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Characterization of $0.93Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.07BaTiO_3$ ceramics derived from a novel $Zn_3Nb_2O_8$ *B*-site precursor

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Abstract

In this work, perovskite relaxor ferroelectric lead zinc niobate–barium titanate (0.93PZN–0.07BT) ceramics were fabricated by using a combination of $Zn_3Nb_2O_8$ *B*-site precursor and reactive sintering process. The effects of sintering condition on phase formation, densification, microstructure and dielectric properties of the final products have been investigated using a combination of X-ray diffraction, Archimedes density measurement, scanning electron microscopy and dielectric measurement techniques. It is seen that pure perovskite phase of PZN-BT solid solutions can be achieved in all samples. Density and average grain size values of sintered samples increased with sintering temperatures and dwell time. With appropriate sintering at 1150 °C for 5 h, 0.93PZN–0.07BT ceramics exhibited a peak dielectric constant of 11,497 and dielectric loss of 0.05 at the Curie temperature of 99 °C measured at 1 kHz.

Keywords: A. Sintering; D. Perovskite; B-site precursor; Lead zinc niobate

1. Introduction

Lead zinc niobate $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) is one of the well-known relaxor perovskite ferroelectrics exhibiting a diffused phase transition. In general, single crystals of PZN can be produced by using the flux method with excellent dielectric and electrostrictive properties, but pure perovskite PZN ceramics are relatively difficult to prepare by conventional mixed-oxide process. Many attempts have been made to prepare pyrochlore-free PZN ceramics, including forming solid solution with more stable perovskite additions. In 1985 Furukawa et al. [1] reported the successful fabrication of pure perovskite PZN by using 15 mol% of $BaTiO_3$ (BT) additive. Later it was confirmed by Halliyal et al. [2] that only 0.07 mol% of BT additive is sufficient to suppress the pyrochlore formation in the fabrication of perovskite PZN-based ceramics. Interestingly, no systematic study on the fabrication of perovskite $0.93Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.07BaTiO_3$ (0.93PZN–0.07BT) ceramics by using a combination of *B*-site precursor $Zn_3Nb_2O_8$ and reactive sintering process is found in the literature. Thus, in the present study, a perovskite solid solution having a composition 0.93PZN–0.07BT was prepared from a novel $Zn_3Nb_2O_8$ *B*-site precursor technique, instead of using a well-known precursor of columbite-type $ZnNb_2O_6$ [2], and it was then fired at various conditions through a reactive sintering process.

2. Experimental procedure

The starting materials were commercially available oxide powders of PbO, ZnO, Nb_2O_5, $BaCO_3$ and TiO_2 (Aldrich, 99% purity) with an average particle size of 3–5 μm. First, ZnO and Nb_2O_5 were reacted at 950 °C for 1 h with heating/cooling rates of 30 °C/min to form $Zn_3Nb_2O_8$. The resulting $Zn_3Nb_2O_8$ powders were vibro-milled (McCrone Micronizing Mill) for 30 min in isopropanol with PbO, Nb_2O_5, $BaCO_3$ and TiO_2 for appropriate stoichiometric ratio of 0.93PZN–0.07BT.

Ceramic pellets were fabricated by uniaxial pressing of the milled powders at 150 MPa into 10 mm-diameter pellets. The samples were placed on the alumina powder-bed in an

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alumina crucible. In order to avoid loss of volatile component e.g. lead, the samples were surrounded with powders of identical chemical composition. Sintering was carried out for 1–5 h at heating/cooling rates of 5 °C/min and various temperatures ranging from 1100 to 1150 °C. Densities of the final sintered products were measured by using the Archimedes principle. Sintered ceramic pellets were examined by X-ray diffraction (Philips PW 1729 diffractometer) using CuK_{α} radiation to identify the phase form at room temperature. The relative composition of perovskite and pyrochlore phases in the samples was determined from XRD patterns by measuring the major peak intensities of perovskite (110) and pyrochlore (222) phases. The microstructure was characterized using scanning electron microscopy (JEOL JSM-840A). The dielectric properties were measured at various frequencies (1–100 kHz) using an LCR meter (TH2819A) at temperatures from 25 to 150 °C.

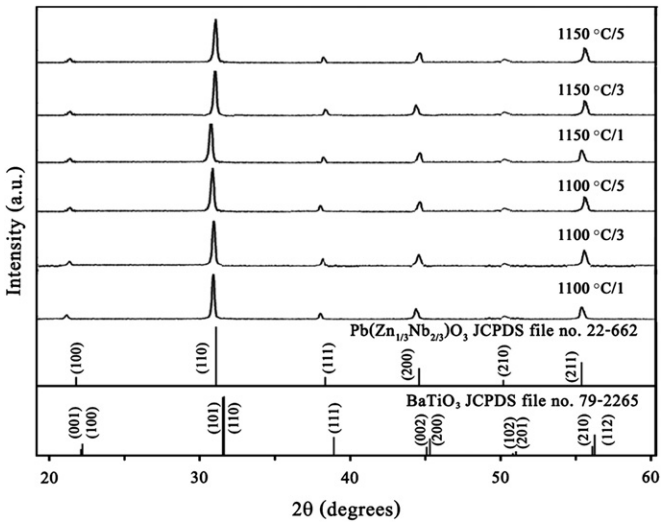

Fig. 1. XRD pattern of 0.93PZN–0.07BT Ceramics sintered at various sintering conditions.

3. Results and discussion

The XRD profiles of the 0.93PZN–0.07BT ceramics, sintered at 1100–1150 °C for 1–5 h are shown in Fig. 1. The strongest reflections in almost all of the XRD traces indicate the formation of the PZN perovskite phase, which could be matched with the standard JCPDS file no. 22-663. The effectiveness of the addition of the high perovskite phase stabilizer ($BaTiO_3$) for the fabrication of perovskite ceramics is confirmed in this study. However, in this study, 0.93PZN–0.07BT ceramics were successfully prepared via a reactive sintering process without involving the calcination step.

As shown in Table 1, the density of sintered ceramics increased with sintering temperatures and dwell-time, similar to that in Srisombat et al. [3]. However, it should be noted that increases in the sintering temperature, up to 1200 °C, caused critical damage to the 0.93PZN–0.07BT samples (with some melted areas). This observation may be attributed to the loss of PbO at high sintering temperatures, which is commonly found in other Pb-based perovskite systems. The optimal sintering condition for the production of 0.93PZN–0.07BT ceramics, with a maximum bulk density, is 1150 °C for 5 h. In comparison with previous work of Halliyal et al. [2], conventional mixed-oxide process and higher sintering temperature are required for 0.93PZN–0.07BT derived from the combination of the $Zn_3Nb_2O_8$ precursor and sintering reaction process, probably due to the lack of a calcination step.

Effects of sintering conditions on the microstructure development of 0.93PZN–0.07BT ceramics are displayed in Fig. 2. In general, sintered surface ceramics with fine grains and non-uniform microstructure were obtained in all samples. In agreement with the previous densification results, highly dense samples exhibited high degrees of grain close-packing, whereas some pores were observed at the surfaces of the lower-density 0.93PZN–0.07BT samples. As also listed in Table 1, the average grain size tended to increase with sintering temperature and dwell time. This is probably due to the grain growth being controlled by boundary diffusion. Moreover, with careful observations (Fig. 2(e) and

Table 1
Physical properties of 0.93PZN–0.07BT ceramics sintered at various conditions.

Compositions	Calcination temperature (°C)/ time (h)	Sintering temperature (°C)/ time (h)	Perovskite phase (±1 wt%)	Relative density (±1%)	Grain size range (mean) (±0.1 μm)
0.93PZN–0.07BT	–	1100/1	100	82	0.9–4.0 (2.4)
	–	1100/3	100	88	0.5–5.0(2.7)
	–	1100/5	100	92	1.5–6.0 (3.7)
	–	1150/1	100	91	1.7–7.0 (4.3)
	–	1150/3	100	93	2.0–8.0 (5.0)
	–	1150/5	100	94	2.0–11.0 (6.5)
0.93PZN–0.07BT [2]	900/4	1100/4	100	94	–
0.95PZN-0.05BT [7]	–	1050/1	95	93	0.8–11.0 (4.5)

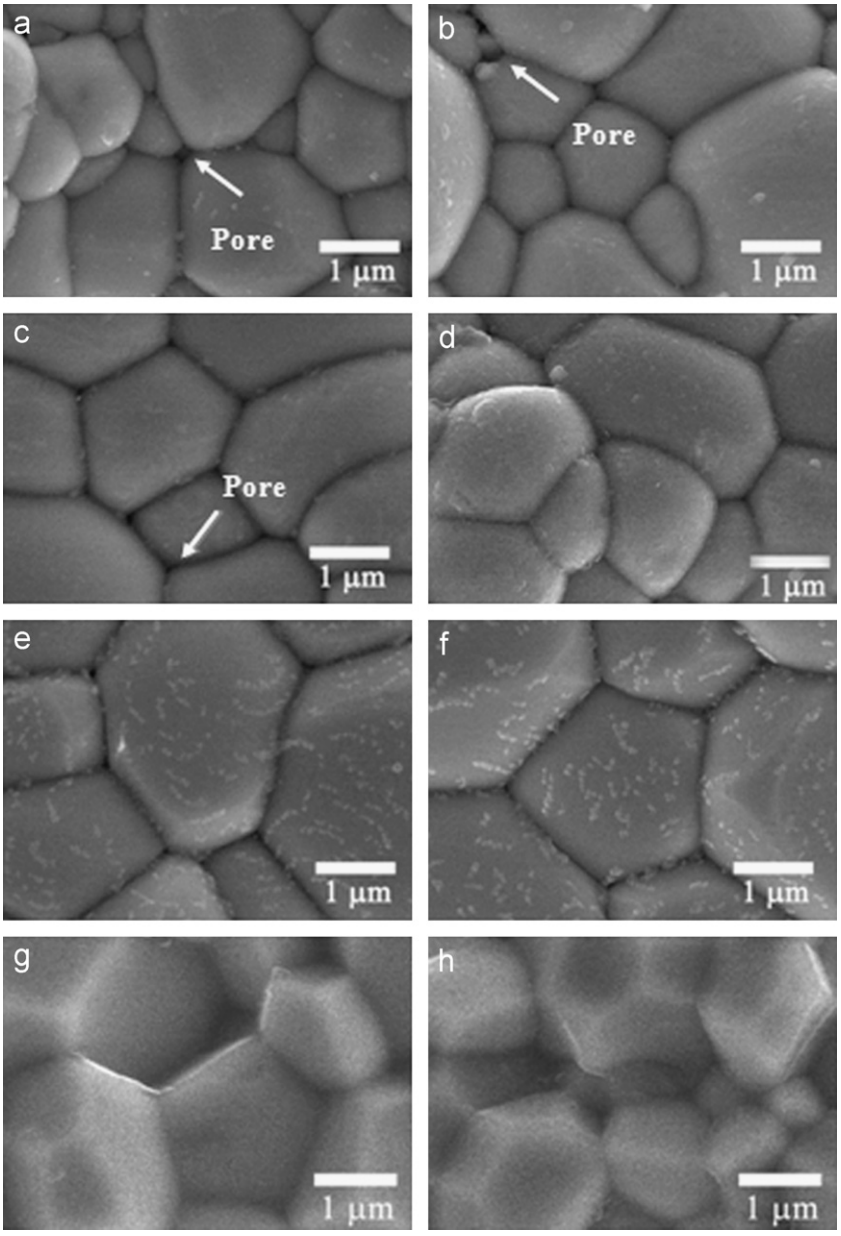

Fig. 2. SEM micrographs of 0.93PZN–0.07BT ceramics sintered at (a) 1100 °C/1 h, (b) 1100 °C/3 h, (c) 1100 °C/5 h, (d) 1150 °C/1 h, (e) 1150 °C/3 h, (f) 1150 °C/5 h, (g) 1150 °C/3 h and (h) 1150 °C/ 5 h.

(f)), nanosized particles could be seen among 0.93PZN–0.07BT grains of reactive sintered samples, similar to the results observed by Liou et al. [4]. Some nanosized particles (~60 nm) were segregated at the surfaces of grains in the samples sintered at 1150 °C, for 3–5 h. These are thought to be pyrochlore-type PZN particles, probably due to PbO evaporation at high temperature.

As shown in Fig. 2(g) and (h), fractured surfaces of 0.93PZN–0.07BT ceramics sintered at 1150 °C for 3 and 5 h revealed no nanosized particles. This observation indicates that the PbO loss may occur only at the samples' surfaces. In addition, 0.93PZN–0.07BT ceramics have an intergranular fracture mechanism, indicating that the grain boundaries are mechanically weaker than the grains, and this is similar to the results observed in conventional mixed-oxide processes [2]

The dielectric properties, e.g. dielectric constant (ε_r) and dielectric loss (tan δ) of 0.93PZN–0.07BT ceramics sintered at 1150 °C for 5 h, were measured as functions of both temperature and frequency, as shown in Fig. 3. Both dielectric constant and dielectric loss exhibited strong temperature–frequency dependence below the transition temperature, indicating typical relaxor ferroelectric behavior, which is in agreement with Cross [5]. In this case, the maximum dielectric constant and dielectric loss had shifted to higher temperature with increasing frequency. The maximum value of the dielectric constant decreased with increasing frequency, while that of the dielectric loss

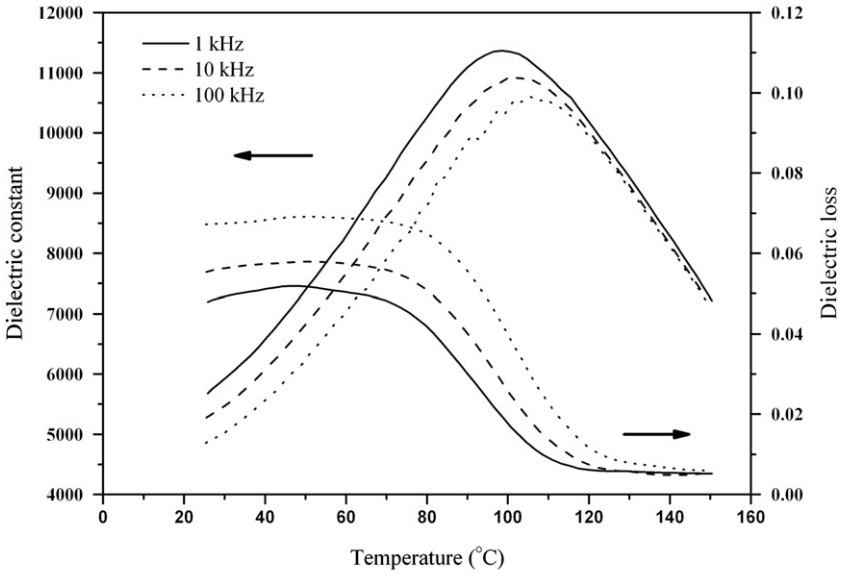

Fig. 3. Variation with temperature of dielectric constant and dielectric loss for 0.93PZN–0.07BT ceramics sintered at 1150 °C for 5 h.

Table 2
Dielectric properties (1 kHz) of 0.93PZN–0.07BT ceramics sintered at various conditions.

Compositions	Calcination (°C)/time (h)	Sintering (°C)/time (h)	T_c (°C)	Dielectric properties (at 30 °C)		Dielectric properties (at T_{max})	
				ε_r	tan δ	ε_r	tan δ
0.93PZN–0.07BT	–	1100/1	90	3175	0.05	3,865	0.04
	–	1100/3	94	3554	0.45	4,200	0.05
	–	1100/5	94	3890	0.05	5,172	0.05
	–	1150/1	98	4516	0.05	7,245	0.05
	–	1150/3	99	4255	0.05	8,183	0.05
	–	1150/5	99	5926	0.05	11,497	0.05
0.93PZN–0.07BT [2]	900/4	1100/4	90	4500	0.06	13,000	0.06
0.95PZN-0.05BT [7]	–	1050/1	–	3105	–	–	–

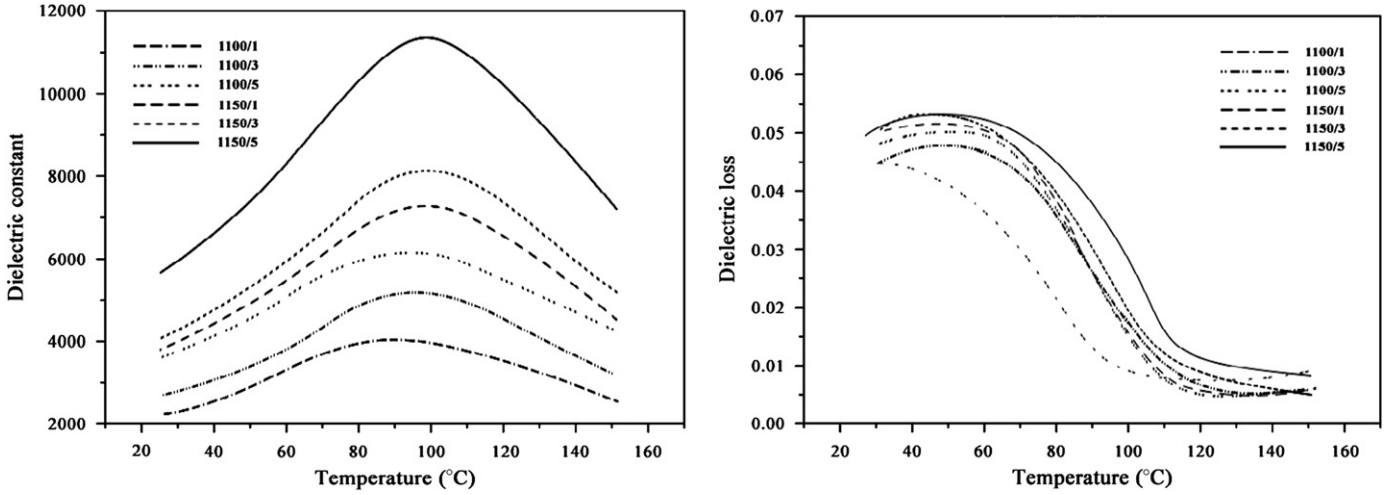

Fig. 4. Temperature dependence of dielectric constant and dielectric loss at 1 kHz for 0.93PZN–0.07BT ceramics sintered at various sintering conditions.

increased, and these are in agreement with the results of Yimnirun et al. [6].

From Table 2, it is clear that at 1 kHz, the maximum dielectric constant was ~11,497 at Curie temperature of ~99 °C, which is slightly lower than those reported by Halliyal et al. [2]. This could be mainly attributed to the effect of different processes including the starting precursor and sintering process. However, the dielectric loss was lower for the samples in this study. Moreover, it should be noted that the dielectric properties at room temperature of the samples obtained in this study were slightly better than those reported in the literature [2,7]. This is probably due to the increase in the dielectric constant at room temperature, which may be related to sintering temperature, dwell time, grain size and density of the ceramics. Temperature dependences of the dielectric constant and dielectric loss of the 0.93PZN–0.07BT ceramics at various sintering temperatures and dwell time are also displayed in Fig. 4. In general, the maximum dielectric constant and dielectric loss gradually increased with increased sintering temperature and dwell time, and are in good agreement with other lead-based perovskite ceramics [6].

4. Conclusion

This study demonstrates the effects of sintering temperature and dwell time on phase formation, densification, microstructure and dielectric properties of 0.93PZN–0.07BT ceramics, prepared by using a combination of $Zn_3Nb_2O_8$ *B*-site precursor and reactive sintering process. The density and average grain size of the sintered samples increased with sintering temperatures and dwell time. With appropriate sintering at 1150 °C for 5 h, sintered 0.93PZN–0.07BT exhibited a peak dielectric constant of 11,497 and dielectric loss of 0.05, at the Curie temperature of 99 °C measured at 1 kHz.

Acknowledgments

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