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Effect of Ti^{4+}:Sn^{4+} ratio on the phase transition and electric properties of PLZST antiferroelectric ceramics

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Abstract PLZST antiferroelectric ceramics were synthesized by the modified coprecipitation method. Effect of variations in the Ti^{4+}:Sn^{4+} ratio on phase and properties were evaluated. The XRD patterns show that with the increasing of Ti^{4+} content, the structure of ceramics changes from tetragonal phase to rhombohedral phase and this was certified by the P–E hysteresis loops. The temperature dependence of dielectric constant of the ceramics was measured. Low frequency dispersion at room temperature disappeared when the temperature increased and the variation of T_m is not linear with the content of Ti^{4+}. These unusual behaviors had been interpreted.

Introduction

The most promising antiferroelectric materials reported in the literature are lead-based materials which can be applied in actuators and high-energy storage capacities. Among all of them, PLZST ceramics and their modification have been studied for potential actuator applications in recent years [1–3]. These materials exhibit attractive characteristics of low induced electric field for antiferroelectric–ferroelectric (AFE–FE) phase transition and high strain (0.85% maximum longitudinal strain) [4]. Antiferroelectric PLZST ceramics with the composition closer to the morphotropic phase boundary (MPB), which separates the tetragonal antiferroelectric (AFE) from the rhombohedral ferroelectric (FE), can be more easily phase switched from AFE to FE by an electric field or a temperature field. The small free energy difference between the two phases near the MPB makes such switching possible [5].

The conventional way to prepare PLZST ceramics is by solid-state method [6]. This method often leads to compositional fluctuation and structural inhomogeneities. To overcome these problems, some different methods have been developed to generate high purity, homogeneous, reactive PLZST ceramic powders, such as sol-gel method [7, 8], molten salt synthesis method [9], and coprecipitation method [10]. In previous research, Xue et al. improved coprecipitation method [11] and prepared $Pb_{0.97}La_{0.02}(Zr_{0.66}Sn_{0.27}Ti_{0.07})O_3$ antiferroelectric ceramics with the composition near the MPB [12]. The purpose of this work is to study electric properties of PLZST ceramics in the vicinity of the MPB using modified coprecipitation method. We changed the ratio of Ti^{4+}:Sn^{4+} perpendicular to the AFE_T-FE_R MPB and discussed the effect of Ti^{4+}:Sn^{4+} on the phase transition and electric properties of the ceramics.

Experimental procedure

The modified coprecipitation method as described by Xue et al. [12] was employed in the synthesis of PLZST ceramics. The starting materials used were reagent grade PbO, La_2O_3, $ZrOCl_2 \cdot 8H_2O$, $SnCl_4 \cdot 5H_2O$ and $TiCl_4$ according to the composition of $Pb_{0.97}La_{0.02}(Zr_{0.66}Sn_{(0.34-x)}Ti_x)O_3$ with an addition of 3 mol% excess PbO (x = 0.07, 0.10, 0.11; hereafter denoted as A1–A3; it is shown in Fig. 1). PbO and La_2O_3 were initially dissolved in acetic acid and

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$ZrOCl_2 \cdot 8H_2O$, $SnCl_4 \cdot 5H_2O$and $TiCl_4$ were dissolved in distilledwater individually. Then the above solutions were mixed to get the PLZST clear solution, which was kept below pH 1 to avoid precipitation. A small amount of hydrogen peroxide was added to the solution. Then the PLZST solution was added dropwise to a continuously stirred bath of cupferron solution (the cupferron to total metal ion ration was 8:1). During the coprecipitation, the pH of the bath was maintained 5.5–5.7 by adding aqueous ammonia as necessary. After the precipitation, the precipitate was filtered and washed several times to eliminate Cl^-, and dried in an oven at 100 °C. The resultant precursor was subsequently calcined at about 700 °C in air. The powders obtained were subjected to axial pressing at 50 MPa to form disc specimens of 10 mm in diameter and of the order of a few millimeters thick. The disc specimens were sintered at 1100 °C for 2 h in a lead-rich atmosphere.

The sintered samples were then polished and covered with silver paste as the electrode for the dielectric measurement. Dielectric properties with temperature were measured using a multi-frequency LCR meter (HP 4192). Frequencies used were 1, 10, and 100 kHz while temperature ranged from –50 to 200 °C with a heating rate of 2 °C/min. Phase analyses were performed by powder X-ray diffraction (XRD, D8 ADVANCE, Brüker, Germany) using Cu Kα radiation. The polarization–electric field (P–E) hysteresis loops was measured using Sawyer–Tower circuit at room temperature.

Results and discussion

Effect of Ti^{4+}:Sn^{4+} ratio on phase structure

Figure 2 shows the X-ray diffraction patterns of A1–A3. The results reveal that all the samples are of the pure perovskite structure. It is known that in the rhombohedral phase, the {200} profile will show a single narrow peak because all the planes of {200} share the same lattice parameters, while in the tetragonal phase, the {200} profile should split into two peaks with the intensity height of one being half of the other because the lattice parameters of (200) and (020) are the same but are slightly different from those of (002). The reported lattice parameters of PLZST single crystals are a = b = 4.120 Å and c = 4.095 Å [13] so the (002) profile is latter than the (200) profile in the XRD patterns of PLZST. Around 2θ = 45 °C as shown in Fig. 2, A1 reveals two obvious lines with the intensity height of the former being nearly twice of the latter indicating that the phase structure of A1 is tetragonal structure. Although there is a peak splitting for A2, the relations between the intensity of two peaks do not correspond to the characters of a typical tetragonal structure, which indicates that there is two-phase coexistence in A2. The single (200) peak of A3 demonstrates that the structure has transferred into rhombohedral phase. Therefore, it can be inferred that with the increasing of Ti^{4+} content, the structure of ceramics changes from tetragonal phase to rhombohedral phase and the characteristic (101), (002), (202) peaks of tetragonal phase disappeared. The structures of the samples close to MPB are very sensible to the variation of the compositions.

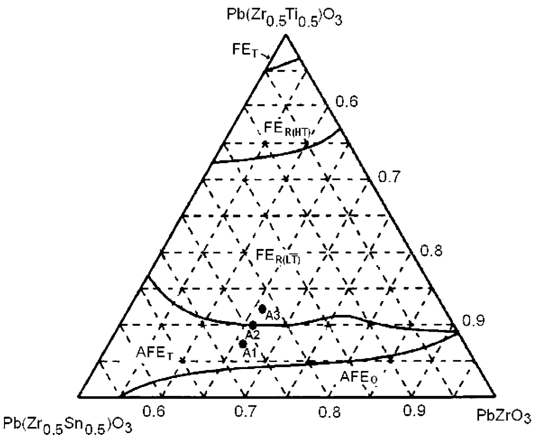

Fig. 1 Ternary phase diagram for the system $(Pb_{0.97}La_{0.02})$ (Zr, Sn, Ti)O_3 [12]

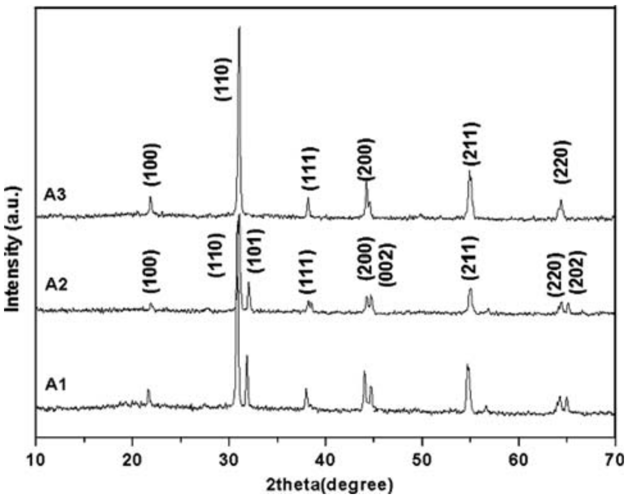

Fig. 2 XRD patterns of PLZST ceramics synthesized by modified coprecipitation method with different Ti^{4+}:Sn^{4+} ratio

Effect of Ti^{4+}:Sn^{4+} ratio on electric properties

The temperature dependence of dielectric constant for A1–A3 samples were measured at different frequencies (1, 10, 100 kHz) as shown in Fig. 3. An unusual phenomenon is that in the low temperature region (–50 to 50 °C), these samples exhibit weak frequency dispersion; while with the

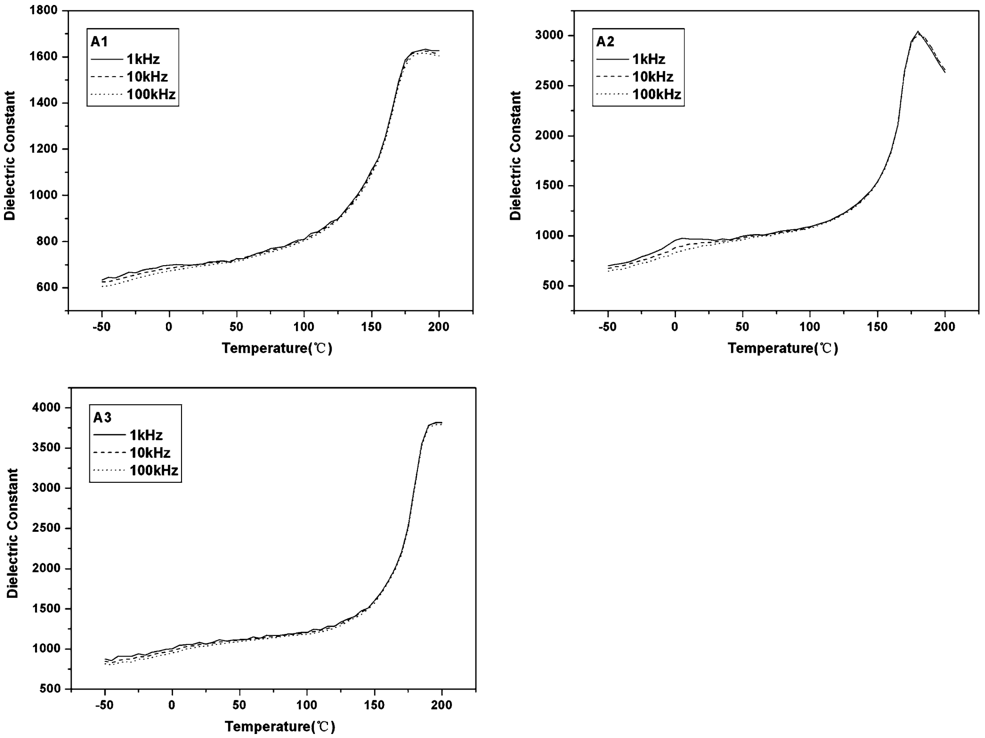

Fig. 3 Temperature dependence of dielectric constants of PLZST ceramics at 1, 10, 100 kHz

increasing of temperature, the dielectric constant increased but the frequency dispersion disappeared. The comparison of dielectric constants of PLZST ceramics with different Ti^{4+}:Sn^{4+} ratio at 1 kHz is shown in Fig. 4. The values of the peak dielectric constant (ε_m) and the corresponding temperature (T_m) at 1 kHz frequency for all samples are shown in Table 1. The results indicate that the dielectric constants rise with the addition of Ti^{4+} in the PLZST ceramics. However, the variation of T_m (the temperature corresponding to the peak dielectric constant ε_m) is not linear with the content of Ti^{4+}, the minimum T_m exists in A2.

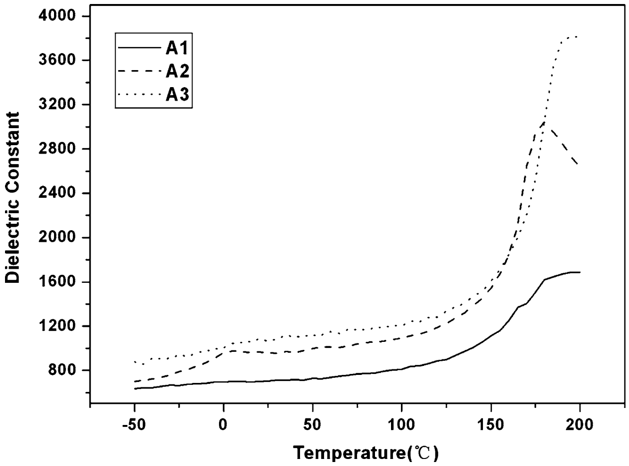

Fig. 4 Temperature dependence of dielectric constants comparison of PLZST ceramics at 1 kHz

According to the diffuse phase transition (DPT) theory proposed by Smolensky [14], for the complex composition of La doped PZST antiferroelectrics, the DPT is considered in terms of a model based on fluctuations in composition. The fluctuations are caused by statistical (disordered) distribution of heterovalent ions in the same crystallographic positions. In crystals of this type, transition to polar state should be gradual. Polar regions of varying composition and Curie temperature emerge and agglomerate into clusters. The polar regions enriched $PbZrO_3$ and $PbSnO_3$ exhibit antiferroelectric characteristic, and the polar regions enriched $PbTiO_3$ come into being strong ferroelectric polar microdomains [15]. Because of the existent of FE microdomains, they occur ''breathing'' movement with the weak electric field applied [16]. The movement is restricted by the condition of FE microdomains which are limited in the base, so the sample exhibits low frequency dispersion at low temperature (Fig. 3). With the temperature rising up, the polar FE microdomains fused into the original base gradually and the frequency dispersion disappear.

Table 1 The peak dielectric constant (ε_m) and the corresponding temperature (T_m) for PLZST ceramics at 1 kHz

Ti^{4+}:Sn^{4+} ratio	ε_m	T_m(°C)
7:27	1634	190
10:24	3038	180
11:23	3804	~200

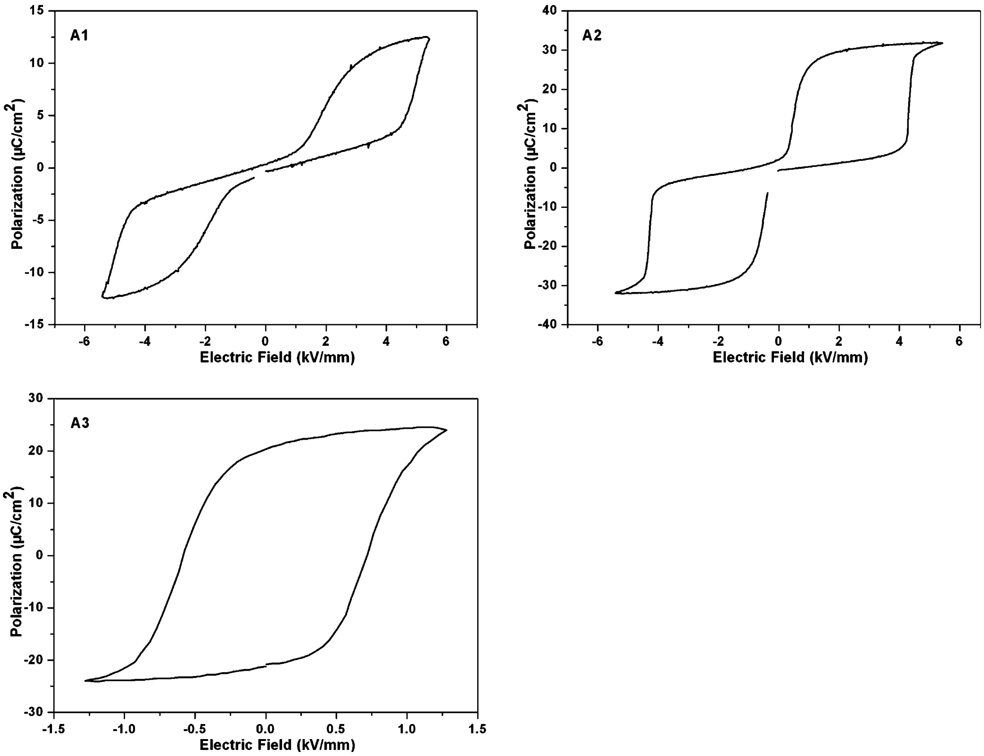

Fig. 5 P–E hysteresis loops for PLZST ceramics

When the content of Ti^{4+} is low (A1), the samples exhibit antiferroelectric tetragonal phase. With the increasing of Ti^{4+} content, polar FE domains enlarge which weaken the antiferroelectric properties accompanied with the AFE–PE phase transition temperature decreased (Fig. 4). After the content of Ti^{4+} exceeds certain proportion, the ferroelectric long-range order is established and the samples transfer to stable ferroelectric rhombohedral phase (A3). FE-PE phase transition occurs and T$_m$ is increased with increasing the content of Ti^{4+}. The certain proportion is called AFE$_T$–FE$_R$–PE$_C$ triple phase point, which generally exists in other doped PZT-system ceramics near the AFE and FE phase [17, 18] and has the lowest phase transition temperature. Compared with the compositions of A1 and A3, A2 is closer to the triple phase point. Therefore, T$_m$ of A2 is lower than that of A1 and A3 (Fig. 4).

The P–E hysteresis loops at room temperature for all the samples are shown in Fig. 5. A1 and A2 represent the typical antiferroelectric double hysteresis loops with maximum polarization of 12.5 and 31.1 μC/cm^2, respectively. The values of forward switching field of A1 and A2 are 4.95 and 4.32 kV/mm, respectively. The switching field increased as the compositions moved further from the MPB, i.e., deeper into the AFE region with decreased Ti^{4+} content. This can be attributed to a material with a more stable, room-temperature AFE phase existing deep within the AFE region that requires a higher field to switch to its FE phase [19]. A3 reveals single hysteresis loop indicating that the structure of A3 is ferroelectric phase. The results of the P–E hysteresis loops are coincident with that of XRD patterns and dielectric constant.

Conclusion

We have prepared PLZST antiferroelectric ceramics using the modified coprecipitation method. Compositions of $Pb_{0.97}La_{0.02}(Zr_{0.66}Sn_{(0.34-x)}Ti_x)O_3$ (x = 0.07, 0.10, and 0.11) were selected to value the effect of Ti^{4+}:Sn^{4+} ratio on the phase transition and electric properties. The XRD patterns reveal that all the samples are of the pure perovskite structure and the structure of ceramics changes from tetragonal phase to rhombohedral phase with the increasing of Ti^{4+} content. Anomalies of frequency dispersion and the temperature corresponding to the peak dielectric constant were attributed to the existence of polar FE microdomains in the AFE base. The mechanism of the effect of FE microdomains was explained. The results of P–E hysteresis loops were coincident with that of XRD patterns and dielectric constant.

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