Properties of pressure-induced phase transition in Nb-doped PZST ceramics

Zhuo Xu · Yujun Feng · Xi Yao

Abstract The structure of Nb-doped $Pb_{0.99}Nb_{0.02}[(Zr_{1-x}Sn_x)_{1-y}Ti_y]_{0.98}O_3$ ceramics can be transformed from ferroelectric to antiferroelectric phase by using hydrostatic pressure. The dependences on both composition and temperature for the phase transition pressure (p_c) are studied. It is found that the p_c increases with increasing composition (y) of Titanium (Ti) if another composition (x) of Stannum (Sn) is fixed, while the p_c decreases with increasing of the composition (x) of Sn if the composition (y) of Ti is fixed. Regarding the influence of the temperature, it is found that the p_c increases with temperature as a linear function.

Keywords Ferroelectric · Antiferroelectric · Phase transition · Hydrostatic pressure

1 Introduction

The hydrostatic pressure can induce the phase transition in ferroelectrics, such as the transformation from ferroelectric state to paraelectric or antiferroelectric states, which is depended on the temperature. For example, the phase transition from ferroelectric to paraelectric phases in $BaTiO_3$ ceramics occurs at 2 GPa hydrostatic pressure at room temperature [1], while such transformation in standard atmosphere pressure occurs at 120 °C. The phase transition from ferroelectric to antiferroelectric phases in PZT 95/5 and La-doped $Pb_{0.98}La_{0.02}$ $(Zr_{1-x}Sn_x)_{1-y}Ti_yO_3$ (PZST) ceramics at room temperature occurs at 200 and 110 MPa

Z. Xu (✉) · Y. Feng · X. Yao
Electronic Materials Research Laboratory, Key Laboratory of the Ministry of the Education, Xi'an Jiaotong University, Xi'an 710049, China
e-mail: xuzhuo@mail.xjtu.edu.cn

hydrostatic pressures, respectively [2–4]. The ferroelectric to paraelectric or antiferroelectric phase transition results in a release of electric energy due to the change in spontaneous polarization, which can be used to generate electric current pulse power, therefore, is very interesting for some applications.

It is reported that the Nb-doped $Pb_{0.99}Nb_{0.02}[(Zr_{1-x}Sn_x)_{1-y}Ti_y]_{0.98}O_3$ (PZST) ceramics at room temperature have rather different structures, such as AFE_O, AFE_T, FE_{RL}, FE_{RH}, FE_T and PE_C. Especially, a meta-stable antiferroelectric phase and a meta-stable ferroelectric phase are found in those ceramics close to the phase boundary between AFE_T and FE_{RL}. For these ceramics, the external electric field can be used to induce the structure change from antiferroelectric to ferroelectric state, while the poled ferroelectric ceramics can be transformed into antiferroelectric state under hydrostatic pressure. Therefore, these ceramics are good candidates for phase transition research. In this paper, the phase transition behaviors of doped-Nb Pb (Sn, Zr, Ti)O_3 ceramics under hydrostatic pressures are reported. The influence of temperature on those behaviors is also studied.

2 Experiments

The polarization and the phase transition pressures of the ceramics change due to the phase transition depend on the temperature and compositions of the ceramics, especially the contents of Ti and Sn. Therefore, the ceramics of $Pb_{0.99}Nb_{0.02}[(Zr_{1-x}Sn_x)_{1-y}Ti_y]_{0.98}O_3$ were studied by: 1) changing the content of Ti from 0.030 to 0.036 with a constant ratio of Zr/Sn; 2) changing the mole ratio of Zr/Sn from 0.80/0.20 to 0.90/0.10 with a fixed content of Ti; 3) changing the temperature of the samples.
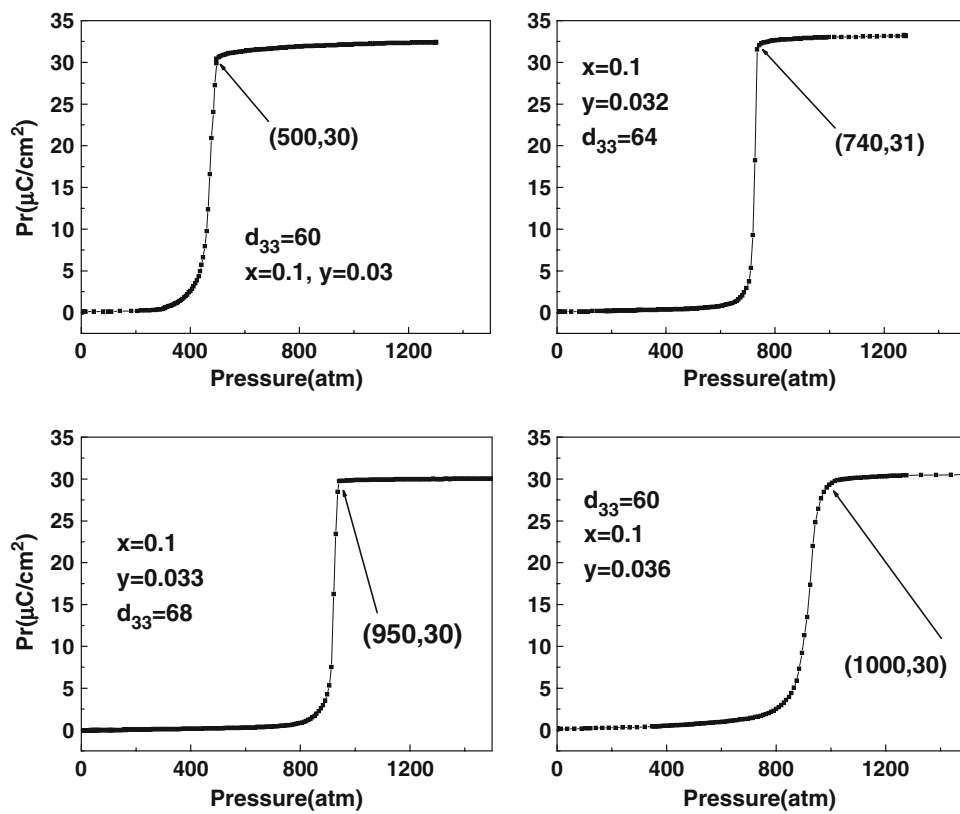
Fig. 1 Remnant polarization vs. hydrostatic pressure for $Pb_{0.99}Nb_{0.02}[(Zr_{1-x}Sn_x)_{1-y}Ti_y]_{0.98}O_3$ ceramics with $x=0.1$ at room temperature
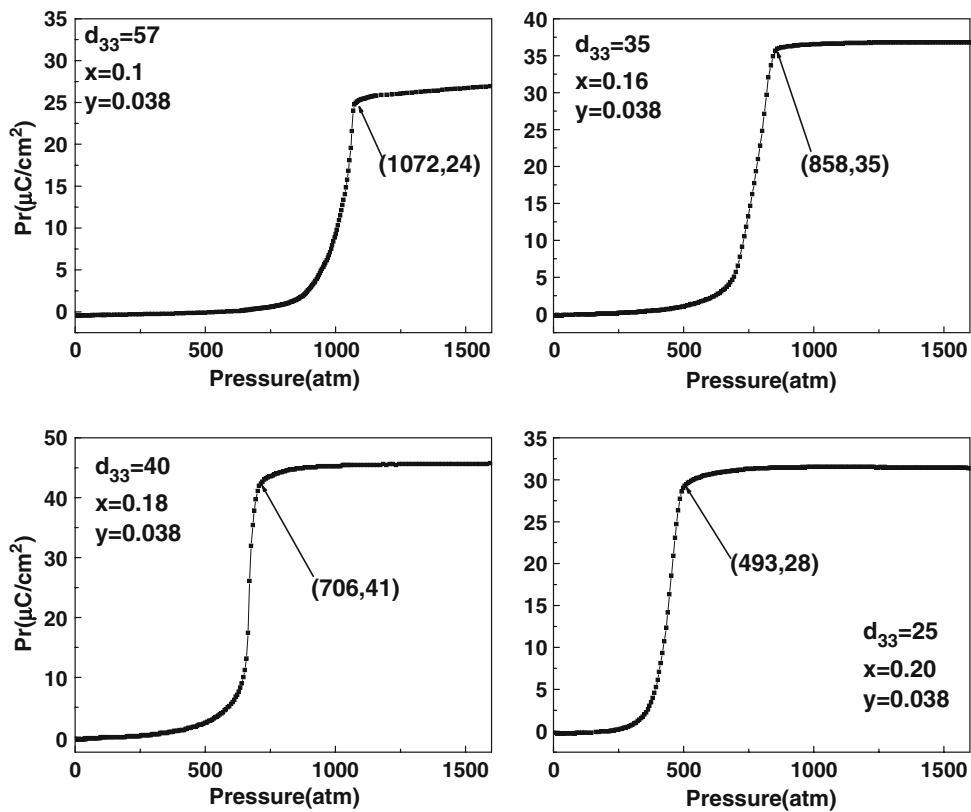
Fig. 2 Remnant polarization versus hydrostatic pressure for $Pb_{0.99}Nb_{0.02}[(Zr_{1-x}Sn_x)_{1-y}Ti_y]_{0.98}O_3$ ceramics with $y=0.038$ at room temperature

Fig. 3 Remnant polarization versus hydrostatic pressure for $Pb_{0.99}Nb_{0.02}[(Zr_{1-x}Sn_x)_{1-y}Ti_y]_{0.98}O_3$ with Zr/Sn=0.90/0.10 and y=0.032 at different temperatures
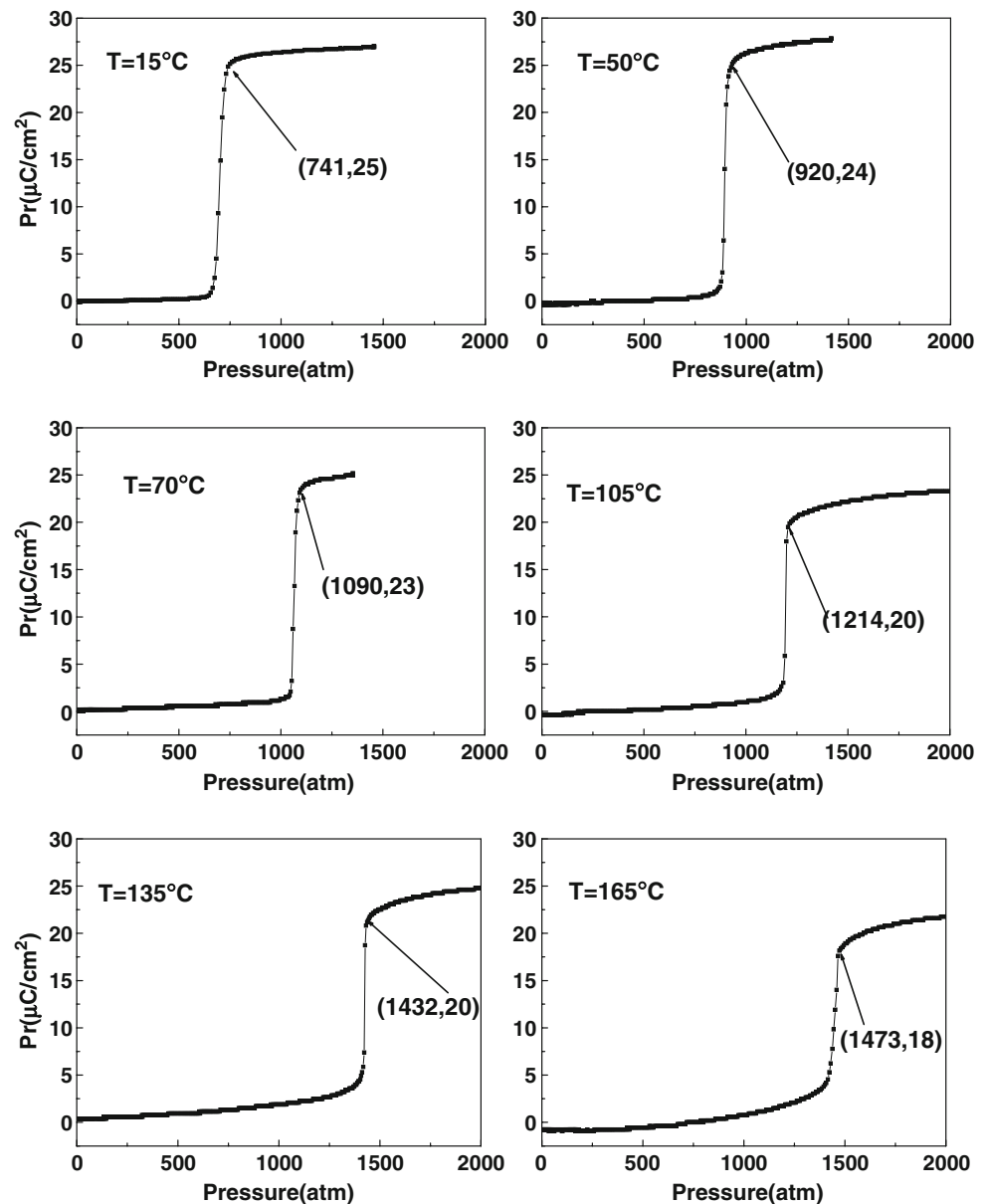
The ceramics were prepared using following process: presintered at 900 °C for 2 h, then sintered at 1200 °C for 2 h in a PbO-rich atmosphere. The density of the specimens was 7.9 g/cm³. All the samples used in this study are disks with a diameter of 10 mm and a thickness of 1 mm. For the polarization measurement, the silver electrodes were prepared on both sides using silver past. The samples were poled at electrical field of 5 kV/mm in silicon oil at 100 °C for 10 min.

The hydrostatic pressure was generated by a piston-cylinder type vessel, which can be compressed in two directions by a 120-ton hydraulic press with double piston and four pillars. Hydraulic oil was used as the pressure-transporting liquid medium. The real pressure on the samples was measured using a manganin wire stress gauge in the pressure cavity. The change in the resistance of the stress gauge with the pressure was used to monitor the pressure, and measured using a computer controlled Keithley 2000 multimeter, which has a relative error less than 0.2%. The temperature of the cavity was heated and controlled using a small resistance-heated furnace.

In order to measure the charges generated by the phase transition, a 10 μF capacitor in series with the sample was used to collect the released charges. The relationship between the remnant polarization and hydrostatic pressure was determined.

3 Results and discussion

3.1 Constant ratio of Zr/Sn

The samples with four compositions were studied: $y=$ 0.030, 0.032, 0.033, 0.036 with a constant ratio of Zr/Sn (=0.90/0.10). First of all, all the samples were poled into ferroelectric states. Then, the hydrostatic pressure would induce phase transition from ferroelectric phase to antiferroelectric phase, the phase change pressures of these poled samples were measured. It is determined that the phase transition pressures (p_c) are 500, 740, 940, and 1,000 atm for y are 0.030, 0.032, 0.033, and 0.036, respectively, as shown in Fig. 1.

It is found that phase transition pressure increases with the value of y. That is, for these ceramics with a fixed ratio of Sn/Zr, the phase transition pressure increases with the content of Ti. This is consistent with the fact that the increase of y results in the ceramics away from AFE/FE phase boundary.

Based on the phase diagram, for the ceramics studied here, the increase of y means that the stability of the ferroelectric phase in the ceramics is enhanced. Therefore, the pressure at which the structure changes from ferroelectric to antiferroelectric increases with the content of Ti.

3.2 The fixed content of Ti

Here, the content of Ti in the ceramics is 0.038. The Zr/Sn mole ratios of 0.90/0.10, 0.84/0.16, 0.82/0.18, and 0.80/0.20 were used in this study. It is found that the phase transition pressures of these four ceramics are 1,072, 858, 706, and 493 atm, respectively, as shown in Fig. 2.

It is indicated that the phase transition pressures p_c decrease as the increase of Sn content and/or the decreases of Zr/Sn ratio. The increase of x means that the stability of the antiferroelectric phase in the ceramics is enhanced. Therefore, when the structures changed from ferroelectric state to antiferroelectric state, the pressures decrease with the increase of x or the content of Sn. Clearly, the result is consistent with phase diagram.

3.3 Influence of temperature on phase transition behaviors

The hydrostatic pressures induced to the phase transition in Nb-doped PZST have been investigated at temperatures of 15, 50, 70, 105, 135, and 165 °C. Since the remnant polarization Pr and FE/AFE phase transition pressure p_c change with temperatures, it is necessary to study the influence of temperature on the phase transition behaviors.

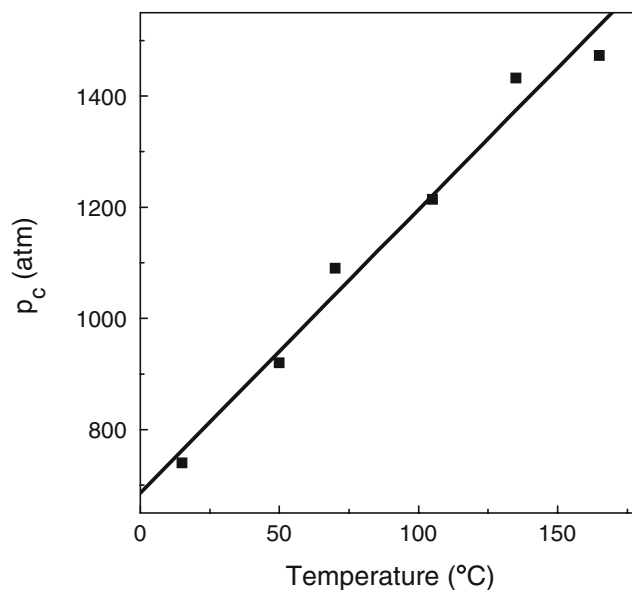The sample used in this experiment was Zr/Sn=0.90/0.10 and $y=0.032$. The experimental results are shown in Fig. 3.

Fig. 4 Phase transition pressure versus temperature for $Pb_{0.99}Nb_{0.02}$ $[(Zr_{1-x}Sn_x)_{1-y}Ti_y]_{0.98}O_3$ with Zr/Sn=0.90/0.10 and $y=0.032$

The experimental results indicate that the phase transition pressures p_c are 740, 920, 1,090, 1,214, 1,432, and 1,473 atm at 15, 50, 70, 105, 135, and 165 °C, respectively. The corresponding remnant polarizations P_r are 25, 24, 23, 20, 20, and 18 μC/cm^2, respectively. Clearly, the phase transition pressures p_c increase and the remnant polarizations P_r decrease with increasing temperature. This is because temperature increase, the ferroelectricity would be weaken, the antiferroelectricity decrease, increasing temperature is unfavorable for the stability of the antiferroelectric phase, so the phase transition pressure of the sample would increase with temperature increasing. The relationship between the p_c and temperature is plotted in Fig. 4. It is very interesting that the p_c shows a linear dependence on the temperature. The results indicate that the hydrostatic pressure induced FE-AFE phase transition will occur in the ceramics as long as the temperature is lower than ferroelectric-paraelectric phase transition temperature. The data shown in Fig. 3 also indicate that the pressure induced FE-AFE phase transition is a first order phase transition, although the feature of first order phase transition weakens with increasing temperature.

4 Conclusions

The hydrostatic pressure which induced ferroelectric to antiferroelectric phase transition behavior in $Pb_{0.99}Nb_{0.02}$ $[(Zr_{1-x}Sn_x)_{1-y}Ti_y]_{0.98}O_3$ ceramics close to the FE-AFE phase boundary is determined at room temperature. It is found that the phase transition pressure increases with the content of Ti

if the Sn/Zr ratio is fixed, while the phase transition pressure decreases with increasing content of Sn if the content of Ti is fixed. For $Pb_{0.99}Nb_{0.02}[(Zr_{1-x}Sn_x)_{1-y}Ti_y]_{0.98}O_3$ ceramics with $Zr/Sn = 0.90/0.10$ and $y = 0.032$, the phase transition pressure p_c increases linearly with increasing temperature. It is also observed that the pressure induced FE-AFE phase transition is a first order phase transition.

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