

Thermal analysis of phase transitions in $\text{PbZr}_{1-x}\text{Sn}_x\text{O}_3$ antiferroelectric single crystals

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Abstract The combined thermal analysis techniques thermal expansion; and differential scanning calorimetry were used to characterize various phase transitions that exist in the solid solutions of $\text{PbZr}_{1-x}\text{Sn}_x\text{O}_3$. Using thermodynamic quantities, i.e., thermal expansion and specific heat to distinguish first-order transitions from second-order ones, we demonstrate that some perovskite antiferroelectrics can exhibit continuous transition at their Curie temperature T_C . We observed such a transition in antiferroelectric crystals of solid solutions based on PbZrO_3 . Although pure PbZrO_3 is a classical example of antiferroelectric crystal with a first-order transition at T_C , the solid solutions of $\text{PbZr}_{1-x}\text{Sn}_x\text{O}_3$ in the range of composition of $x > 0.25$ seem to exhibit a second-order phase transition.

Keywords Antiferroelectrics · Phase transitions · Specific heat · Thermal expansion

Introduction

$\text{PbZr}_{1-x}\text{Sn}_x\text{O}_3$ (PZS) belongs to the family of $\text{AB}'\text{B}''\text{O}_3$ perovskite solid solutions based on well-known antiferroelectric material PbZrO_3 . Phase diagram showing different

phases that exist in PZS with $0 < x < 0.4$ obtained on the basis of dielectric, optic and thermodynamic measurements was already reported [1]. The substitution of Sn^{4+} ions at the Zr^{4+} sites in PZS single crystals does not alter the basic structure of PbZrO_3 which crystallizes in an orthorhombic structure at room temperature RT. The stability and range of the existence of subsequent phases, namely A1 (orthorhombic)–A2 (orthorhombic)–IM (multiple cell cubic)–PE (cubic), depend strictly on the composition. Such rich phase diagram of PZS compound and its potential possibilities of applications (especially the PZS compounds enriched with Ti ions) have attracted the interest of many researchers [2–5]. It was found that mechanism of the A1–A2 phase transition is of purely displacive character for all investigated compositions [6]. In a case of phase transition at T_C , above $x = 0.2$ a gradual change from order–disorder to displacive character also takes place. Despite the efforts made, the nature of phase transitions is still not clear. Numerous experiments revealed distinct differences in physical properties of single crystals with compositions of x below and above 0.25. It is believed that all of this is due to the so-called tricritical point, the existence of which was postulated in early studies [7]. It means that around this concentration, the change from the first- to second-order phase transition at T_C takes place. Simultaneously, the large value of the dielectric permittivity at T_C which is observed in both PbZrO_3 and $\text{PbZr}_{1-x}\text{Sn}_x\text{O}_3$ single crystals with $x < 0.25$ considerably decreases in the compositions with $x > 0.25$ and another intermediate phase—IM, called also “multiple cell cubic” [5]—appears. In our earlier studies of specific heat [7], we found that above the value of $x = 0.25$, the latent heat at T_C at PE–IM phase transition is absent suggesting the change of the character of the phase transition to a second order in these crystals. However, in this paper,

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IM phase was erroneously identified as ferroelectric one. In later studies, we found that this intermediate phase is ferroelastic one [1]. Later, Brillouin scattering measurements made in $\text{PbZr}_{0.72}\text{Sn}_{0.28}\text{O}_3$ pointed to enhanced fluctuations in coupling between local polarization and strain which occurs due to Sn replacing in Zr-site [8]. Such large fluctuations of order parameter are expected near the second-order phase transition, and electrostrictive coupling between the strain and fluctuations of local polar regions seems to be the origin of the anomalous behavior of the temperature dependence of the relaxation time of this polar regions— τ_{LA} [8].

Since all previous studies do not definitely prove that second-order phase transition can exist in perovskite materials with antiferroelectric phase transition, we undertook a detailed study to be able to unequivocally confirm the suggestion. For the purposes of this study newly acquired high quality, transparent crystals were selected for the experiment. Three crystals with values of x chosen from different points of the phase diagram were selected, namely 0.04, 0.09 and 0.3. The stoichiometry of the compounds and thus quality of the crystals were verified with X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS). Additionally, the Mössbauer effect was made in the crystal with high amount of Sn ions as an additional verification of the oxidation state of Sn in the compound. In the next step, precise investigations of thermal expansion were undertaken. It is worth to mention that an accurate thermal expansion experiments were made for those crystals for the first time. For comparative purposes, calorimetric (DSC) and dielectric measurements had to be repeated in order to meet the same conditions of the experiment.

According to thermodynamic criterion for first-order phase transitions, a discontinuity in the first derivative of the free energy with respect to thermodynamic quantities takes place which is absent in second-order–continuous phase transitions and becomes visible only in the second derivative of the free energy. It is known that thermal expansion reveals distinct anomalies at the phase transitions. Particularly, in measurements of thermal expansion a distinct anomaly is observed at the first-order phase transition point which is connected with the structural volume change of the primitive cell. In a case of second-order phase transition, the volume discontinuity at the phase transition is eliminated. At the same time, when measuring the temperature dependence of specific heat, a latent heat is a quantity present only in first-order transitions, and therefore, its presence or absence is also a direct proof of the nature of a transition. Peaks of first-order phase transitions are usually sharp and narrow (δ -shape). For a second-order phase transition, the anomaly is small and

assumes a look of λ -shape [9]. The goal of this paper is the final outcome of the existence of the phase transition of second order in perovskite crystals with antiferroelectric phase transition.

Experimental

$\text{PbZr}_{1-x}\text{Sn}_x\text{O}_3$ single crystals with x between 0.04 and 0.3 were grown by flux method. The detailed description of crystallization can be found elsewhere [1, 10]. The obtained crystals were in form of thin transparent plates with the thickness ranging from 0.05 to 1.5 mm. After the crystallization process, the chemical composition and stoichiometry of the investigated crystals were verified using X-ray photoelectron spectroscopy (XPS) and energy-dispersive X-ray spectroscopy (EDS). EDS analysis was made with scanning electron microscope (SEM) Hitachi S-4700 with Noran Vantage system. XPS spectra were obtained with monochromatized Al $K\alpha$ radiation at the temperature 470 K using a PHI 5700 ESCA spectrometer. The Mössbauer effect was measured with commercial ^{119}Sn gamma ray source, and the data were collected at room temperature using a MsAa-1 spectrometer.

Thermal expansion (TE) experiments were made on a crystal with thickness of $x \sim 1.5$ mm. The measurements were taken by a capacitance method. The sample was placed in an air-tight brass block within which the temperature was stabilized with an accuracy of ± 0.1 K. The thermal expansion of the sample was transmitted by a quartz rod. The upper end of the movable rod carried one plate of an air capacitor. Thus, a change in the sample thickness results in a change of the air capacitor. The capacitance was measured with the digital, self-balancing, three terminal commercial Andeen-Hagerling AH2700A capacitance bridge with accuracy 10^{-15} F and heating rate was set to be 0.5 K min^{-1} . Each measurement was repeated three times.

The calorimetric experiments were performed by heating the sample from room temperature to 620 K and cooling back. As previously, the rate of temperature change was selected to be 0.5 K min^{-1} . For the accurate determination of the background (lattice) heat capacity, the measurements were also taken down to low temperatures (to 120 K). The temperature dependence of the specific heat was measured by the commercial Netzsch DSC F3 Maia calorimeter. The specimen consisted of single piece of crystal of the average mass 20 mg which was placed in an alumina crucible. For dielectric measurements, the crystal plate was covered by silver electrodes and the capacity of the sample was measured with E4980A Precision LCR Meter at the frequency 1 MHz.

Fig. 1 Elemental composition from EDS measurements for $\text{PbZr}_{1-x}\text{Sn}_x\text{O}_3$ single crystals **a** $x = 0.04$, **b** $x = 0.09$, **c** $x = 0.30$

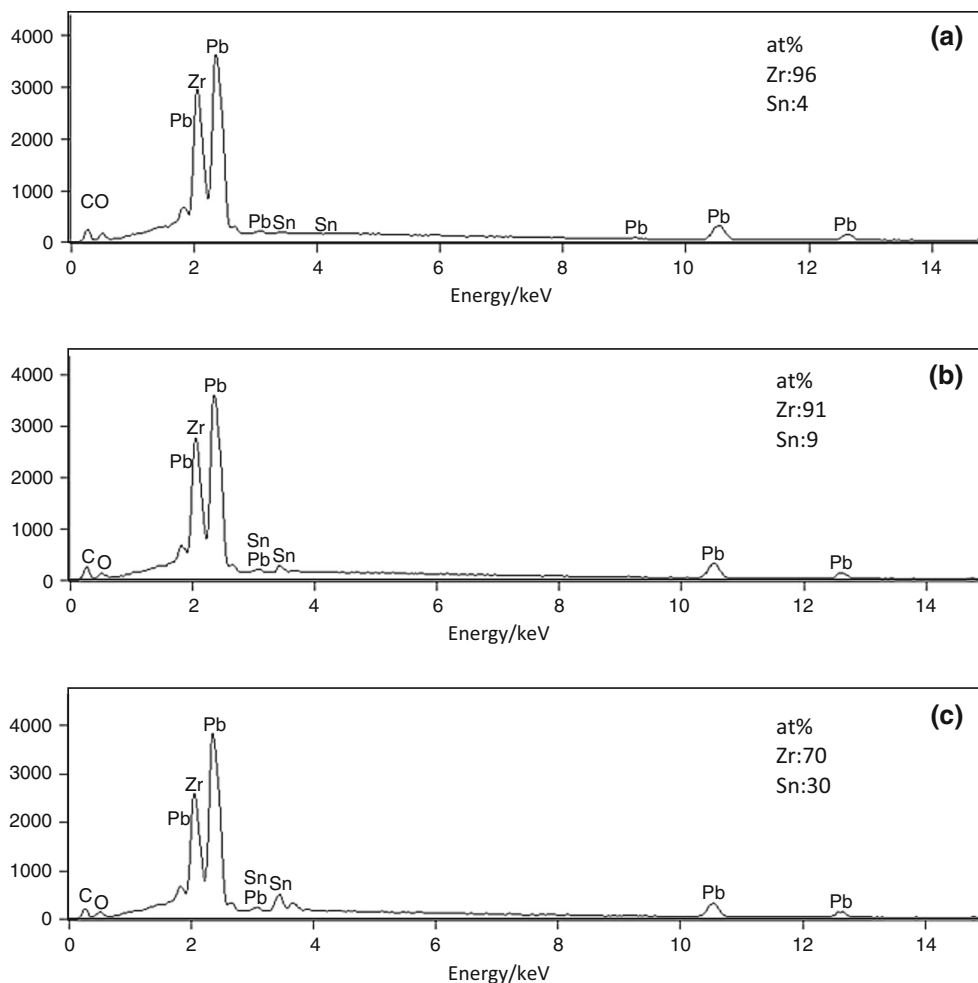
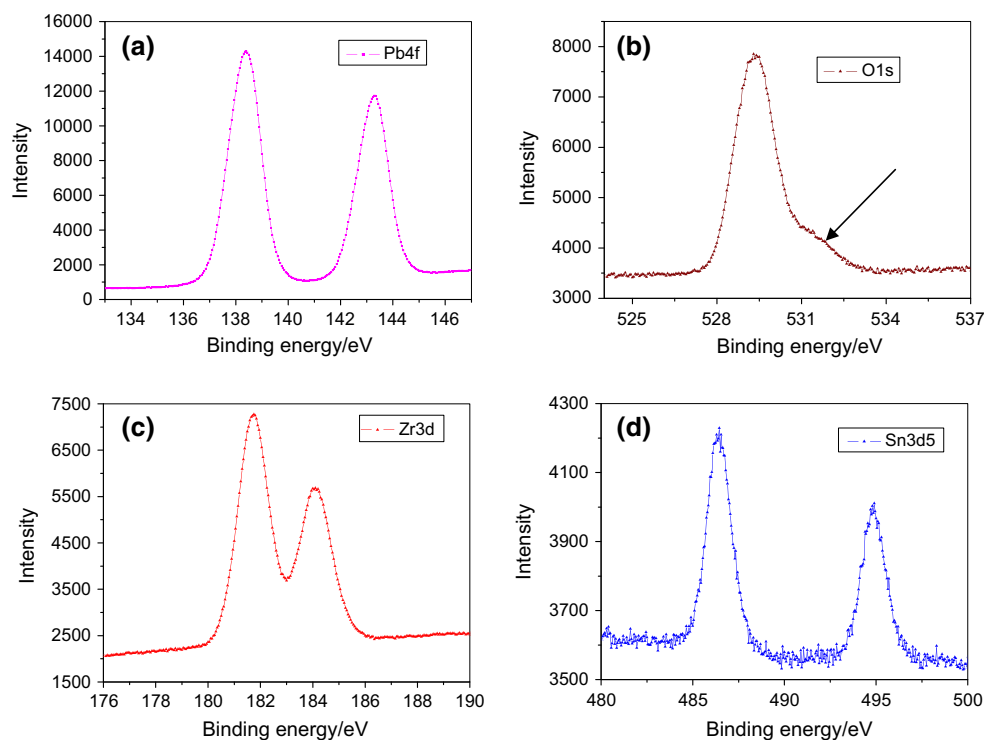


Fig. 2 Representative XPS spectra for $\text{PbZr}_{0.96}\text{Sn}_{0.04}\text{O}_3$ single crystal **a** Pb4f, **b** O1s, **c** Zr3d, **d** Sn3d5 core lines



Results

The real chemical composition for each crystal was established on the basis of X-ray spectroscopy (EDS). The qualitative EDS spectra (Fig. 1) show the presence of main elements (Pb, Zr, Sn) but also of an artifact related to the presence of C used for the specimen preparation.

X-ray photoelectron spectroscopy (XPS) has shown that $\text{PbZr}_{1-x}\text{Sn}_x\text{O}_3$ single crystals are globally stoichiometric. The spectra presented in Fig. 2 for chosen sample indicate that the components possess an appropriate oxidation state and homogeneous chemical compositions. Only the O1h core line presents an additional broadness which suggests multiple overlapping components. According to Ref. [11], the additional component (indicated by an arrow) can be regarded as chemisorbed CO or CO₂ and/or physisorbed OH or H₂O.

Figure 3c shows the specific heat of single crystal $\text{PbZr}_{0.96}\text{Sn}_{0.04}\text{O}_3$ measured in the range 490–510 K. The sharp anomalies observed as peaks on the temperature dependence of excess specific heat— $\Delta c_p(T)$ —perfectly correspond with temperatures of anomalies of dielectric

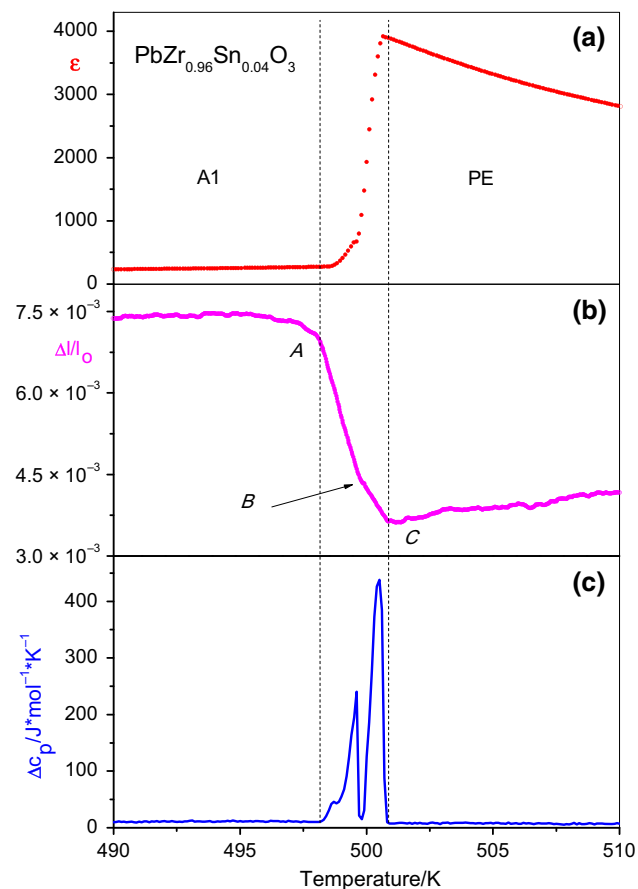


Fig. 3 Dependence of dielectric constant (red) (a), thermal expansion (magenta) (b) and excess specific heat (blue) (c) in function of temperature for $\text{PbZr}_{0.96}\text{Sn}_{0.04}\text{O}_3$ single crystal. (Color figure online)

permittivity. The two Δc_p peaks are of the shape characteristic for the first-order phase transition, i.e., they are large and narrowly centered. Moreover, the latent heat accompanied the lower phase transition ($E = 650 \text{ J mol}^{-1}$) is twice smaller than that related to the higher temperature phase change ($E = 1320 \text{ J mol}^{-1}$). According to the phase diagram reposted in [1], there are two very close phase transitions, i.e., phase transformation from low-temperature antiferroelectric–orthorhombic A1 phase to paraelectric–cubic phase PE is realized via very thin transient A2 phase which is also antiferroelectric and orthorhombic but with incommensurate modulations. Small latent heat accompanying the lower transition confirms the fact that both phases possess similar structures, i.e., orthorhombic.

At the same time, clear anomaly of the thermal strain (magenta line in Fig. 3b) in the range of both transitions is typical for first-order phase transition. Namely, it shows an abrupt decrease (contraction) and follows the linear relationship above transition temperature T_C . The contraction process takes place in two stages, i.e., at point B a small change of slope of the AC segment is noticeable indicating for a slight structural change at A1–A2 phase. The observed contraction is related to the structural change between orthorhombic and cubic phases and diminution of the unit cell. Outside the phase transitions region TE is increasing function of temperature.

Calorimetric measurements made for the next sample $\text{PbZr}_{0.91}\text{Sn}_{0.09}\text{O}_3$ (Fig. 4c) clearly revealed two well-separated phase transitions: (1) from low-temperature antiferroelectric phase A1 to antiferroelectric A2 phase and (2) from the A2 to PE phase. Calorimetric measurements indicated also that near phase transitions, there exist temperature ranges (indicated in Fig. 4c) in which two phases coexist. The phase coexistence is a characteristic feature of the first-order phase transitions. Stepped changes of $\Delta l/l_0$, i.e., TE (Fig. 4b) in the phase transition ranges correlate well with both dielectric and specific heat runs and are characteristic for the first-order PT (phase transitions). The observed smaller contraction is observed between two orthorhombic phases A1–A2, whereas larger volume change is observed in A2–PE phase transition. In [12], it was reported that octahedral rotations of the oxygen ion framework in perovskite oxides have been shown to be accompanied by an anomalous TE even though the transitions are displacive with very small changes of the lattice constants as compared to those of the cubic high-temperature phase.

Completely different behavior was observed for the $\text{PbZr}_{0.7}\text{Sn}_{0.3}\text{O}_3$ crystal, i.e., sample with high concentration of Sn ($x = 0.3$) presented in Fig. 5. Namely, two large anomalies connected with two low-temperature phase transitions, i.e., A1–A2 and A2–IM are observable on $\Delta c_p(T)$ dependence (Fig. 5c). Their shapes are typical for

first-order phase transitions. Contrary to that a very small anomaly of λ shape is observed on $\Delta C_p(T)$ dependence corresponding to the temperature in which maximum of dielectric permittivity exists, i.e., at T_C . The measurements of thermal expansion show a significant discontinuity at A1–A2 phase transition and an abrupt decrease near A2–IM phase transitions, whereas continuous change was observed in the temperature range where dielectric permittivity takes its maximal value. This continuous change is in agreement with the remark made in [5]. The authors of [5] claim that “the intermediate—MCC—phase displays a much higher thermal expansion rate, eliminating the volume discontinuity between the antiferroelectric and the cubic paraelectric phase. Therefore, the first-order transition—at T_C —is replaced by two second-order transitions.” Outside the phase transitions range $\Delta l/l_0$ is increasing function of temperature. In Figs. 3a, 4a and 5a, the dependences of $\varepsilon(T)$ were presented for comparison purposes to show the correlation between the temperatures of phase transitions obtained by different techniques, all these

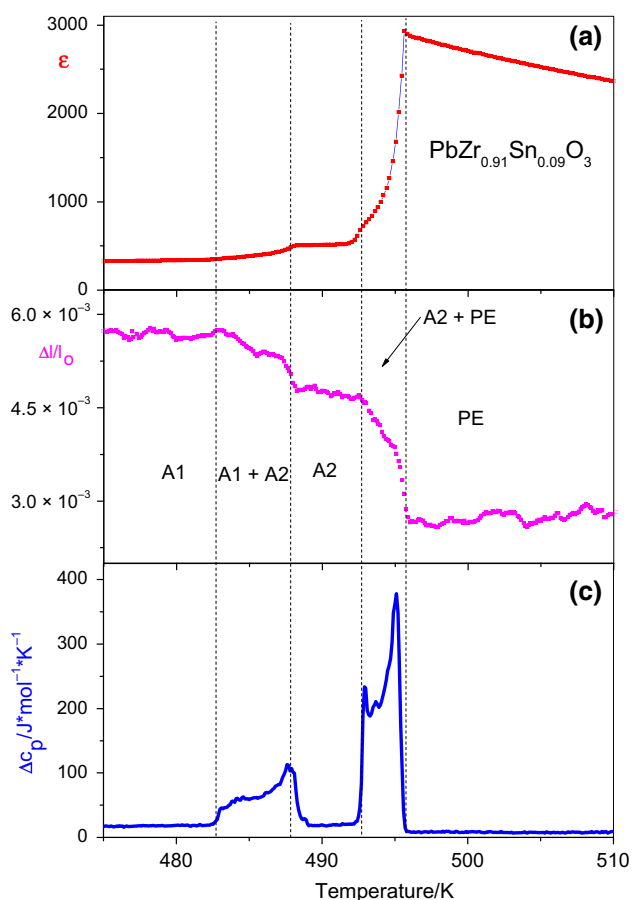


Fig. 4 Dependence of dielectric constant (red) (a), thermal expansion (magenta) (b) and excess specific heat (blue) (c) in function of temperature for $\text{PbZr}_{0.91}\text{Sn}_{0.09}\text{O}_3$ single crystal, with indication of subsequent transitions and phases coexistence. (Color figure online)

prove that the phase transition between IM and PE phase tends to be of the second order.

It can appear the supposition that for high concentrations of tin in PZS compound, the problem of the site occupancy of Sn (A or B position in the ABO_3 structure) can arise, and hence, the diffusion of the phase transition can appear revealing similar thermodynamic effects as described above. One should not confuse diffuse phase transition which is associated with the disorder in one of sublattice sense with the continuous phase transition in thermodynamic sense. Indeed, tin can exist in two oxidation states, +2 and +4, and therefore may occupy positions of A (Sn^{2+}) or B (Sn^{4+}) or both of them in the perovskite ABO_3 unit cell. According to our XPS measurements, tin displays a tendency to exist only in the +4 oxidation state. However, the study by XPS concerns mainly the surface to ensure, especially in the case $\text{PbZr}_{0.7}\text{Sn}_{0.3}\text{O}_3$ compound which

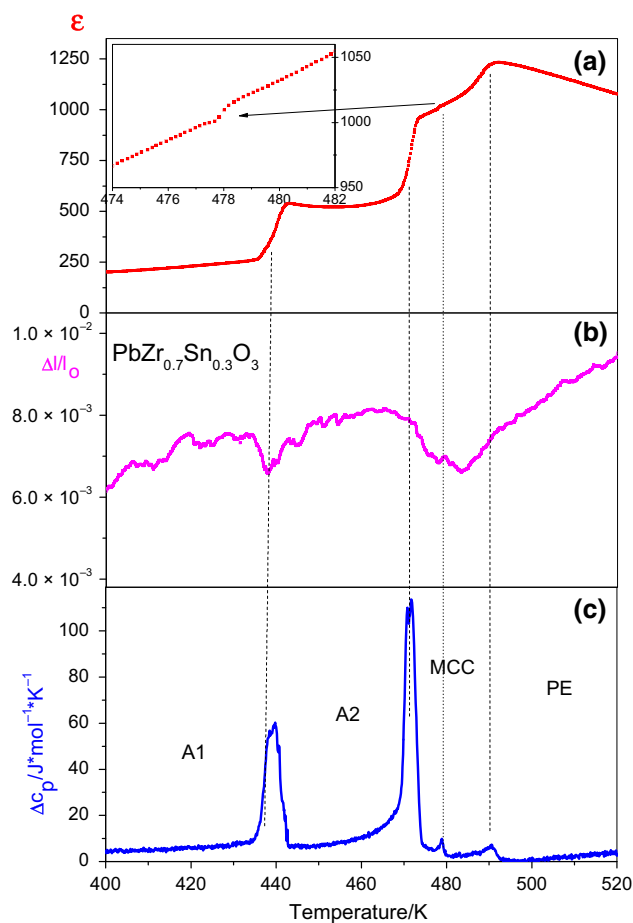


Fig. 5 Behavior of the dielectric constant (red) (a), thermal expansion (magenta) (b) and excess specific heat (blue) (c), in function of temperature for $\text{PbZr}_{0.7}\text{Sn}_{0.3}\text{O}_3$ single crystal. Dotted lines indicate additional small anomalies on $\Delta C_p(T)$ dependence with respect to $\varepsilon(T)$ and $\Delta l/l_0(T)$ dependences. The inset shows more precisely a temperature in which additional dielectric anomaly exists. (Color figure online)

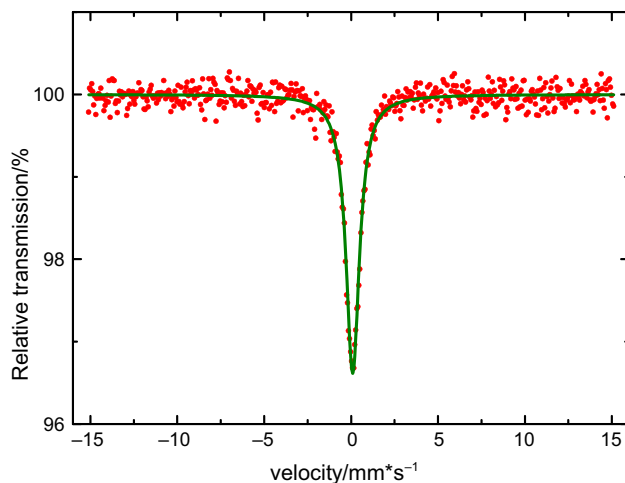


Fig. 6 Mössbauer spectrum of $\text{PbZr}_{0.7}\text{Sn}_{0.3}\text{O}_3$ single crystal at room temperature. The spectrum shows only one single absorption peak in the central region relating to Sn^{4+} oxidation state

contains a significantly large amount of tin, an additional test was made, i.e., the measurement of Mössbauer effect. The representative Mössbauer spectrum at 300 K for the sample of $\text{PbZr}_{0.7}\text{Sn}_{0.3}\text{O}_3$ is shown in Fig. 6. The sharp single-line spectrum was obtained for this crystal with the value of isomer shift (0.09 mm s^{-1}) which is characteristic for Sn^{4+} [13].

Interestingly, there exists another small anomaly on $\Delta C_p(T)$ dependence of $\text{PbZr}_{0.7}\text{Sn}_{0.3}\text{O}_3$ (Fig. 5c). An accurate measurements of dielectric permittivity (with the heating rate of 0.1 K min^{-1}) showed a slight discontinuity on $\epsilon(T)$ dependence (see inset in Fig. 5a) at the same temperature. We do not know the origin of this anomaly at this moment, and however, it may be thought that this kind of anomaly may be associated with a significant rebuilding of the domain structure visible under the polarizing microscope without change of the structure and increased polarization fluctuations strictly induced by local strains. Similar effects were observed for single crystal— $\text{PbZr}_{0.72}\text{Sn}_{0.28}\text{O}_3$ —by optic (birefringence) and electromechanical (electrostriction) measurements [1]. It is also worth to mention here that the maximum of piezoelectric activity (measured by piezoresponse force microscopy—PFM) was detected for the same crystal not at the T_C temperature nor at the temperature corresponding to IM–A2 phase transition, but between these two points [1].

Conclusions

In summary, we have determined that although both $\text{PbZr}_{0.96}\text{Sn}_{0.04}\text{O}_3$ and $\text{PbZr}_{0.91}\text{Sn}_{0.09}\text{O}_3$ compounds show a first-order phase transition at T_C , the behavior of $\text{PbZr}_{0.7}\text{Sn}_{0.3}\text{O}_3$ is completely different. It was detected that the

character of the transition at T_C is very sensitive to Sn doping. Thus, the introduction of the Sn ions into PbZrO_3 lattice is directly responsible for the change of the character of phase transition at T_C . While for small concentrations of Sn in $\text{PbZr}_{1-x}\text{Sn}_x\text{O}_3$, the first-order character of phase transition is maintained, together with increasing of x it gradually changes into the second-order one (in Ref. [7] it was postulated that this change will start near $x = 0.25$). This was directly evidenced by the thermal expansion measurements, supported by specific heat measurements and decrease in the sharpness of the transition.

Thus, in this study thermal expansion (TE) experiments appeared to be a convincing tool to draw conclusions about the nature of a structural phase transition in PZS compounds, since the structural changes associated with phase transitions and associated changes in lattice constants frequently become apparent just by volumetric discontinuities.

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