Release of charges under external fields of $PbLa(Zr,Sn,Ti)O_3$ ceramic*

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This paper investigates the pyroelectric of poled antiferroelectric (AFE) ceramic $Pb_{0.97}La_{0.02}$ $(Zr_{0.69}Sn_{0.196}Ti_{0.114})O_3$ and its remnant polarization dependence of hydrostatic pressure. The results show that the bound charges of poled sample can be released in short time by temperature field or pressure field. The released charge abruptly forms a large pulse current. The phenomena of released charge under external fields result in the ferroelectric-AFE phase transition induced by temperature or hydrostatic pressure.

Keywords: antiferroelectric ceramic, pyroelectric, hydrostatic pressure, phase transition

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1. Introduction

A great deal of attention has been focused on La-modified Pb(Zr, Sn, Ti)O_3 (PLZST) antiferroelectric (AFE)-ferroelectric (FE) ceramics for its various excellent dielectric properties: high electric field-induced longitudinal strain and large volume expansion.[1,2] Especially, those compositions near the morphotropic phase boundary (MPB) between the FE and AFE phases are very sensitive to electric field and temperature,[3,4] exhibiting more phase transition associated with good properties induced by E-field or temperature. Except for E-field and temperature, pressure has strong influence on PLZST ceramics as well. Samara *et al.* found that the relaxor was induced by pressure in PLZT12/40/60 ceramic,[5] and pressure induced phase transition in PZT95/5-2Nb ceramic.[6] Our previous research work revealed that hydrostatic pressure could affect the dielectric properties of PLZST ceramics.[7−9] In this paper, we investigate the released charge characteristics of PLZST ceramic induced by temperature and hydrostatic pressure.

2. Experimental procedure

The composition used in our experiments is $Pb_{0.97}La_{0.02}(Zr_{0.69}Sn_{0.196}Ti_{0.114})O_3$ (PLZST). The bulk ceramics were fabricated by using the traditional solid-state ceramic processing route. The raw materials were first mixed and pre-sintered at 850 °C for 2 h, and then sintered at 1240 °C for 2 h in a PbO-rich atmosphere. The sintered bulk ceramics were cut into circle disc with a diameter of 10 mm and a thickness of 0.7 mm, and the silver paste was applied as electrodes for the measurements of pyroelctric and remanent polarization. The pyroelectric current was detected by a Keithley-6485 picoammeter contacted with a computer. The heat rate is 3 °C/min. The pressure was generated in the pressure apparatus by using transformer oil as the pressure transmitting media. The pressure measurements were calculated from the resistance of a manganin wire stress gauge in the pressure cavity using a computer controlled Keithley 2000 multimeter with an accuracy better than 0.2%. The specimens were polarized under the 2 kV·mm^{-1} electric field in silicon oil for 15 min. The piezoelectric constant d_{33} was measured by a Mode ZJ-2 d_{33} meter. A 10-μF capacitance was in series with a specimen

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to collect the released charge of the specimen so as to obtain the curve of remanent polarization vs. hydrostatic pressure for the pressure-induced phase transition (as shown in Fig. 1).

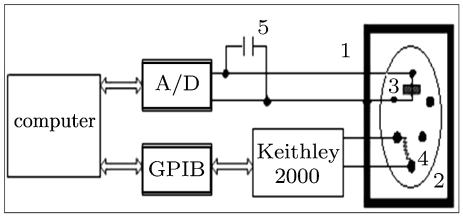


Fig. 1. Schemes of released charge measurement induced by pressure: 1 hydraulic press; 2 high pressure cavity; 3 sample; 4 manganin wire resistance; 5 10-μF standard capacitor.

3. Results and discussion

3.1. Pyroelectric

The P–E behavior is shown in Fig. 2, where dashed line *oab* corresponds to the initial loops. The loops display an AFE–FE phase transition when electric field is 0.708 kV/mm. The switch electric field is as large as the coercive electric field ($E_{\rm C}$) because the sample is very close to the MPB. The maximum remnant polarization ($P_{\rm r}$) of poled sample is 28.6 μC/cm^2.

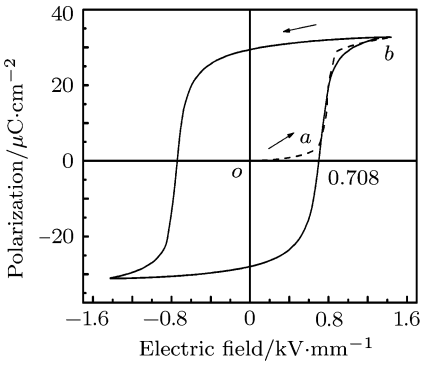


Fig. 2. The P–E loop of PLZST ceramic.

The dependence of dielectric constant ε' and loss $\tan\delta$ on temperature for poled sample is measured (shown in Fig. 3). It can be seen that sample undergoes two phase transitions. The first peak at about 123 °C corresponds to FE to AFE phase transition. The second peak at about 177 °C corresponds to AFE to paraelectric (PE) phase transition. After being poled, the FE phase is improved and kept till the electric field is removed, and the piezoelectric coefficient is $d_{33} = 96$ pC/N.

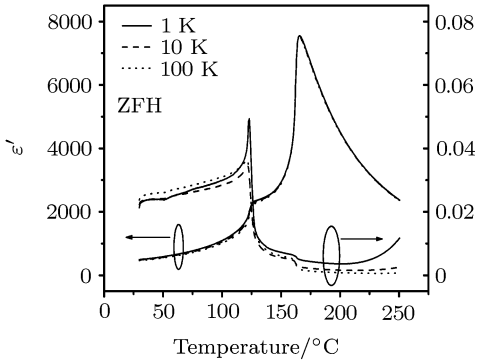


Fig. 3. Dependence of dielectric constant ε' and loss $\tan\delta$ on temperature of PLZST ceramic.

The pyroelectric curve is shown in Fig. 4. It can be seen clearly that only one large and sharp current pulse appears at 123 °C. The peak value approaches to 170 nA/cm^2. The discharge peak just corresponds to the FE–AFE phase transition, while in cool process no discharge peak is found. The poled sample is in FE state and the dipoles are oriented with large polarization. While in AFE state, the antiparallel dipoles neutralize each other's polarization, forming a zero polarization structure. Accordingly, a significant current is released when the poled sample undergoes the FE to AFE phase transition. The calculated pyroelectric coefficient maximum can reach 340×10^{-8} C $\cdot$ cm^{-2} $\cdot$ K^{-1}. The pyroelctric coefficient is much larger than that of conventional pyroelectric materials (PZT: 18×10^{-8} C $\cdot$ cm^{-2} $\cdot$ K^{-1}), PZT film (48 nC$\cdot$cm$^{-2}\cdot$K^{-1})[10] and relaxor ferroelectric PMN–PT (PMN–PT crystal: 12.4×10^{-8} C $\cdot$ cm^{-2} $\cdot$ K^{-1}).[11] The sum of released charges were calculated from released current versus time curve by

$$Q = \int_0^{t_{\rm m}} I{\rm d}t, \tag{1}$$

where $t_{\rm m}$ is released current time, and I is current intensity. The sum of released charge is 24.28 μC.

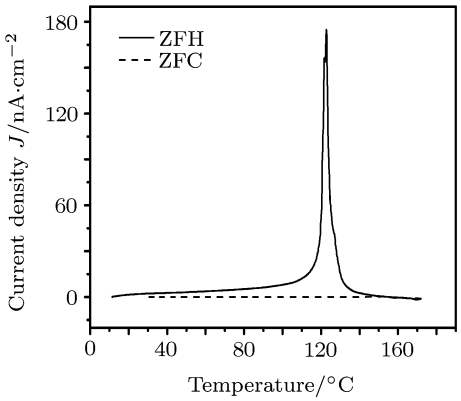


Fig. 4. Pyroelectric current density vs. temperature of PLZST ceramic.

3.2. Hydrostatic pressure induced release charges

To gain a further insight into the discharge property, the hydrostatic pressure-induced released current was also measured. The sample is poled again under the same condition as previous measurement. The remanent polarization under pressure is calculated by

$$P_{\mathrm{r}} = \frac{Q}{A} = \frac{C_0 U}{A}, \tag{2}$$

where C_0 is a 10-μF standard capacitor, U is the voltage of standard capacitor C_0. When the standard capacitor is larger than the sample's capacitance, the released charges are completely collected almost by the C_0. Figure 5 shows the curves of remanent polarization P_{r} and released current with hydrostatic pressure. It can be seen from Fig. 5 that the P_{r} curve changes sharply at about 250 MPa. The bound charge is released at first and a large current pulse appears. At about 320 MPa, the specimen switches to AFE state and the bound charge was completely released. With a further increase of pressure up to 570 MPa, the P_{r} does not decrease any more. Similarly to the temperature-induced FE–AFE phase transition, hydrostatic pressure-induced FE–AFE phase transition takes place under a certain pressure and the bound charge is released in a very short time period. The maximum release current density can reach 42 mA/m^2. The calculated sum of released charge is 24.22 μC, which is as much as the released charge induced by temperature FE–AFE phase transition. The experimental results can promote PLZST AFE ceramics to be widely utilized in energy converter and ignition system with electric pulse.

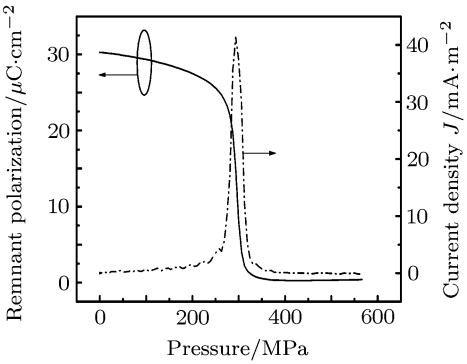


Fig. 5. Remnant polarization (solid line) and electrodischarge current density (dash–dot line) vs. hydrostatic pressure.

4. Conclusion

The released charge properties induced by temperature and hydrostatic pressure of La-doped Pb(Zr, Sn, Ti)O_3 ceramic have been systematically investigated. Experimental results show that both temperature and hydrostatic pressure can induce poled PLZST ceramic to undergo FE–AFE phase transition associated with large and sharp current pulse. Furthermore, the current pulse induced by pressure is remarkably large.

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