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The crystalline and dielectric properties of $(1-x)Pb(Sc_{1/2}Ta_{1/2})O_3$–$(x)PbTiO_3$ ceramics prepared by one-step-sintering-method

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Abstract

The solid solutions of lead scandium tantalate–lead titanate, $(1-x)Pb(Sc_{1/2}Ta_{1/2})$–$xPbTiO_3$ (PSTT(x)) were synthesized by a conventional mixed-oxide method (or named as one-step-sintering-method) using lower sintering temperature (1200–1300 °C). The experimental results showed the percent of the perovskite phase of the PSTT(x) ceramics could be as high as 90%, the highest was up to 100%. The SEM observation showed the crystalline grains were dense and well-stacked, and the grain boundaries were well clear. It was found that the Curie temperature T_c of the PSTT(x) ceramics synthesized by one-step-sintering-method were usually higher than that of the references reported. The thermal hysteretic temperature ΔT_c were changed from 6 to 12 °C with different x concentration, and the Curie constants c^* were 3.7–$(8.3 \times 10^6)K^2$.

Keywords: D. Perovskite; Relaxor ferroelectric ceramics; PSTT

1. Introduction

$Pb(Sc_{1/2}Ta_{1/2})O_3$ (PST) ceramics is one of the typical relaxor ferroelectrics, and has excellent dielectric, ferroelectric, piezoelectric, and pyroelectric properties [1–3]. However, the Curie temperature T_c of PST is rather low (about −10 to 26 °C according to the order degree of B site ions) and the PST ceramics needs higher sintering temperature (about 1500 °C) [4–6]. If $PbTiO_3$ which T_c is about 490 °C could be added into PST to form the solid solution with complex lead perovskite structure, the T_c of PST system could be increased and the sintering temperature decreased. So the application fields of PST ceramics system could be enlarged [7,8]. Due to the difficult preparation of the Pb-based complex perovskite relaxor ferroelectric ceramics, many authors employed the two-step-sintering-method to produced PST ceramics. That means at the first step, a wolframite $ScTaO_4$ precursor was synthesized using Ta_2O_5 and Sc_2O_3. Then at the second step, added PbO into $ScTaO_4$ powders to synthesize PST ceramics. However, a conventional mixed-oxide method or named as one-step-sintering-method was easier to be used in industrial production.

In this paper, the $(1-x)Pb(Sc_{1/2}Ta_{1/2})$–$xPbTiO_3$ (PSTT(x)) with high perovskite phase were prepared by using one-step-sintering method, and the crystalline and dielectric properties were measured. The Curie temperatures, the thermal hysteretic temperature and the Curie constants of the PSTT(x) ceramics were obtained. The initiatory explain was also given for the preparation of PSTT(x) ceramics by using one-step-sintering-method.

2. Experimental procedure

In our study, PSTT(x) ceramics were prepared by one-step-sintering-method involving the use of high purity starting compounds PbO, TiO_2, Sc_2O_3, Ta_2O_5, added excessive PbO, a long preserving heat time (9 h), and controlled lead atmosphere sintering. The detail experimental procedures are reported elsewhere [9].

The crystalline properties of PSTT(x) ceramics were characterized by X-ray diffraction (DX-1000) and scanning

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electron microscopy (Hitachi S450), and a wide-frequency LCR meter (TH2816) was employed to measure the dielectric properties.

3. Results and discussion

Fig. 1 is a typical XRD patterns of PSTT(x) ceramics sintered at different temperatures. From Fig. 1, it was found that some samples showed the pure perovskite phase, and others showed the coexistence of perovskite and pyrochlore phase. The volume fraction of perovskite phase was determined by using the ratio of related intensities of the (2 2 2) pyrochlore peak ($I_{(222)\text{Pyro}}$) and the (2 2 0) perovskite peak ($I_{(220)\text{Perov}}$) of PSTT(x) ceramics, as given by the following equation [3]:

$$\text{perovskite phase (\%)} = \frac{I_{(220)\text{ perovskite}}}{I_{(220)\text{ perovskite}} + I_{(222)\text{ pyrochlore}}} \times 100.$$

The percentage of the perovskite phase content of PSTT(x) ceramics as a function of sintering temperature and composition was shown in Fig. 2. The perovskite phase of the PSTT(x) ceramics, which were prepared by one-step-sintering-method, usually surpass to 90%, and the highest was up to 100%, such as PSTT(30), PSTT(35), and PSTT(45) ceramics. The perovskite content of the PSTT(30) changed greatly with different sintered temperature. PSTT(30) ceramic samples sintered at 1175 °C showed pure perovskite phase. However, when sintering temperature rose up to 1275 °C, the perovskite phase content of PSTT(35) was only 94% or less. The perovskite phase content of the PSTT(40) changed least. The perovskite phase content was about 97.5–98.5% when the sintering temperature changed from 1120 to 1250 °C.

Fig. 3 shows the optimum sintered temperature with the highest perovskite phase content of PSTT(x) ceramics. From

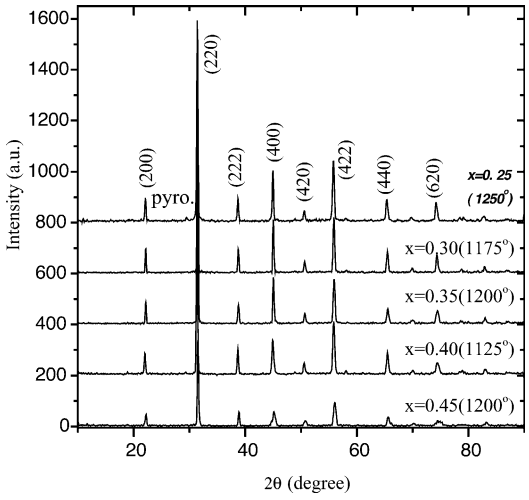

Fig. 1. The typical XRD patterns of PSTT(x) ceramics.

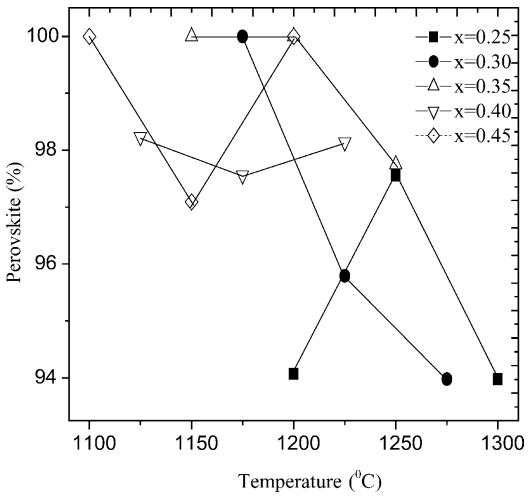

Fig. 2. The perovskite phase content of PSTT(x) ceramics dependence of sintering temperatures and composition.

Fig. 3, it was found that the perovskite phase content of PSTT(x) ceramics was closely dependent on the sintered temperature and composition. When x is 0.25, 0.45, the optimum sintered temperature is about 1250, and 1100 °C, respectively.

Fig. 4 shows the surface morphology of PSTT(30) ceramics sintered at 1275 °C. From Fig. 4, it was found that the PSTT(30) ceramics was dense, good crystalline and well-stacked. The average size of crystal grains was about 1.5–5.0 μm. The crystal boundary was well clear, and the crystal grain had plump outward appearance, and showed complete growth. This was on account of higher sintered temperature, longer preserve-heat time, so that the crystal grains grew completely, and some of grains became bigger. It was expected that the PSTT(x) ceramics with more dense and smaller grains could be obtained by using optimum sintering processing.

The dielectric constant measured at 10 kHz is showed as a function of temperature in Fig. 5 for poled specimens. From

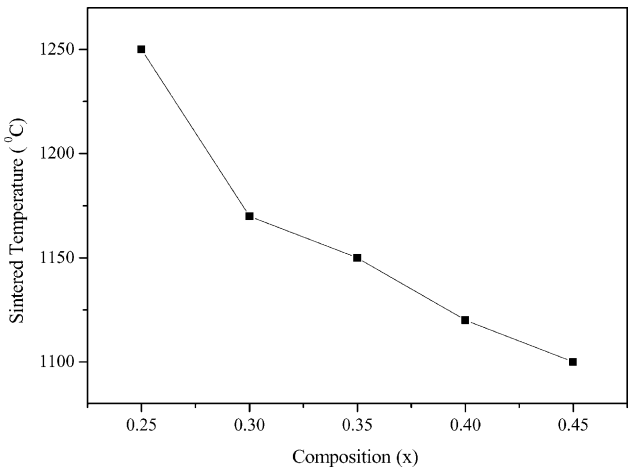

Fig. 3. The dependence of optimum sintered temperature on composition of PSTT(x) ceramics.

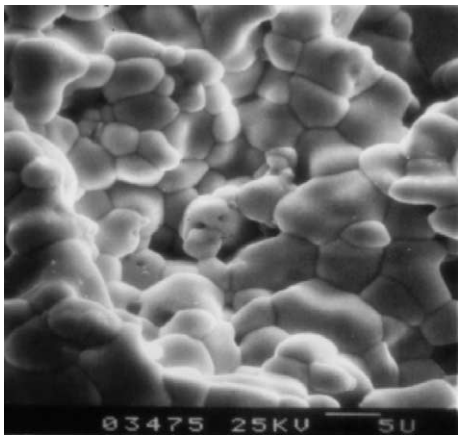

Fig. 4. The SEM observation of PSTT(30) ceramics sintered at 1275 °C.

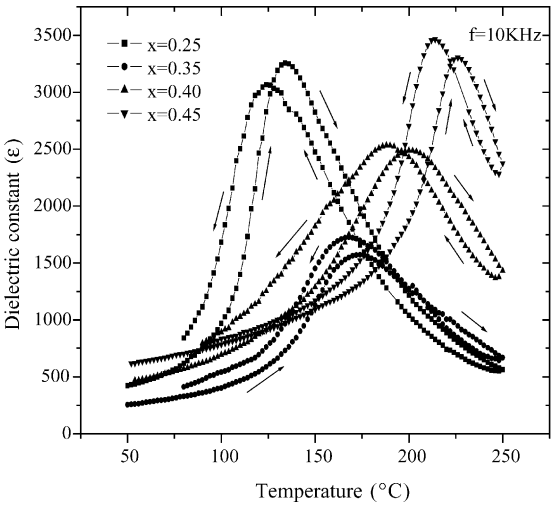

Fig. 5. The temperature dependence of dielectric constant of PSTT(x) ceramic.

Fig. 5, T_c was obtained of the PSTT(x) ceramics when it was heating or cooling process and their difference value ΔT_c—the thermal hysteresis temperature. The changes of the dielectric constant of PSTT(x) ceramics at the peak temperature were quite a large, and showed the typical characteristic of the diffuse phase transition. Table 1 shows the dependence of T_c and ΔT_c of PSTT(x) ceramics with composition x. From Table 1, it was found that ΔT_c of PSTT(x) ceramics was changed from 6 to 12 °C. The peak temperature of the dielectric constant of PSTT(x) ceramics in heating process was larger that that of PSTT(x) ceramics in cooling process. This result was consistent with other ferroelectrics with first phase transition. With increasing of the composition x, the T_c of PSTT(x) ceramics increased too, from 134 °C at $x = 0.25$ to 200 °C at $x = 0.40$. It was reported that the T_c of PSTT(0.30), PSTT(0.40) ceramics prepared by two-step-sintering-method was 136 and 180 °C, respectively [10].The changes in T_c of PSTT(x) ceramics may be caused by the different processing. The two-step-sintering-method required the reaction of Sc_2O_3 and Ta_2O_5 to produce $ScTaO_4$ at higher temperature. It can be inferred that $ScTaO_4$ had the influence to decrease the T_c of PSTT(x) ceramics.

Table 1
The T_c, ΔT_c, and c^* of PSTT(x) ceramics in heating or cooling process measured at 10 kHz

	Process	$x = 0.25$	$x = 0.35$	$x = 0.40$	$x = 0.45$
T_{c1} (°C)	Heating	134	174	200	226
T_{c2} (°C)	Cooling	124	168	188	214
ΔT_c (°C)	–	10	6	12	12
c^* ($\times 10^6 K^2$)	Heating	4.3492	3.6814	6.9411	3.9591
	Cooling	5.6045	3.9487	8.3043	5.0751

The dependence of the reciprocal of dielectric constant on the temperature T of relaxor ferroelectrics is as follows [11]

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_0} + \frac{(T - T_c)^2}{c^*}.$$

From Fig. 5, it was derived the relationship of $1/\varepsilon$ with T, and the Curie constant c^* could be calculated, as shown in Table 1. For the same composition, it was found that c^* was larger in cooling than that in heating process. For the same heating or cooling process, the minimum c^* was 3.7–3.9 $\times 10^6 K^2$ when $x = 0.35$; and the maximum c^* was 3.7–3.9 $\times 10^6 K^2$ when $x = 0.40$. The mechanisms of produced different c^* of PSTT(x) ceramics in different processing are studied in progress.

It is, therefore, assumed at this time that Sc^{3+} and Ta^{5+} could easier enter B site when Ti^{4+} existed during a longer time sintering. It was also beneficial to the movement of Pb^{2+} for a longer time sintering, thereby promoted the forming of the perovskite phase. On the other sides, compensating $PbZrO_3$ pellets could efficiently control the loss of PbO during the sintering process of PSTT(x) ceramics. So, the PSTT(x) ceramics could be synthesized by one-step-sintering-method. A more thorough investigation of the intrinsic mechanism is required to determine more accurately the origin and exact nature of the preparation of PSTT(x) ceramics by using one-step-sintering-method.

4. Conclusions

The PSTT(x) ceramics with pure perovskite phase could be produced by one-step-sintering-method. The processing was simple, so it was expected that this process would be used in industrialized production. The SEM observation showed that the crystalline grains of the PSTT(x) ceramics were well-stacked and the grain boundaries were well clear. The T_c of the PSTT(x) ceramics prepared by one-step-sintering-method was usually higher than that of the references reported. The ΔT_c of the PSTT(x) were changed from 6 to 12 °C with different x concentration. The c^* of the PSTT(x) ceramics were 3.7–8.3 $\times 10^6 K^2$. The initiatory explain was also given for the preparation of PSTT(x) ceramics by using one-step-sintering-method.

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