

Dielectric and pyroelectric properties of $(1-x)$ PST- x PZT ferroelectric ceramics

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Abstract $\text{Pb}(\text{Sc}_{1/2}\text{Ta}_{1/2})\text{O}_3$ (PST) ceramics were investigated greatly in the world for their unique pyroelectric, ferroelectric and dielectric properties and comprehensive applications on uncooled focal plane arrays, infrared detectors and other electronic devices. However, the PST ceramics doped with other perovskite ferroelectrics showed more excellent electrical and electronic properties. In this paper, $(1-x)$ PST- x PZT(PSTZT) ferroelectric ceramics were prepared by conventional solid state process. The experiment results demonstrated that the PSTZT ceramics had pure perovskite phase. The temperature dependence of permittivity of PSTZT ceramics was investigated in detail, which indicated that PSTZT was not a complete diffusive phase transition ferroelectric ceramics. At room temperature, the pyroelectric coefficient of PSTZT ($x=0.1$) ceramics was about $15 \cdot 10^{-8} \text{C}/(\text{cm}^2 \text{K})$.

Keywords PSTZT ceramics · Relaxor ferroelectric · Pyroelectricity

1 Introduction

$\text{Pb}(\text{Ta}_{0.5}\text{Sc}_{0.5})\text{O}_3$ (PST) is a complex perovskite relaxor ferroelectric ceramics [1, 2] with high permittivity (about

25000), large electrostrictive effect, and good pyroelectricity, therefore PST ceramics could have comprehensive applications on uncooled focal plane arrays, infrared detectors and other electronic devices [3, 4]. However, PST ceramics were always doped some other ions to promote their properties for more complex applications.

Usually, $\text{Pb}(\text{B}', \text{B}'')\text{O}_3$ complex ferroelectric ceramics, such as PST ceramics, were prepared by the precursor method to avoid formation of pyrochlore phase which deteriorated the properties of perovskite ceramics. However, the conventional solid state process (named as one-step-sintering method, OSSM) in which all starting oxides are mixed directly to fabricate electronic ceramics is rather simple and suitable to industry production [4, 5].

In this paper, $(1-x)$ PST- x Pb($\text{Zr}_{0.52}\text{Ti}_{0.48}$) O_3 (PSTPZT) relaxor ferroelectric ceramics were prepared by OSSM. The crystalline, dielectric and pyroelectric properties of PSTZT ceramics were measured and discussed.

2 Experimental procedure

Ceramics with the normal composition $(1-x)\text{Pb}(\text{Sc}_{0.5}\text{Ta}_{0.5})\text{O}_3$ - x Pb($\text{Zr}_{0.52}\text{Ti}_{0.48}$) O_3 ($x=0.1, 0.2, 0.3, 0.4, 0.5$) were synthesized by using conventional solid state process. The starting materials used in this study were Sc_2O_3 and Ta_2O_5 of 99.99% purity, TiO_2 of 99.8% purity, PbO of 99.8% purity, and ZrO_2 of 99.8% purity. The mixture powders were calcined at 850°C for 2 h. The calcined powders were milled, and the poly(vinylalcohol) was added into these powders as a binder. The granulated powders were subsequently granulated and pressed into disks of 10 mm diameter and 1 mm thickness under 16 MPa pressure. These powder compacts were fired in air at selected

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temperatures, depending on their x values, in the range between 1200 °C and 1350 °C for 4 h. $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ pellets were used to compensate the volatilization of PbO during sintering of PSTZT ceramics. For electrical characterization, the PSTZT ceramics were polished and pasted silvers as electrodes, and then immersed in silicon oil and poled in a 4.0 kV/mm electric field. The electric field was applied under the Curie temperature for about 15–30 min depending on their x values. The samples were aged for 24 h before test. The phase structure of samples was determined by X-ray diffraction (DX-1000); Surfaces were observed by SEM (HitachiS-450). The value of d_{33} was measured with a Burlincourt-style d_{33} meter (ZJ-3A, Institute of Acoustic Academia Sinica). The dielectric properties were measured by using a high temperature system (GJW-I) and a precision LCR meter (HP4282A, Agilent). The pyroelectric coefficients of PSTZT ceramics were measured by using a Keithely 6517 electrometer.

3 Experimental results and discussion

3.1 XRD analysis

The XRD patterns of PSTZT ceramics sintered at 1250 °C and 1300 °C by OSSM were illustrated in Fig. 1. From Fig. 1, it was found that the pyrochlore phase existed in the samples sintered at different temperature. However, when x is 0.5, no pyrochlore phase was found in samples at all four sintering temperatures. Because of high activity, PbO firstly reacts with constituents at B site to form pyrochlore during sintering of Pb-base relaxor ceramics, and then changes into perovskite with sintering temperature increasing [6, 7]. So, when excessive PbO is added into oxides mixture, pyrochlore phase formed at lower temperature is enough unstable to form more stable perovskite phase at higher temperature. The perovskite content of PSTZT ceramics can be calculated roughly as follows [8]:

$$\text{Perovskite content}(\%) = \frac{I_{\text{per max}}}{\sum_n I_{n \text{ max}}} \times 100\%$$

In the equation, $I_{\text{per max}}$ is the intensity of the strongest XRD peak line of perovskite phase, and $I_{n \text{ max}}$ is the intensity of the strongest XRD peak line of No. n phase. It was found that the perovskite content of PSTZT ceramics was rather high, from 92 to 100%. It was also found that the content of perovskite phase in PSTZT ceramics was affected in some degree by sintering temperature. The content of perovskite phase of PSTZT ceramics increased

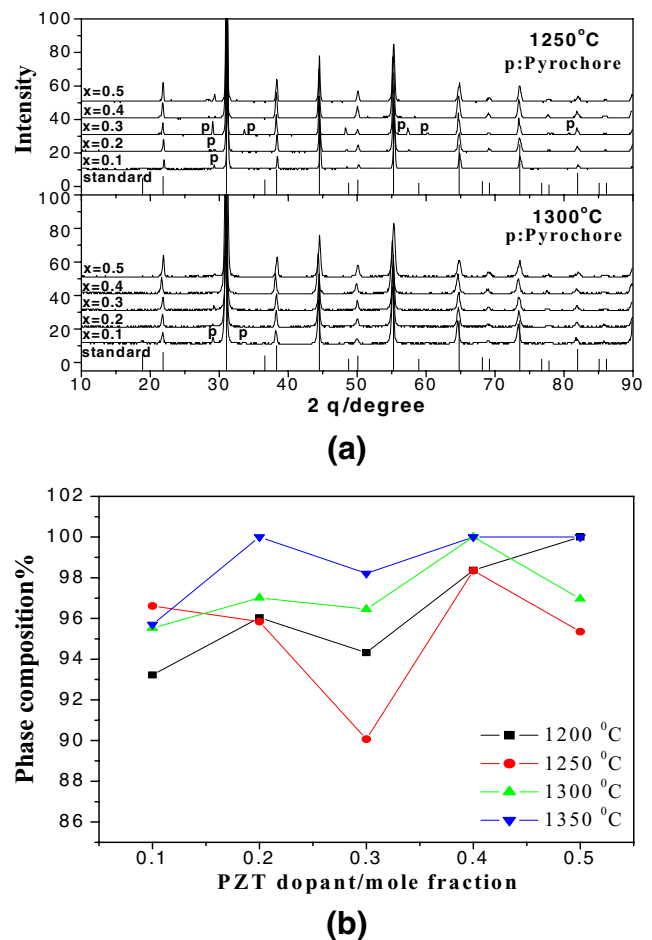


Fig. 1 The crystalline properties of PSTZT ceramics prepared by OSSM (a) patterns and (b) perovskite content

basically in most of samples with increasing the sintering temperature.

3.2 Dielectric properties

The temperature dependences of permittivity and dielectric loss of PSTZT ceramics were measured at several frequencies from 25 to 250 °C. Figure 2(a)–(c) show these experiment results of PSTZT ceramics sintered at 1200 and 1300 °C, with $x=0.2$, 0.4 and 0.5, respectively. It could be found from Fig. 2 that the frequency diffusion of PSTZT ceramics was rather weak. The difference, ΔT_m , between peak permittivity temperature at high frequency and one at low frequency, and the temperature difference, $\Delta T(1 \text{ KHz})$, between the temperatures at half of peak permittivity, can represent frequency diffusion (FD) and diffusive phase transition (DPT), respectively. Table 1 showed the FD and DPT values of PSTZT ceramics.

The temperature dependences of ϵ_r and $\tan\delta$ of PSTZT ceramics demonstrated that PZT dopant had a main important effect on T_m : T_m increased with the increasing

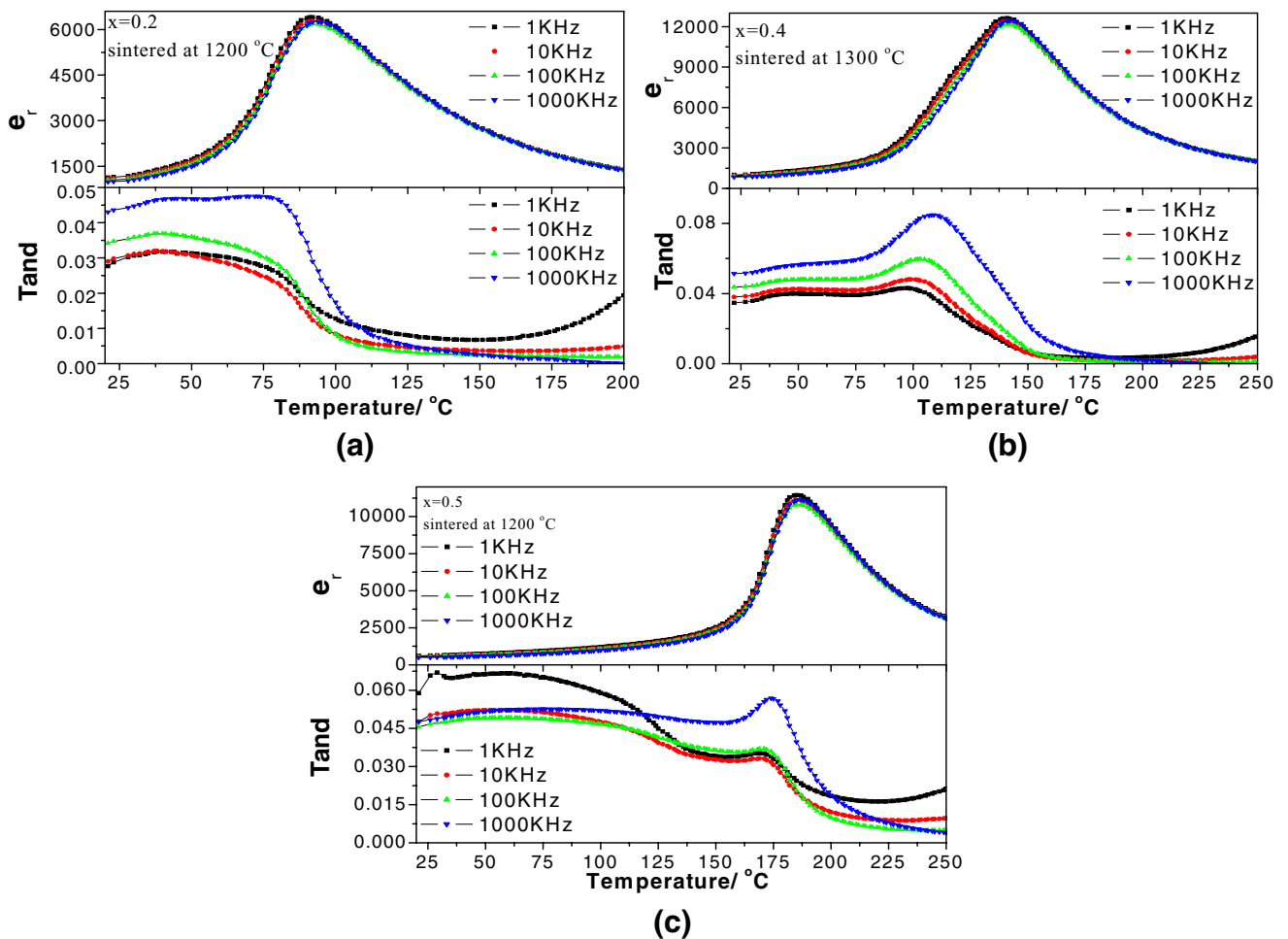


Fig. 2 The temperature dependences of permittivity and loss of PSTZT ceramics (a) sintered at 1200 °C, x=0.2, (b) sintered at 1200 °C, x=0.5, and (c) sintered at 1300 °C, x=0.4

of PZT dopant; permittivity decreased with the increasing of PZT dopant. For ceramics prepared by using conventional solid state process, the composition of ceramics could not be well distributed at the atoms' level and a little amount of impurity is unavoidable. The ion radius of Ta⁵⁺, Sc³⁺, Ti⁴⁺, Zr⁴⁺ is 0.064, 0.075, 0.061, 0.072 nm, respectively, so for close size of ions, a stable uniform phase could be achieved more easily. When PZT was doped into PST, the amount of impurity was decreased, and the space charge from inhomogeneous phase composition was reduced, and its attribution to polarization got smaller, which resulted in permittivity decreased with increased dopant of

PZT. Because the Curie temperature of Pb(Zr_{0.52}Ti_{0.48})O₃ is about 380 °C, the Curie temperature of PSTZT ceramics is enhanced, and the more PZT is doped into PST, the higher the Curie temperature of PSTZT is.

3.3 Pyroelectric properties

Figure 3 showed the temperature dependences of pyroelectric properties of PSTZT ceramics. From Fig. 3(a), it was found that when sintering temperature increased, the pyroelectric coefficient of PSTZT(x=0.3) ceramics increased except for sintered at 1350 °C. It might be due to the formation of glass phase in PSTZT ceramics sintered at high temperature as to 1350 °C. The temperature dependences of pyroelectric coefficients of PSTZT ceramics sintered at 1300 °C with different PZT dopant were shown in Fig. 3(b) and (c). Obviously, the pyroelectric coefficient of PSTZT ceramics decreased when increasing PZT dopant because the pyroelectric property of PZT was much weaker than that of PST ceramics. It was found that the pyroelectric coefficient of PSTZT(x=0.1) ceramics at room temperature

Table 1 FD and DPT values of PSTZT ceramics sintered at different temperature for 2 h.

Samples	x=0.2,1200 °C	x=0.4,1300 °C	x=0.5,1200 °C
ΔT _m / °C	2	1	2
ΔT/ °C	72	73.5	53.5

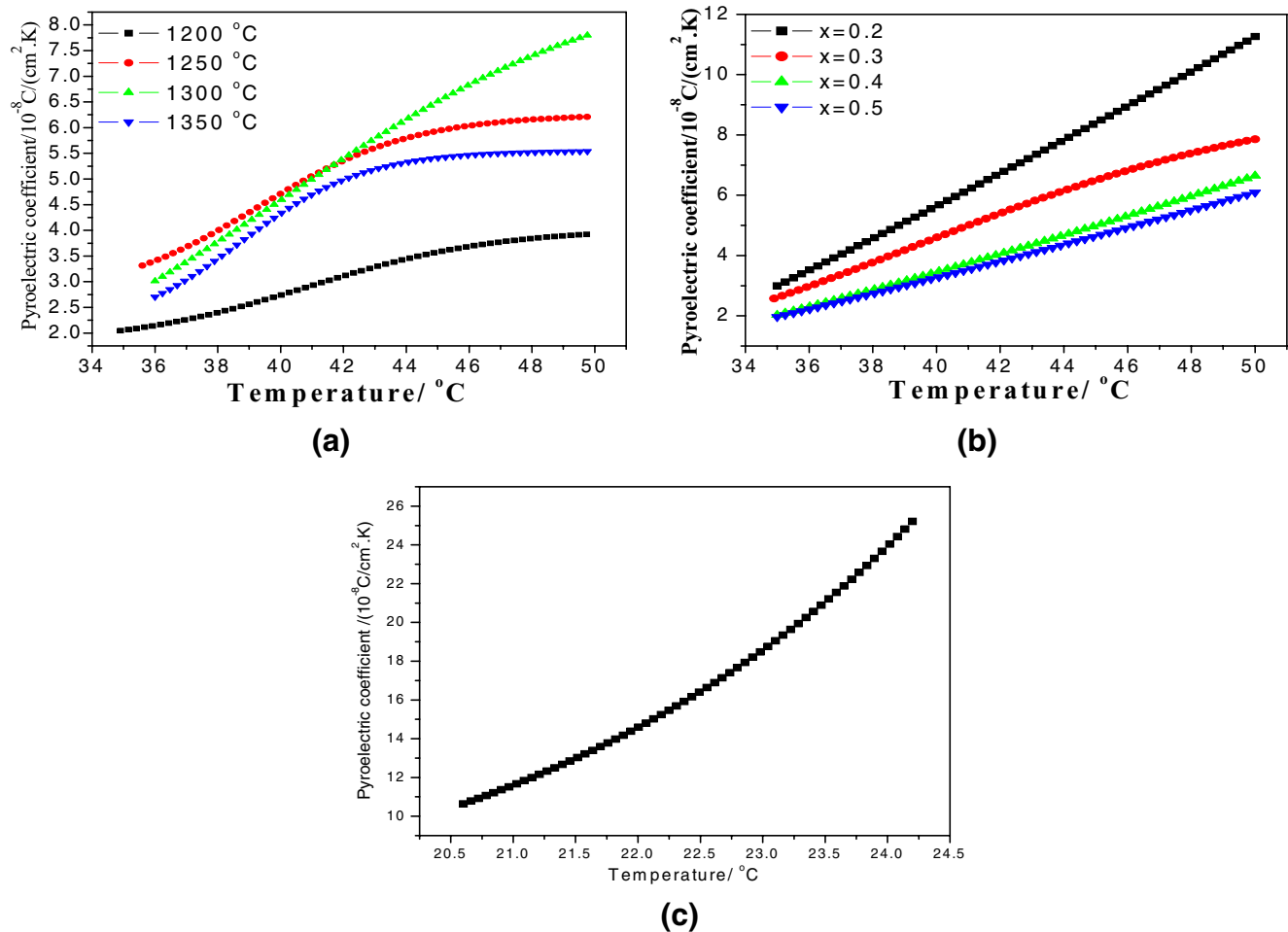


Fig. 3 The temperature dependences of pyroelectric coefficients of PSTZT ceramics (a) $x=0.3$, sintered at different temperature; (b) $x=0.2-0.5$; and (c) $x=0.1$ sintered at 1300 $^{\circ}\text{C}$

was much higher, which could be as to $15 \cdot 10^{-8} \text{ C}/(\text{cm}^2 \cdot \text{K})$. That meant PSTZT ceramics had a promising application in the infrared detector field.

4 Summary

With oxides as starting materials, $(1-x)\text{PST}-x\text{PZT}$ ceramics were prepared by conventional solid state process. The PSTZT ceramics without pyrochlore could be acquired when sintered for 4 h at 1350 $^{\circ}\text{C}$ and at 1200 $^{\circ}\text{C}$ when $x=0.5$ for 4 h. According to the temperature dependence of ϵ_r and $\tan\delta$ of PSTZT ceramics, it was found that PSTZT ceramics was a ferroelectric ceramics with a limited DPT: T_m increased, and ϵ_{rm} increased firstly, then decreased with frequency increasing. T_m was affected greatly by the amount of PZT doped and increased with PZT dopant increasing. The amount of PZT dopant had an important main effect on the pyroelectric coefficient of PSTZT

ceramics: the pyroelectric coefficient of PSTZT ceramics decreased with PZT dopant increasing.

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