Effect of 0.5PbO-0.5B_2O_3 Glass Additionon the Microstructure and Electrical Properties of $Pb_{0.87}Ba_{0.1}La_{0.02}(Zr_{0.68}Sn_{0.26}Ti_{0.06})O_3$ Anti-ferroelectric Ceramics Fabricated by Hot-press Sintering Method

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Abstract. The sintering temperature of lead-basedanti-ferroelectric (AFE) ceramics is always as high as1230°C，which leads to the volatilization of lead and deterioration of performance. In order to bring down the sintering temperature and preventthe deterioration of electrical properties of AFE ceramics, $Pb_{0.87}Ba_{0.1}La_{0.02}(Zr_{0.68}Sn_{0.26}Ti_{0.06})O_3$(PBLZST) AFE ceramics with various amount of 0.5PbO-0.5B_2O_3 glass have been fabricated by the hot-press sintering method. The sintering temperature of AFE ceramics is reduced to 1150°Cand the density of all samples is enhanced. When the content of glass addition is 0.1 wt.%, the high density of 8.17 g/cm^{3}is obtained. And when the content of glass addition is 0.3 wt.%, the saturate polarization of 42.4 μC/cm^2 is achieved.The combination of glass addition and the hot-press sintering method reduced the sintering temperature and simultaneouslypromoted the density and saturate polarization of PBLZST AFE ceramics.

Introduction

Recently, PBLZST anti-ferroelectric (AFE) ceramics were widely used in high energy storage density capacitor, high strain actuators, energy transducers and infrared detectors owing to their particular electric field-induced anti-ferroelectric to ferroelectric (AFE-FE) phase transition and adjustable dielectric properties[1-4].However, PBLZST AFE ceramics belong to lead-based ceramics and the sintering temperature is from 1200°C to 1300°C[5], which is so high that it gives rise to the volatilization of lead and finally results in the decrease of density, stoichiometric deviation, deterioration of performance and environmental pollution[6].The methods currently in common used, such as adding excess PbO and atmosphere sintering, can only reduce the stoichiometric deviation, but are not able to fundamentally eliminate the volatilization of PbO and inhibit the appearance of pore caused by lead volatilization. The effective and feasible approach to inhibit the volatilization of PbO is to bring down the sintering temperature of AFE ceramics. Adding low-melting-point glassand hot-press sintering areeffective methods to realize low-temperature sintering of lead-based ceramics. In addition, both of the addition of glassand hot-press sintering are favorable to improve the density. Although some work has reported the influence of glass addition on the microstructure and electrical properties of lead-based AFEs sintered by conventional solid-state method[7,8], few studies have been conducted on the effect of glass addition on the AFE ceramics fabricated by hot-press sintering. Because the sintering process of conventional method and hot-press method are different, the effect of the glass addition during the hot-press sintering is different from the conventional solid-state reaction method. Thus, it is necessary to systemically investigate the effect of glass addition on the AFE ceramics fabricated by the hot-press sintering.

In order to reduce the possibility of reaction to produce new crystalline structure and improve the matching of temperature coefficient of expansion between AFE ceramics and glass, 0.5PbO-0.5B_2O_3 glass is designed for the PBLZST anti-ferroelectric ceramics in this work.$Pb_{0.87}Ba_{0.1}La_{0.02}(Zr_{0.68}Sn_{0.26}Ti_{0.06})O_3$(PBLZST) AFE ceramics containing various amounts of

$0.5PbO$-$0.5B_2O_3$ glass are fabricated by the hot-press sintering method. The microstructure and the electrical properties of the PBLZST samples with various contents of glass additives have been investigated. When the glass is added, the density of the AFE ceramics sintered by hot-pressing method increases. The saturate polarization of the specimen with glass additive is also enhanced.

Experimental

$Pb_{0.87}Ba_{0.1}La_{0.02}(Zr_{0.68}Sn_{0.26}Ti_{0.06})O_3$ (PBLZST) powder was prepared using the conventional solid-state method. 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%), SnO_2(99.6%) and H_3BO_3(99.5%). The PBLZST powders were weighed and then thoroughly milled for 4h. A 7mol% excess of lead was added to the powders to compensate for lead loss during annealing. The dried slurries were calcined at 900°C for 3h, and then ball milled again for 4h.

The composition of the glass is $0.5PbO$-$0.5B_2O_3$. Calculated amount of PbO and H_3BO_3 (H_3BO_3 can dehydrate and generate B_2O_3 at 300°C)for the glass composition were weighed, mixed, and melted in an Al_2O_3 crucible at 800°C for 1h. The molten glass was quenched in water and then ball milled to a fine powder.

The glass powder was mixed with $Pb_{0.87}Ba_{0.1}La_{0.02}(Zr_{0.68}Sn_{0.26}Ti_{0.06})O_3$ powder according to the following chemical composition: $Pb_{0.87}Ba_{0.1}La_{0.02}(Zr_{0.68}Sn_{0.26}Ti_{0.06})O_3$+x wt.% $0.5PbO$-$0.5B_2O_3$, where x=0, 0.1, 0.3, 0.5, 0.7, 0.9 and 1.0 ,respectively. The mixed powders were ball milled for 4h. After drying the powders, polyvinyl alcohol (PVA) was added to the mixtures as a binder for granulation, and the compacts were pressed at about 10 MPa with the diameter of 20mm. Then the samples were sintered by the hot-pressing sintering approach. The compact were placed in silicon carbide die, and sintered at 1150°C for 2.5h with a pressure of 50 MPa. The specimens with 0 wt.%, 0.1 wt.%, 0.3 wt.%, 0.5 wt.%, 0.7 wt.%, 0.9 wt.% and 1 wt.% were donated as PBLZST(g1), PBLZST(g2), PBLZST(g3), PBLZST(g4), PBLZST(g5), PBLZST(g6), PBLZST(g7), respectively.

The crystal structures of the samples were determined by using an X-ray diffractometer (XRD). The microstructure of the specimens was observed by a scanning electron microscopy (SEM). The bulk density was determined by the Archimedes method. The versus electric field hysteresis loops were measured by a standard Sawyer-Tower circuit with high voltage power supply.

Results and Discussion

Microstructure

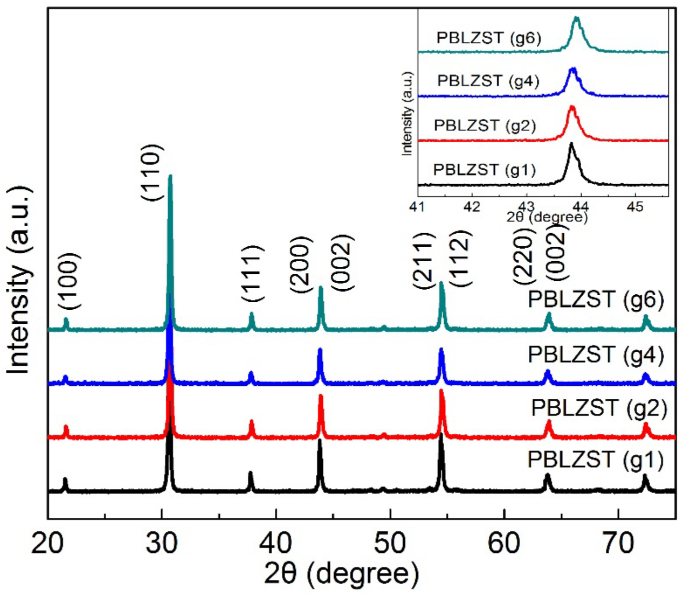


Fig.1 XRD diffraction patterns of the PBLZST ceramics with various contents of $0.5PbO$-$0.5B_2O_3$ glass.The inset shows the fine scanning

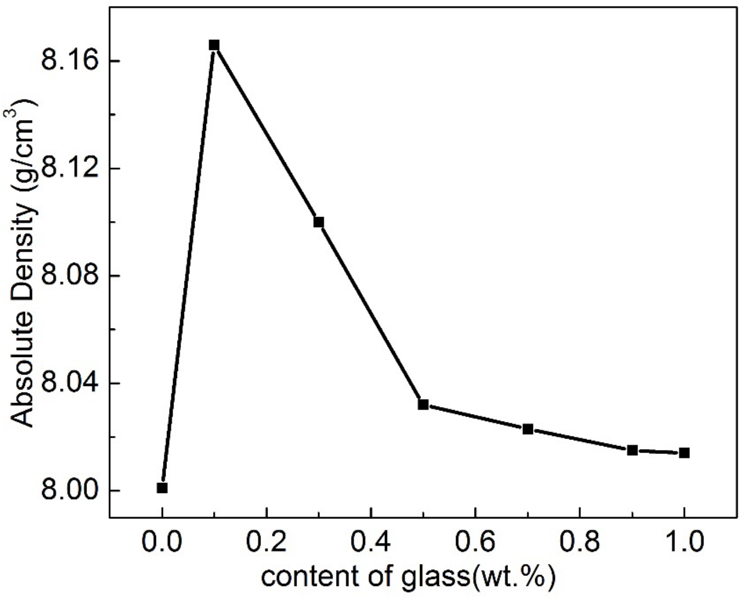
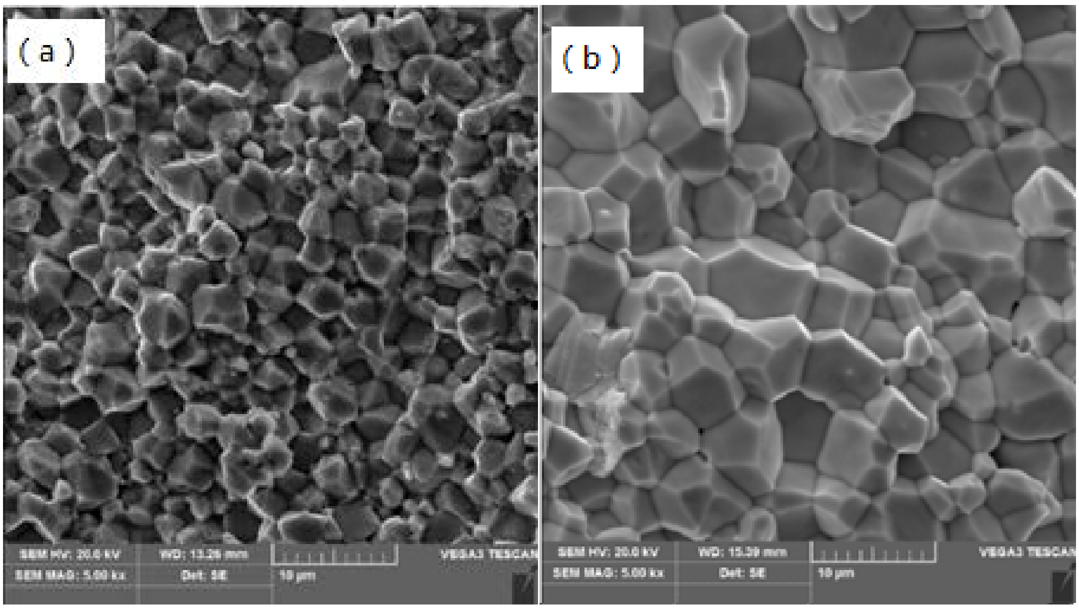


Fig. 2. Density of PBLZST ceramics with various contents of 0.5PbO-0.5B_2O_3 glass

Fig.1shows the XRD patterns of PBLZST ceramics with various contents of 0.5PbO-0.5B_2O_3 glass sintered by hot-press sintering.From the Fig. 1, it can be seen that there is only perovskite structure in all specimens, without additional impurity phase. In the inset of Fig. 1, when the amount of glassincreased, the diffraction peak around $2\theta=44^{o}$slightlyshift tohigh diffraction angle, which means that the lattice constant decrease. It maybe that the Ti^{4+} ion (ion radius 0.0605nm) is substituted by B^{3+} ion (ion radius 0.02nm), which result in the decrease of cell volume [8].

Fig.2 shows the density of PBLZST AFE ceramics with various contents of 0.5PbO-0.5B_2O_3 glass fabricated by hot-press sintering method. It is obvious that the addition of 0.5PbO-0.5B_2O_3 glass can significantly improve the density of PBLZST AFE ceramics. When the addition of 0.5PbO-0.5B_2O_3 is 0.1 wt.%, the density of the specimen reached its maximum value of 8.17g/cm^3. This is because that the addition of 0.5PbO-0.5B_2O_3 glass encourages the formation of liquid phase, which is favorable for the densification of samples. However, when the content of glass exceed 0.1 wt.%, the densities of all the samples decreased. This can be attributed to the excess liquid phase formed in the samples, which results in the appearance of closed pores. As a result, the densification of ceramic decreases.



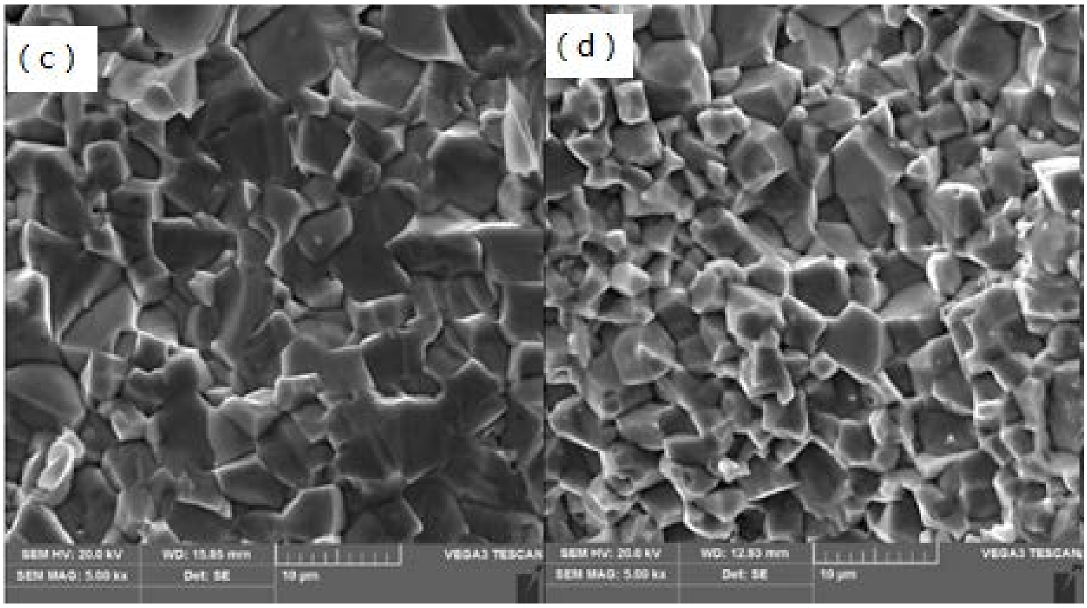


Fig. 3. Cross-sectional scanning electron micrographs of (a) PBLZST (g1), (b) PBLZST(g2), (c) PBLZST(g4), (d) PBLZST(g6) with various contents of 0.5PbO-0.5B_2O_3 glass

The cross-sectional view of the samples with various contents of 0.5PbO-0.5B_2O_3 glass is shown in Fig. 3. When the content of 0.5PbO-0.5B_2O_3 glass is less than 0.5wt.%, the grain size of samples obviously increases with the increase of glass content. This is possible that when the content of 0.5PbO-0.5B_2O_3 is less, there issmall amount of liquid phase in the specimen, which is beneficial for the dissolution-precipitationprocessandgrain growth [9]. However, with the content of glass further increasing, the grain size of ceramic samples decreases. This means that a too large amount of 0.5PbO-0.5B_2O_3 glass liquid phase hinder the grain growth during the sintering process.In addition, the excessive glass liquid phase brings about an initial rapid densification and leaves lots of closed pores in the ceramics, which canreduce the densification of the anti-ferroelectric ceramics and deteriorate the anti-ferroelectric properties of samples.

Anti-ferroelectric properties

Fig. 4 shows the hysteresis loops of the PBLZST ceramics with various contents of 0.5PbO-0.5B_2O_3 glass sintered by hot-pressing methods. All samples show the double hysteresis loops, which indicates all samples are anti-ferroelectric. The influence of the glass additions on saturate polarization is obvious. When the glass additive is increase from 0 to 0.3wt.%, the saturate polarization increases from 33.1$\mu C/cm^2$ to 42.4$\mu C/cm^2$. With the increasing of glass addition content, the porosity of the ceramics decreases. This means the increase of the anti-ferroelectric ceramics and hence the saturate polarization increases. In addition, with the increase of the glass content, the grain size increase. As a result, the internal stress between the ceramics grains decrease[10], and the decreased stress reduce the lattice distortion and enlarge the relative displacement of B-site cations. It is reported that spontaneous polarization of anti-ferroelectric materials is depended on the relative displacement of the B-site cations (for PBLZST, Zr^{4+}, Sn^{4+}, and Ti^{4+} are the B-site cations), and the larger relative displacement between the O^{2-} ions and B-site ions, the higher saturation polarization[11], thus the saturate polarization of the samples is increased. However, the saturate polarization decrease with the further increase of glass additions. This is because the grain size decreases and the internal stress increases between grains when the glass content further increases, and the stress distort the lattice and limit the relative displacement of B-site cations. Consequently, the saturate polarization decreases. In addition, it can be observed that the phase transition field is inclined to first decreases and then increases with the increase of the glass content. When the content of glass additives is less than 0.5wt.%, the grain size increases with the glass content increasing. This means that the amount of grain boundaries decreases and effective electric field on thegrains increases[12]. Thus, the phase transition field decreases. With the further increase of glass addition, the grain size decreases again and thus the phase transition increases. Furthermore, more B^{3+} cations substitute for Ti^{4+} on B-site resulting in the generation of oxygen vacancies. The existence of oxygen vacancies have an effect of "pinning" on the domain[6]. As a result, the phase transition field increases.Therefore, appropriate amount of glass addition is conductive to the improvement of anti-ferroelectric properties of PBLZST AFE ceramics.

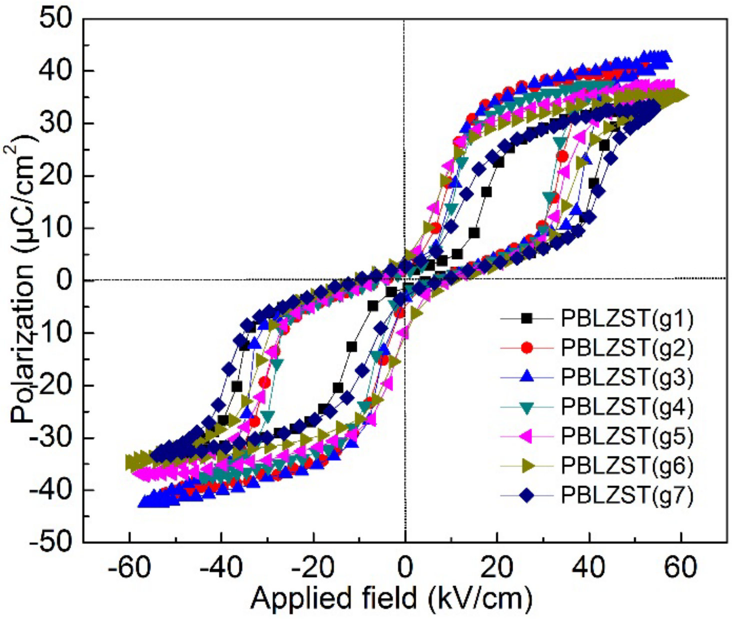


Fig. 4. Hysteresis loops of the PBLZST ceramics with various contents of $0.5PbO\text{-}0.5B_2O_3$ glass

Conclusions

In this work, the effect of glass addition on the PBLZST anti-ferroelectric ceramics fabricated by hot-press sintering method has been systematically studied. The microstructure and anti-ferroelectric properties have been analyzed. Firstly, the sintering temperature of AFE ceramics has been successfully reduced to 1150°C by the method of combining adding appropriate glass with hot-press sintering. Secondly, the addition of $0.5PbO\text{-}0.5B_2O_3$ glass improved the density of all samples, and when the content of glass addition is 0.1 wt.%, the high density of 8.17 g/cm^3 is obtained. Thirdly, with the increasing of content of glass, the saturate polarization of AFE ceramics first increase and then decrease. And when the content of glass addition is 0.3 wt.%, the maximum saturate polarization is 42.4 μC/cm^2. These results indicate that the combination of adding appropriate glass and hot-press sintering is an effective method to improve the density and promote the anti-ferroelectric properties of PBLZST ceramics.

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Reference

[1]G. Li, T. Q. Yang, J. F. Wang, S. C. Chen, X. Yao. Preparation of PLZST antiferroelectric ceramics by hydroxide coprecipitation method,Ceram. Int.39 (2013) S345-S348.

[2]X.H. Hao, J.W. Zhai and X. Yao. Improved energy storage performance and fatigue endurance of Sr-doped $PbZrO_3$ antiferroelectric thin films, J. Am. Ceram. Soc. 92 (2009) 1133-1135.

[3]M. S. Mirshekarloo, K. Yao and T. Sritharan. Large strain and high energy storage density in

orthorhombic perovskite ($Pb_{0.97}La_{0.02}$)($Zr_{1-x-y}Sn_xTi_y$)O_3 antiferroelectric thin films,Appl. Phys. Lett. 97 (2010) 142902-3.

[4]H.L. Zhang, X.F. Chen, F. Cao, G.S. Wang, et al. Low thermal hysteresis pyroelectric response near the ferroelectric/antiferroelectric phase transition in $Pb_{0.97}La_{0.02}(Zr_{0.42}Sn_{0.40}Ti_{0.18})O_3$ ceramics, J. Appl. Phys. 108 (2010) 086105-086105-3.

[5]L. Wang, C. L. Mao, G. S. Wang, G. Du, R. H. Liang, andX. L. Dong, Effect of CuO addition on the microstructure and electric properties of low-temperature sintered 0.25PMN-0.40PT-0.35PZ ceramics, J. Am. Ceram. Soc. 96 (2013) 24–27.

[6]J.Q. Yi, S.L. Jiang, S.S. Liu, L. Zhang, and J.G. He, Effects of $LiBiO_2$ addition on themicrostructure and piezoelectricproperties of CuO-doped PNN–PZT ceramics, Phys. Status Solidi A. 211 (2014) 2552-2557.

[7]X.H. Hao, P. Wang, X.F. Zhang, J.B. Xu, Microstructure and energy-storage performance of PbO–B2O3–SiO2–ZnO glassadded ($Pb_{0.97}La_{0.02}$)($Zr_{0.97}Ti_{0.03}$)O_3 antiferroelectric thick films, Mater. Res. Bull. 48 (2013) 84-88.

[8]Q.F. Zhang , S.C. Chen, Y.Y. Zhang, M.Y. Fan, S.L. Jiang, T.Q. Yang, J.F. Wang, G. Li, X. Yao,Effects of glass additions on high pyroelectric response of low-temperature sintered $Pb_{0.87}Ba_{0.1}La_{0.02}(Zr_{0.7}Sn_{0.24}Ti_{0.06})O_3$ antiferroelectric ceramics, Mater. Res. Bull. 48 (2013) 1324-1327.

[9]S.C. Chen, T.Q. Yang, J.F. Wang, X. Yao, Effects of glass additions on the dielectric properties and energystorage performance of $Pb_{0.97}La_{0.02}(Zr_{0.56}Sn_{0.35}Ti_{0.09})O_3$antiferroelectric ceramics, J Mater Sci: Mater Electron, 24 (2013)4764–4768.

[10] W.F. Rao, Y.U.Wang. Grain size effect of phase coexistence around morphotropicphase boundary in ferroelectric polycrystalline ceramics, Appl.Phys. Lett.92 (2008) 102905.

[11]X.L. Tan, C. Ma, J. Frederick, S. Beckman, KG. Webber. Theantiferroelectric–ferroelectric phase transition in lead-containing and lead freeperovskite ceramics. J. Am. Ceram. Soc. 94 (2011) 4091–107.

[12]L. Zhang, S.L. Jiang, Y.K. Zeng, M. Fu, K. Han, Q. Li,Q. Wang, G.Z. Zhang, Y dopingandgrainsizeco-effectsontheelectricalenergy storageperformanceof($Pb_{0.87}Ba_{0.1}La_{0.02}$)($Zr_{0.65}Sn_{0.3}Ti_{0.05}$)$O_3$anti-ferroelectric ceramics, Ceram. Int. 40 (2014) 5455-5460.