

Microstructure and electrical properties of $(\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02})(\text{Zr}_{0.68}\text{Sn}_{0.24}\text{Ti}_{0.08})\text{O}_3$ anti-ferroelectric ceramics fabricated by the hot-press sintering method

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Abstract

$(\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02})(\text{Zr}_{0.68}\text{Sn}_{0.24}\text{Ti}_{0.08})\text{O}_3$ anti-ferroelectric ceramics with various amounts of excess PbO have been fabricated by the conventional solid-state reaction process and the hot-press sintering method, and the dependence of microstructure, ferroelectric and dielectric properties on sintering approaches and lead volatilization conditions has been studied. When an appropriate quantity of excess PbO is added, the lead volatilization effect can be compensated and the content of pyrochlore phase is decreased. Hot-pressed anti-ferroelectric ceramics exhibit much higher densities than conventionally sintered samples. The spontaneous polarization and maximum dielectric constant of the AFE ceramics decrease when the hot-press sintering method is used. The dielectric loss can be obviously reduced by using the hot-press sintering method and adding a proper amount of excess PbO. The systemic investigation of the lead volatilization effect and the hot-press sintering method will contribute to the development of high properties of anti-ferroelectric ceramics in practical applications.

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1. Introduction

The anti-ferroelectric (AFE) ceramics exhibiting the electric field-induced anti-ferroelectric-to-ferroelectric (AFE–FE) phase transition have attracted more and more research attention¹ due to their potential use in micro-actuators,^{2,3} high-energy storage capacitors,^{4,5} and infrared detectors.^{6–8} In recent years, scientists do not give much focus on the doping effect but on the relationship between the microstructure and the electrical properties of the AFE ceramics.^{9–11} Among all these microstructure parameters, density is the one of utmost importance. When the AFE ceramics are used as the field-induced strain material in micro-actuators, the high porosity decreases the field-induced strain and deteriorates the fatigue property.¹² When the ceramics are used for high-energy storage capacitors, the low density of the AFE ceramics leads to the decrease of breakdown field strength and dielectric constant and finally the

low energy density.⁴ For infrared sensors, the AFE ceramics are used as pyroelectric materials. AFE ceramics of high porosity have low pyroelectric coefficient and large dielectric loss, and cannot be easily used in infrared focal plane array for their poor mechanical strength at the final device thickness.¹³ Therefore, it is necessary to increase the density for practical applications of high performance AFE ceramics.

In order to increase the density of the ceramics, several methods, such as adding sintering aids and changing the sintering atmosphere, have been widely used. However, these methods have their drawbacks. Sintering aids are usually doped to decrease the sintering temperature and increase the density,^{14,15} but the electrical properties of ceramics are deteriorated. Changing the sintering atmosphere can also increase the density of ceramics,^{13,16} but the densification capacity is limited. There are different sintering atmosphere modulations on different materials or the material with various dopants, and the sintering atmosphere modulation effect on the microstructure and electrical properties is not easily controllable. Moreover, the hot-press sintering is an effective method to fabricate high density ceramics.^{17–20} Barium titanate ferroelectric ceramics, for instance, have been hot-pressed by researchers,²⁰ usually for

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attaining high density with small grain size and thus obtaining a high dielectric constant or a high dielectric breakdown strength. However, there are few reports on the microstructure and electrical properties of AFE ceramics fabricated by the hot-press sintering method. Besides, most of the AFE materials belong to the lead zirconate titanate system, the electrical properties of the AFE materials are seriously affected by the lead volatilization during the sintering process.^{6,21} As evidenced by our previous work, the deviation of stoichiometry caused by PbO loss during high temperature processing leads to the formation of pyrochlore phase, and then the poor dielectric and dc electric-field-induced pyroelectric properties.⁶ While much work has reported the effect of excess PbO on the electrical properties of AFE materials sintered by the conventional method, few studies have been conducted on the lead volatilization effect of AFE ceramics prepared by the hot-press sintering method. When the green pellets are hot-pressed in the mold, they cannot be buried in the PbO powders and fired in a closed alumina crucible as being sintered in the muffle furnace, so the lead volatilization conditions of hot-pressed AFE ceramics are different from those of samples prepared by the common solid-state reaction process. Therefore, in order to obtain hot-pressed AFE ceramics with high properties, an appropriate amount of excess lead is important, and the lead volatilization effect during the hot-pressing process must be systemically investigated.

In this paper, $(\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02})(\text{Zr}_{0.68}\text{Sn}_{0.24}\text{Ti}_{0.08})\text{O}_3$ (PBLZST) AFE ceramics containing various amounts of excess PbO are prepared by the conventional solid-state reaction process and the hot-press sintering method, respectively. The microstructure (density, grain size, phase structure) and the electrical properties (anti-ferroelectric and dielectric properties) of the PBLZST specimens with various contents of excess PbO and fabricated by the two different sintering approaches have been systematically investigated. The analysis in this paper is also applicable for other FE and AFE ceramics of the lead zirconate titanate system fabricated by hot-press and spark plasma sintering methods.

2. Experimental

The starting materials were analytical-grade metal oxides and carbonate powders: PbO(99.9%), La_2O_3 (99.9%), TiO_2 (99.8%), ZrO_2 (99.6%), BaCO_3 (99.8%), and SnO_2 (99.6%). The powders were weighed according to the formula $(\text{Pb}_{0.87}\text{Ba}_{0.1}\text{La}_{0.02})(\text{Zr}_{0.68}\text{Sn}_{0.24}\text{Ti}_{0.08})\text{O}_3$ with x mol% excess PbO (x is from 0 to 13) and then thoroughly milled for 4 h. The dried slurries were calcined at 900 °C for 3 h, and then ball milled again for 4 h. Polyvinyl alcohol (PVA) was added to the mixtures as a binder for granulation. The compacts were pressed at about 5 MPa in a disk with the diameter of 20 mm. Next, the samples were sintered with different methods. By the conventional sintering method, the specimens were buried in the PbO powders and sintered at 1250 °C in the muffle furnace for 3 h, in a closed alumina crucible. The specimens with 0 mol%, 4 mol%, 7 mol%, 10 mol%, and 13 mol% excess PbO were denoted as PBLZST(c1), PBLZST(c2), PBLZST(c3), PBLZST(c4), and PBLZST(c5), respectively. By

the hot-press sintering approach, the compacts were placed in a silicon carbide die, and sintered at 1150 °C for 2.5 h with a pressure of 50 MPa. The specimens with 0 mol%, 4 mol%, 7 mol%, 10 mol%, and 13 mol% excess PbO were denoted as PBLZST(h1), PBLZST(h2), PBLZST(h3), PBLZST(h4), and PBLZST(h5), respectively.

The crystal structures of the samples were determined through using an X-ray diffractometer. The microstructure of the PBLZST specimens was observed by a scanning electron microscopy (SEM). The bulk density was determined by the Archimedes method. Polarization versus electric field (P–E) hysteresis loops were measured with a standard Sawyer–Tower circuit connected to a high voltage power supply. And the dielectric properties with variation of temperature were measured at the frequency of 1 kHz using a LCR analyzer (HP 4192; Hewlett Packard Ltd., Palo Alto, CA).

3. Results and discussion

3.1. Microstructure characteristics

Fig. 1 shows the XRD patterns of the PBLZST ceramics with various excess PbO contents sintered by different methods. For samples sintered in the muffle furnace, in addition to the diffraction peaks from perovskite phase, two weak reflections from the pyrochlore phase are observed in the XRD patterns of PBLZST ceramics when the content of excess PbO is less than 10 mol%. The intensity of pyrochlore phase characteristic peaks decreases with the increase of excess PbO. This means that the amount of pyrochlore phase decreases when the content of PbO increases. The pyrochlore phase is easily formed by the vaporization of PbO during the sintering process.^{22–25} The XRD patterns indicate that the lead vaporization effect can be compensated by adding excess PbO. The variation in the intensity of the pyrochlore phase characteristic peaks of hot-pressed PBLZST specimens depending on the amount of excess PbO shows a similar tendency with that of the samples sintered in the muffle furnace. However, when the same content of excess PbO

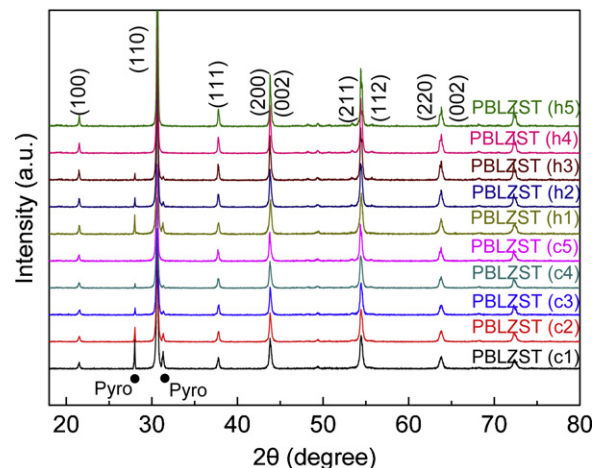


Fig. 1. XRD diffraction patterns of the PBLZST ceramics with various contents of excess PbO sintered by conventional and hot-press sintering methods.

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