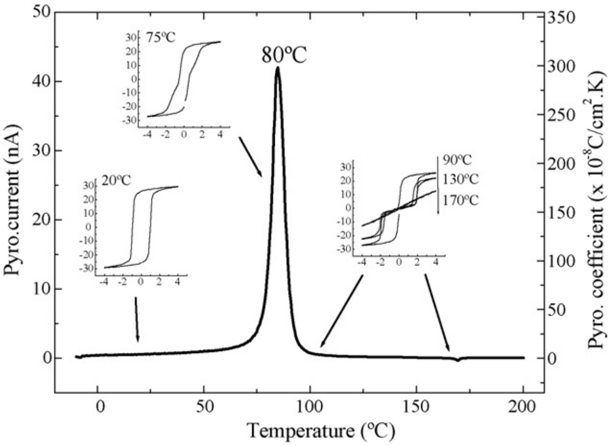

Fig. 3. Temperature dependence of pyroelectric properties of metastable FE phase.

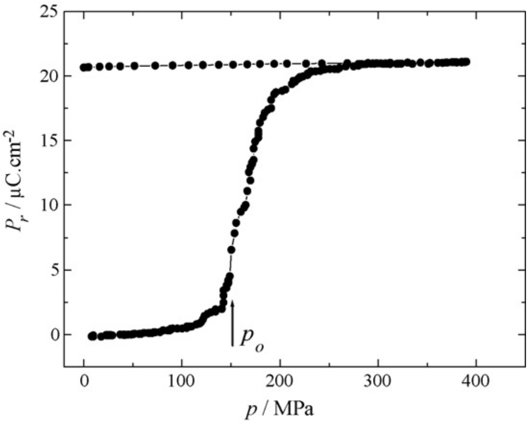

Fig. 4. Charge release of remnant polarization P_r with hydrostatic pressure from metastable FE phase to AFE phase at room temperature.

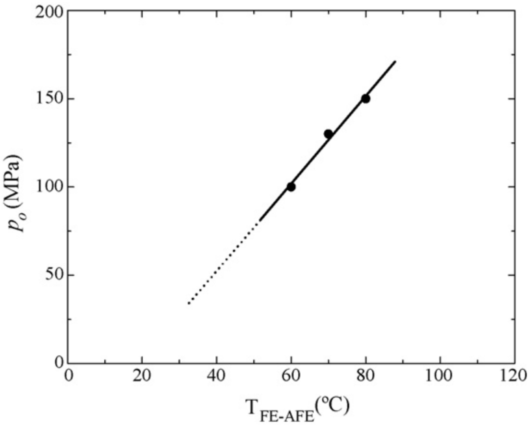

Fig. 5. Relationship between the critical hydrostatic pressure p_o and $T_{\text{FE-AFE}}$ at room temperature.

gradually. When the pressure increased more than the critical parameter p_o of 150 MPa, the charge was released rapidly. Due to the instantaneous release of charge, this property could be utilized for shock-wave transducers [8,9]. When the pressure increased more than 250 MPa, most of charge has been released. We noted that the total release of charge was about 21 μC/cm^2, which was smaller than the P_r of remanent polarization due to the loss of current leakage in the measurement. After forced by hydrostatic pressure, the polarization-electric field hysteresis loop with first circle of this sample was measured again. The curve of P–E loop with forward switch field $E_{\text{AFE-FE}}$ was observed, which was the same as shown in Fig. 2. From above results, it suggested the metastable FE phase recovered to AFE phase again after forced by hydrostatic pressure.

The p_o, shown in Fig. 4, is a critical parameter of pressure-induced FE to AFE phase transition. The value of p_o depends on the stability of metastable FE phase. In practical application, p_o with lower value is desired for high power supply [10]. In the further study, we found the p_o was close relative with the $T_{\text{FE-AFE}}$. For different compositions, the $T_{\text{FE-AFE}}$ was different, so the p_o was also changed. Fig. 5 shows the relation between p_o and $T_{\text{FE-AFE}}$. As shown, the p_o decreased linearly with the decreasing of $T_{\text{FE-AFE}}$. Therefore, it is possible to tailor the critical parameters of pressure-induced phase transition through $T_{\text{FE-AFE}}$ with different compositions [6].

4. Conclusions

Metastable ferroelectric phase induced by electric field in PZST antiferroelectric ceramics could remain when electric field was removed, but it was unstable. As the increase of temperature and hydrostatic pressure, the metastable FE phase recovered to AFE phase again at temperature of $T_{\text{FE-AEF}} \approx 80$ °C and critical pressure of $p_o \approx 150$ MPa, respectively. Large charge release from remnant polarization of metastable FE phase was accompanied. The p_o was observed to be dependent strongly on $T_{\text{FE-AFE}}$, which decreased linearly with the decreasing of $T_{\text{FE-AFE}}$.

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