

Phase transition and dielectric properties of $\text{PbLa}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$ antiferroelectric ceramics under hydrostatic pressure

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Abstract The influences of temperature and hydrostatic pressure on the dielectric constant (ϵ_r) and loss ($\tan\delta$) of $\text{PbLa}(\text{Zr},\text{Sn},\text{Ti})\text{O}_3$ antiferroelectric ceramics have been studied. Temperature-induced transition from tetragonal antiferroelectric phase to cubic paraelectric phase and low-temperature frequency dispersion are observed. The dielectric behavior as a function of temperature was determined by XRD measurement. It has been found from experimental results that the ferroelectric–antiferroelectric phase transition temperature decreased and antiferroelectric–paraelectric phase transition temperature increased with increasing pressure.

Keywords Hydrostatic pressure · Frequency dispersion · Phase transition · PLZST

1 Introduction

Under different conditions, there are plenty of phase structures including antiferroelectric ferroelectric and paraelectric phases in the antiferroelectric (AFE) lead lanthanum zirconate stannate titanate (PLZST). PLZST ceramics will exhibit complicated phase transformations under the changes of temperature ac bias and pressure [1–5]. From 1970s, there are many studies on PLZST ceramics. Antiferroelectric PLZST ceramics can undergo transformation from antiferroelectric phase to ferroelectric phase with big volume change under external ac bias. The maximal

longitudinal strain reached as large as 0.87% [6]. These high-strain phenomena have been investigated for applications including charge-storage capacitors, large displacement actuators and shape memory devices [7]. Poled antiferroelectric PLZST release the electric charge instantly for the FE/AFE phase transformation induced by the high pressure. It's a good kind of energy transformation materials and potential candidates for other applications.

In the ternary phase diagram of $\text{Pb}_{0.98}\text{La}_{0.02}(\text{Zr},\text{Ti},\text{Sn})\text{O}_3$ system, antiferroelectric ceramics near AFE/FE phase boundary undergo transformation between antiferroelectric and ferroelectric phase under low ac bias or pressure. Transition between antiferroelectric and ferroelectric can be induced by the change of temperature, electric field, or hydrostatic pressure. Despite a number of studies [6, 8, 9] concerning electrostriction, kinetics of dielectric polarization, and induced strain of the PLZST solid solution system, relative little attention has been paid to the composition 67/23/10 under temperature and hydrostatic pressure. In this paper we report on phase transformation and dielectric properties studies in the $\text{Pb}_{0.98}\text{La}_{0.02}(\text{Zr},\text{Ti},\text{Sn})\text{O}_3$ system under temperature and hydrostatic pressure. At first we ascertained phase transformation of this ceramics by X-ray diffraction method in heating process. Then we summarized the influence of hydrostatic pressure to temperature inducing phase transformation.

2 Experiment

The composition $\text{Pb}_{0.97}\text{La}_{0.02}(\text{Zr}_{0.67}\text{Sn}_{0.23}\text{Ti}_{0.10})\text{O}_3$ was chosen to characterize AFE-FE phase switching behavior. This composition is located near the boundary between the tetragonal AFE (AFE_{Tet}) and rhombohedral FE (FE_{Rh}) phases. These ceramics were prepared by traditional solid-

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state reaction process. The sintering process was conducted at 1240°C for two and half hours in a lead-rich environment to minimize lead evaporation. As showed in Fig. 1, the A_O region is the antiferroelectric orthorhombic region, the $F_R(LT)$ region is the low-temperature ferroelectric rhombohedral region and the A_T region is the antiferroelectric tetragonal region. The compositions in the A_O region are not suitable for this study because the transition field from the antiferroelectric state to the ferroelectric state is so high that the transition is difficult to be accomplished by a realizable applied external field. However, in the antiferroelectric tetragonal region, the compositions are so energetically close to those of the ferroelectric form that the switching between the antiferroelectric and ferroelectric form can be accomplished by an applied temperature electric field or hydrostatic pressure.

The piezoelectric constant d_{33} was measured by a Model ZJ-2 d_{33} meter. To study the dielectric properties with increasing pressure at different temperatures, these specimens were mounted in the pressure vessel, heated by a small resistance-heating furnace, and simultaneously recorded by a HP4274 LCR meter at a frequency of 1 kHz. The phase structure of sintered specimens was analyzed using a Rigaku D/max-2400 X-ray diffraction system. Powder XRD was obtained by scanning a 2θ range of 43.5°~45.5°. Low-temperature dielectric properties were measured with frequencies from 1 to 100 kHz by HP4274ALCR Low-temperature dielectric property system that the temperature ranged from -100 to 200°C at a 3°C/min rate.

The hydrostatic pressure was produced in a piston-cylinder type vessel with two pistons and four pillars, which could be compressed in two directions by a 120 ton hydraulic press. Hydraulic oil was used as the pressure liquid medium. The pressure was calculated from the resistance of a manganin wire stress gauge in the pressure cavity using a computer controlled Keithley 2000 multimeter with an

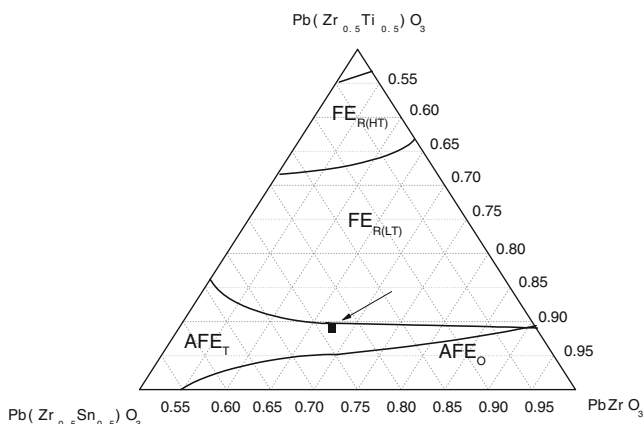


Fig. 1 Ternary phase diagram of PLZST showing composition in this work

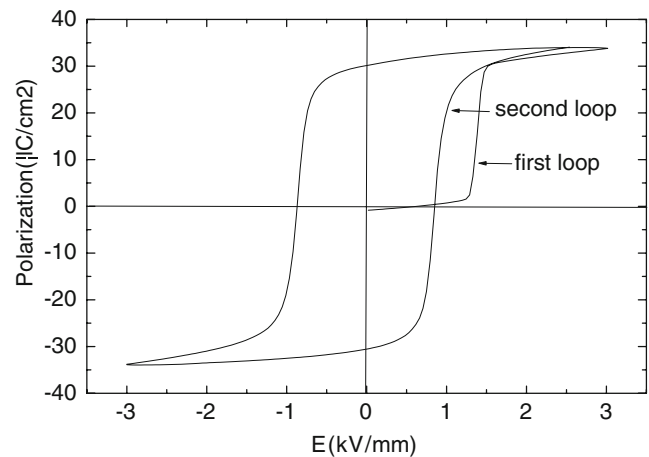


Fig. 2 Electric hysteresis loops of aboriginal specimen

accuracy better than 0.2%. To polarize these ceramic samples, the specimens were put in silicon oil under the 3 kV/mm electrical field at room temperature for 10 min.

The P - E hysteresis loops of the aboriginal sample are illustrated in Fig. 2. The first loop was taken from a virgin sample and had a small slope (dP/dE) typical of AFE behavior. A step-like transition from AFE state to the field-induced FE state takes place at $E \sim 14$ kV/cm. Afterward the system displays the “classical” ferroelectric hysteresis loop in the second loop. The induced FE state is metastable.

3 Results and discussion

3.1 Temperature induced phase transition

Figure 3 shows dielectric constant and loss vs temperature for the PLZST ceramics specimen. Measurements frequency was from 1 to 100 kHz and the temperature were from -100 to 200°C. Dielectric constant increased slowly near low temperature and the prominent peak where AFE/PE phase transformation was observed. Dielectric constant has little frequency dispersion at low temperature and decreased linearity after reaching peak value 4438 where temperature is 161°C. Dielectric frequency dispersion behavior implies the evidence of microdomain structures in the specimen. These microdomain structures may be caused by composition fluctuations.

In the high-temperature paraelectric phase, dielectric constant ϵ_r obeys Curie–Weiss law: $\epsilon_r = C/(T - T_0)$, in which C is Curie constant and T_0 is Curie–Weiss temperature. The linear temperature variation of $1/\epsilon_r$, the values of Curie–Weiss temperature T_0 and AFE/PE transition temperature T_c are indicated at 10 kHz. From Fig. 3, Curie–Weiss temperature is 99°C and Curie constant is 1.9×10^5 . It is obvious that the phase transition is first order phase transition and this ferroelectric is displacement ferroelectric.

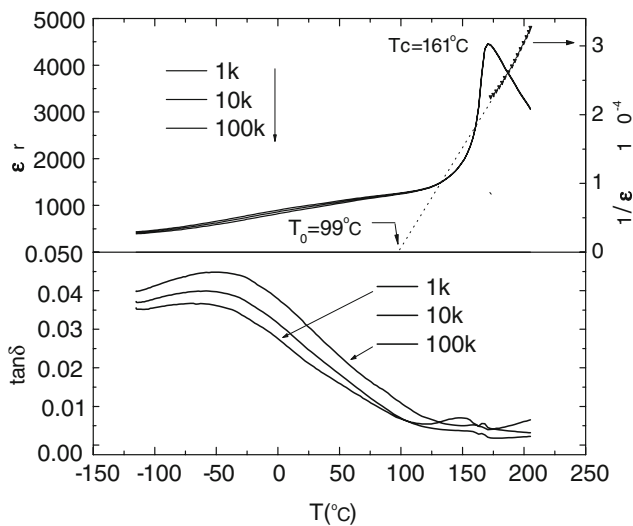


Fig. 3 Dielectric constant and loss vs temperature for PLZST ceramics specimen

4 X-ray diffraction of sample

The X-ray diffraction pattern ($2\theta=43.5^\circ\sim 45.5^\circ$) and microstructures at different temperature and zero electric field are shown in Fig. 4. In all the fits, the $k_{\alpha 2}$ diffraction fake peak and $k_{\alpha 1}$ diffraction fake peak was eliminated. It is observed from Fig. 4 that there exists an anomalous change in the X-ray diffraction pattern. As can be seen from the figure, the (200) peak and (002) peak was divided distinct at 25°C . This is no doubt due to a preferred AFE tetragonal phase domain structure at this temperature. As the temperature increased, the two peaks closed more and more and finally united to one peak at 200°C . It is indicated that in PLZST ceramics a phase transition from tetragonal antiferroelectric to cubic paraelectric happened as temperature increased. But this transformation was not in a certain temperature and it was a gradual process as temperature varied. This can be

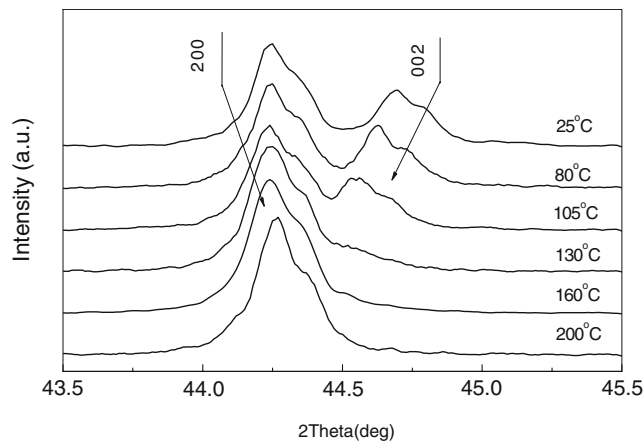


Fig. 4 XRD patterns of specimen at different temperature

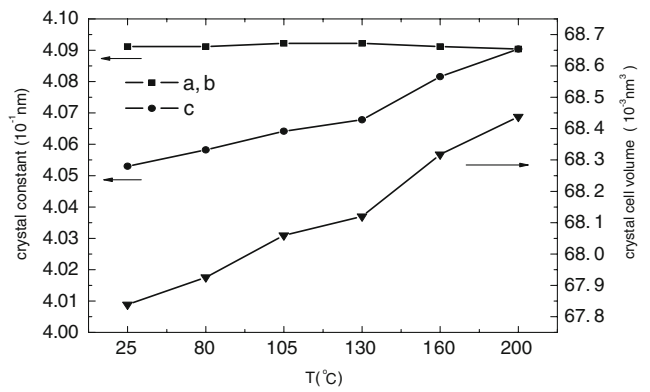


Fig. 5 Crystal lattice constant vs temperature for PLZST ceramics specimen

confirmed by the change of crystal cell parameters in the process. Using in situ X-ray diffraction, direct observations of the microstructures in the AFE with parameter $a=b=4.0910\text{ \AA}$ and $c=4.0528\text{ \AA}$ at 25°C . This rule is $a = b > c$ and it is continued until 160°C , and subsequent Cubic paraelectric phase has been identified with parameters $a=b=c=4.0903\text{ \AA}$ when temperature reached 200°C . In this process, cell parameter c was more and more bigger and cell parameter a and b were more and more smaller. The cell volume of poled sample was 68.8725 \AA^3 , so comparing with the cell volume of AFE and PE crystal in Fig. 5 we can draw a conclusion: $V_{\text{FE}} > V_{\text{PE}} > V_{\text{AFE}}$.

4.1 The effects of hydrostatic pressure on dielectric constant and phase transition temperature

The temperature dependence of the dielectric constant for the polarized specimens at 1 kHz under different hydrostatic pressures of $1 \times 10^5\text{ Pa}$, 30 MPa and 60 MPa were measured. It was found that the AFE/PE phase transformation temperature increased under increasing pressure from

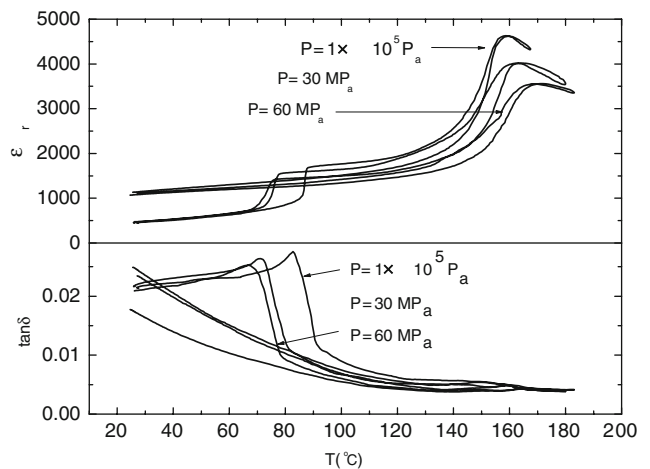


Fig. 6 Temperature dependence of dielectric constant of polarized specimen under hydrostatic pressures

159°C at 1×10^5 Pa to 171°C at 60 MP_a, with $dT_m/dp=2^\circ\text{C}/10$ MP_a. It indicated that the phase transition temperature increased with increasing pressure, which is consistent with the observations of antiferroelectric PbZrO₃. The peak of the dielectric constant ϵ_m decreased when hydrostatic pressure increased. The peak broadening of dielectric constant from the diffused phase transition was obvious with increasing pressure. When ϵ_m decreased continuously, the dielectric constant curves became more and more flat, and the abnormality near T_m decreased distinctly. The relationship between ϵ_r and temperature do not obey Curie–Weiss law but as follows:

$$\epsilon_r = \frac{k}{(T - T_m)^\alpha} \quad (1)$$

where k is rate coefficient, T_m is the temperature of maximal ϵ_r , $\alpha > 1$. The phase transition has diffusion characteristic. At the same time, the FE/AFE phase transformation temperature decreased with increasing pressure from 87°C at 1×10^5 Pa to 74.5°C at 60 MP_a, with $dT_m/dp = -2.1^\circ\text{C}/10$ MP_a, as shown in Fig. 6. dT_m/dp of PbZrO₃ is $0.42^\circ\text{C}/10$ MPa, dT_m/dp of PbTiO₃ is $-0.67^\circ\text{C}/10$ MPa and dT_m/dp of PZN–PT–BT is $-0.4^\circ\text{C}/10$ MPa [10, 11]. This specimen is more sensitive to pressure than those materials.

5 Summary

Dielectric properties from -100°C to 200°C and X-ray diffraction in different temperature for the PbLa(Zr,Sn,Ti)O₃ antiferroelectric ceramics near tetragonal antiferroelectric phase and rhombohedral ferroelectric phase boundary have been studied. X-ray diffraction for PbLa(Zr,Sn,Ti)O₃ antiferroelectric ceramics verified that a phase transition in the ceramics took from tetragonal AFE phase to cubic PE

phase and the phase transition is a gradual process with increasing temperature. The volume relation of these cells is as $V_{\text{FE}} > V_{\text{PE}} > V_{\text{AFE}}$. The relationship of dielectric properties with temperature and hydrostatic pressure has been obtained from this experiment. The poled ceramics underwent FE/AFE phase transition in low temperature and underwent AFE/PE phase transition in higher temperature. Hydrostatic pressure will be beneficial to making the cell volume of PLZST antiferroelectric ceramics towards smaller. The higher the hydrostatic pressure is, the more obvious the feature of the diffraction phase transition feature is.

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References

1. L.E. Cross, S.J. Jang, R.E. Newnham, S. Nomura, K. Uchino, *Ferroelectrics* **23**, 187 (1980)
2. C.T. Blue, J.C. Hicks, *Appl. Phys. Lett.* **21**, 68 (1996)
3. R.E. Newnham, G.R. Rusehan, *Am. Ceram. Soc. Bull.* **75**, 51 (1996)
4. P. Liu, T.Q. Yang, Z. Xv, L. Y. Zhang, X. Yao, *Chin. Sci. Bull.* **23**, 2563 (1998)
5. X.H. Dai, A.D. Giovanni, D. Viehland, *J. Appl. Phys.* **74**, 5 (1993)
6. W.Y. Pan, C.Q. Pan, Q.M. Zhang, L.E. Cross, *J. Appl. Phys.* **66**, 6014 (1989)
7. E.N. Robert, R.R. Gregory, *Am. Ceram. Soc. Bull.* **10**, 51 (1996)
8. Pan, Q. Zhang, A. Bhalla, L.E. Cross, *J. Am. Ceram. Soc.* **72**, 570 (1989)
9. W.Y. Pan, W.Y. Gu, L.E. Cross, *Ferroelectrics*, **99**, 185 (1989)
10. I. W. Chen, *J. Phys. Chem. Sol.* **61**, 197 (2000)
11. X. V. Zhuo, S. G. Zhen, Z. X. Yue, *Chin. Sci. Bull.* **46**, 1409 (2001)