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Synthesis and properties of $(Ba_xPb_{1-x})(Zn_{1/3}Nb_{2/3})O_3$ relaxor ferroelectric ceramics using a reaction-sintering process

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Abstract

$(Ba_xPb_{1-x})(Zn_{1/3}Nb_{2/3})O_3$ (BPZN; $x = 0.06$–0.1) relaxor ferroelectric ceramics produced using a reaction-sintering process were investigated. Without any calcination involved, the mixture of raw materials was pressed and sintered directly. BPZN ceramics of 100% perovskite phase were obtained. Highly dense BPZN ceramics with a density higher than 98.5% of theoretical density could be obtained. Maximum dielectric constant K_{max} 13,500 (at 75 °C), 19,600 (at 50 °C) and 14,800 (at 28 °C) at 1 kHz could be obtained in 6BPZN, 8BPZN and 10BPZN, respectively. Dielectric maximum temperature (T_{max}) in BPZN ceramics via reaction-sintering process is lower than BPZN ceramics prepared via B-site precursor route.

Keywords: $Pb(Zn_{1/3}Nb_{2/3})O_3$; Reaction-sintering process; Dielectric

1. Introduction

Lead zinc niobate $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) is a relaxor ferroelectric with a perovskite structure [1–3]. The structure of PZN is rhombohedral at room temperature and undergoes a phase transition to cubic at about 140 °C [1]. It exhibits excellent dielectric properties and is hence a candidate material for applications in multilayer capacitors [2,4]. In preparing the lead-based perovskites, pure PZN is the most difficult to obtain. Stable cubic pyrochlore phase always existed in PZN ceramics via the conventional mixed oxide method or the columbite route under atmospheric pressure [4,5]. Powders of perovskite PZN could be synthesized only under a very high pressure of 2.5 GPa [6]. Single phase of perovskite structure can only be obtained in PZN by adding an appropriate amount of perovskite compound, such as $BaTiO_3$ (BT) (>6 mol%) [5], $SrTiO_3$ (ST) (>9 mol%) [4,7], $PbTiO_3$ (PT) (>25 mol%) [7,8] and $Ba(Zn_{1/3}Nb_{2/3})O_3$ (BZN) (>15 mol%) [9]. Swartz and Shrout proposed a columbite route for pyrochlore-free $Pb(Mg_{1/3}Nb_{2/3})O_3$ (PMN) ceramics. Two calcination steps were involved, $MgNb_2O_6$ columbite formed first and followed by formation of perovskite [10]. Liou and Wu proposed an effective and simplified method to obtain pyrochlore-free PMN ceramics. The mixture of $MgNb_2O_6$ and PbO was pressed into pellets and sintered directly to form PMN ceramics. The second calcination and pulverization stages in the columbite route were bypassed [11]. In the study of Han and Kim, PMN powder with >99% perovskite phase was prepared by adding an aqueous $Mg(NO_3)_2$ solution rather than MgO to the alcoholic slurry of PbO and Nb_2O_5, followed by calcination at 950 °C for 2 h [12]. Liou et al. further proposed a reaction-sintering process to prepare PMN and $Pb(Fe_{1/2}Nb_{1/2})O_3$ (PFN) ceramics [13,14]. The mixture of PbO, $Mg(NO_3)_2$ (or $Fe(NO_3)_3$) and Nb_2O_5 was pressed and sintered directly into PMN and PFN ceramics. These are the first successful synthesis of perovskite relaxor ferroelectric ceramics without having to go through the calcination step. Recently, this effective process has also been used to produce some microwave dielectric ceramics such as $BaTi_4O_9$, $(BaSr)(Zn_{1/3}Nb_{2/3})O_3$ and $CaNb_2O_6$ [15–17].

In this study, the reaction-sintering process was used to prepare pyrochlore-free $(Ba_xPb_{1-x})(Zn_{1/3}Nb_{2/3})O_3$ (BPZN) perovskite ceramics.

2. Experimental procedures

The composition of BPZN ceramics investigated in this study is $(Ba_xPb_{1-x})(Zn_{1/3}Nb_{2/3})O_3$ ($x = 0.06$, 0.08 and 0.1;

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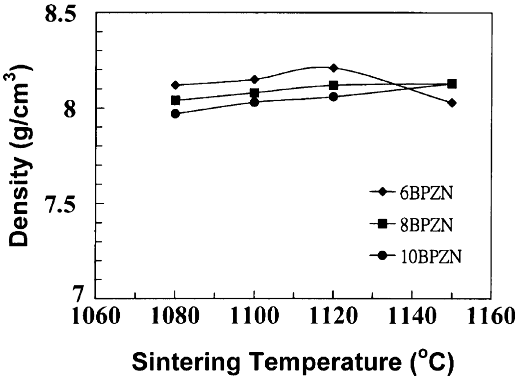

Fig. 1. Variation of density for BPZN ceramics sintered at various temperatures for 2 h.

6BPZN, 8BPZN and 10BPZN). All samples were prepared from reagent-grade powders: $BaCO_3$ (99.4%, J.T. Baker, USA), PbO (99.9%, J.T. Baker, USA), $Zn(NO_3)_2\cdot6H_2O$ (99%, Kanto Chemical, Japan), Nb_2O_5 (99.8%, High Purity Chemicals, Japan). Appropriate amounts of $BaCO_3$, PbO, $Zn(NO_3)_2$ and

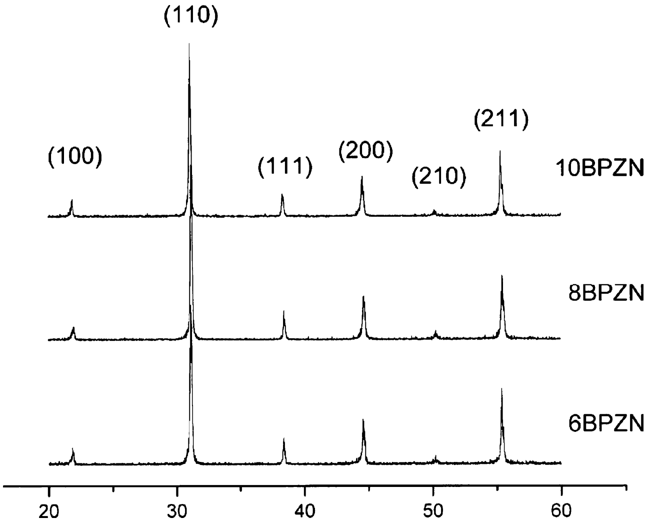

Fig. 2. XRD profiles of BPZN ceramics sintered at 1080 °C for 2 h.

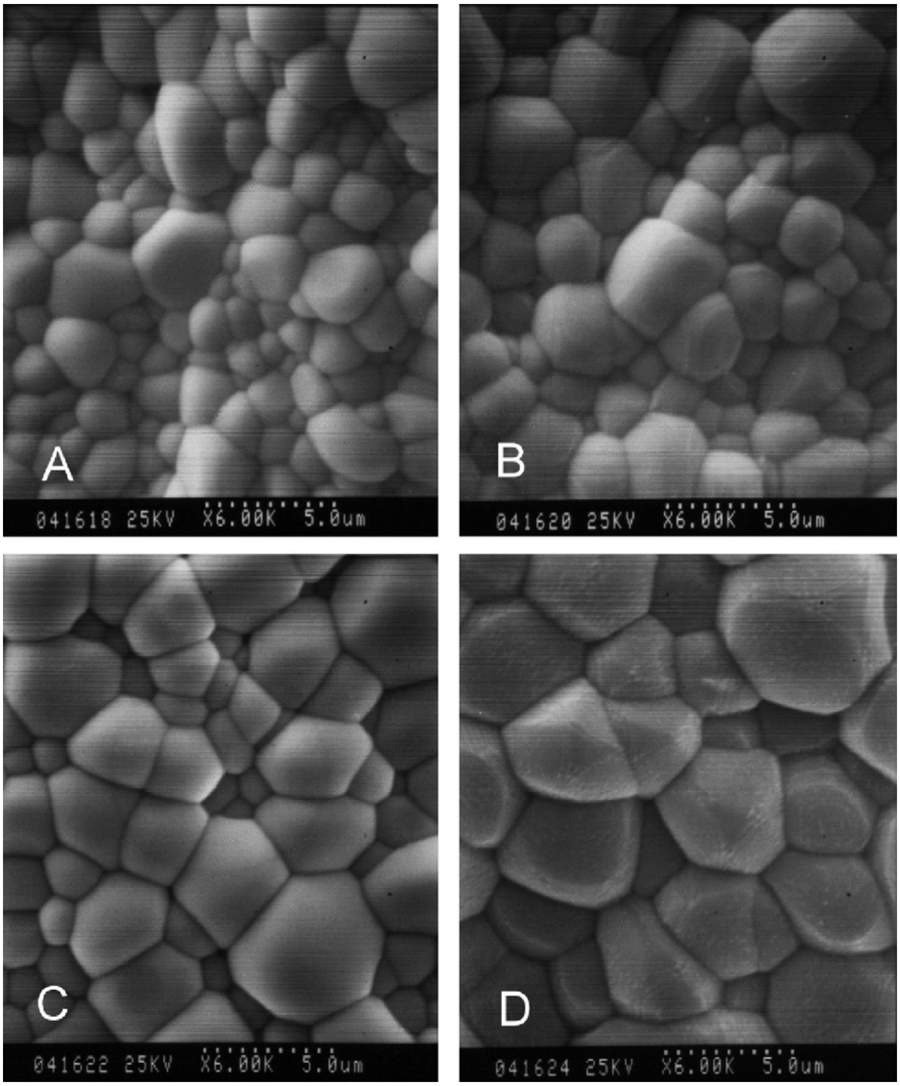

Fig. 3. SEM photographs of as-fired 6BPZN ceramics sintered at (A) 1080 °C, (B) 1100 °C, (C) 1120 °C and (D) 1150 °C for 2 h.

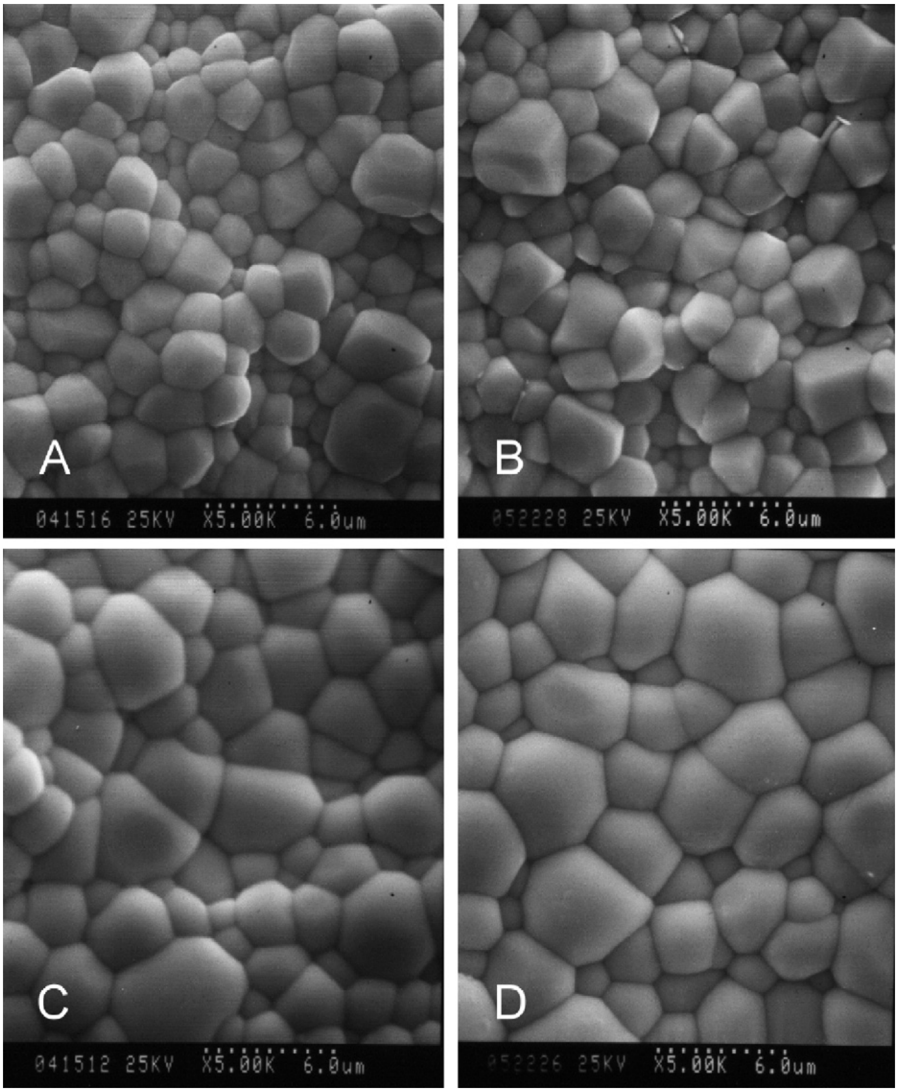

Fig. 4. SEM photographs of as-fired 8BPZN ceramics sintered at (A) 1080 °C, (B) 1100 °C, (C) 1120 °C and (D) 1150 °C for 2 h.

Nb_2O_5 for BPZN were milled in acetone with zirconia balls for 12 h. After the slurry was dried and pulverized, the powder was pressed into pellets 12 mm in diameter and 1–2 mm thick. The pellets were heated at a rate 5 °C/min to temperatures in a range from 1080 to 1150 °C and sintered for 2 h in a covered alumina crucible in air. To prevent PbO loss from the pellets, a PbO-rich atmosphere was maintained by adding 5 wt.% PbO powder beside the pellets.

The sintered BPZN ceramics were analyzed by X-ray diffraction (XRD) for the amount of perovskite phase. Microstructures were analyzed by scanning electron microscopy (SEM). The density was measured by the Archimedes method. After polishing, the dimensions were measured before silver electrodes were deposited on the pellets. Dielectric properties were measured with an HP4194A impedance analyzer.

3. Results and discussions

Fig. 1 shows the variation of density for BPZN ceramics sintered at various temperatures. Density increases slightly from 1080 °C to 1150 °C for 8BPZN and 10BPZN. In 6BPZN, it reaches a maximum 8.21 g/cm^3 (99.1% of theoretical density) at 1120 °C and decreases at 1150 °C due to the increased PbO evaporation. For 8BPZN, a maximum value 8.13 g/cm^3 (98.5% of theoretical density) was obtained at 1150 °C. As in 10BPZN, density 8.13 g/cm^3 (99% of theoretical density) was obtained at 1150 °C. This proves that highly dense BPZN ceramics could be produced using this simple reaction-sintering process. In the study of Ahn and Kim, 93.7–95.4% of theoretical density were obtained in $(Ba_xPb_{1-x})(Zn_{1/3}Nb_{2/3})O_3$ ceramics synthesized via

Table 1
Dielectric constant at room temperature of BPZN ceramics sintered at various temperatures for 2 h

	Sintering temperature (°C)			
	1080	1100	1120	1150
6BPZN	7,200	8,800	9,700	10,200
8BPZN	9,600	12,600	14,100	17,900
10BPZN	12,500	13,200	14,500	14,700

Table 2
Properties of BPZN ceramics obtained via columbite route and reaction-sintering process

	Columbite route process (sample from [9])			Reaction-sintering process (sample from this work)		
Calcination temperature/time	1150 °C/2 h and 900–1000 °C/2 h			No calcining		
Composition	5BPZN	8BPZN	10BPZN	6BPZN	8BPN	10BPZN
Sintering temperature/time	1000–1400 °C/1 h			1120 °C/2 h	1150 °C/2 h	1150 °C/2 h
Perovskite content	≥92%	99.9%	100%	100%	100%	100%
Relative density	93.7–95.4%			99.1%	98.5%	99%
K_{max}	~6050 (1 kHz)	10,400 (1 kHz)	~8730 (1 kHz)	13,500 (1 kHz)	19,600 (1 kHz)	14,800 (1 kHz)
T_{max}	~93 °C	56 °C	~33 °C	75 °C	50 °C	28 °C

B-site precursor route (columbite route) [9]. Therefore, reaction-sintering process is more effective in producing dense BPZN ceramics than the B-site precursor route. XRD profiles of polished surfaces of BPZN ceramics sintered at 1080 °C for 2 h are shown in Fig. 2. The peaks of pyrochlore phase were not detected in the patterns. BPZN ceramics of 100% perovskite phase could be obtained by the reaction-sintering process. Ahn and Kim reported that $(Ba_xPb_{1-x})(Zn_{1/3}Nb_{2/3})O_3$ of 99.9% perovskite phase was obtained at $x = 0.08$ and 100% at $x \geq 0.1$ [9]. Kang et al. reported that more than 10 mol% BZN was needed to stabilize the 100% perovskite phase with a spray-drying method [18]. Reaction-sintering process is simple and effective in producing pyrochlore-free and dense BPZN ceramics with 6–10 mol% barium substitution.

The SEM photographs of as-fired 6BPZN ceramics sintered at 1080–1150 °C for 2 h are illustrated in Fig. 3. No pyrochlore phase was found in these 6BPZN pellets. Grain size increased with sintering temperature. It is also noted that more uniform

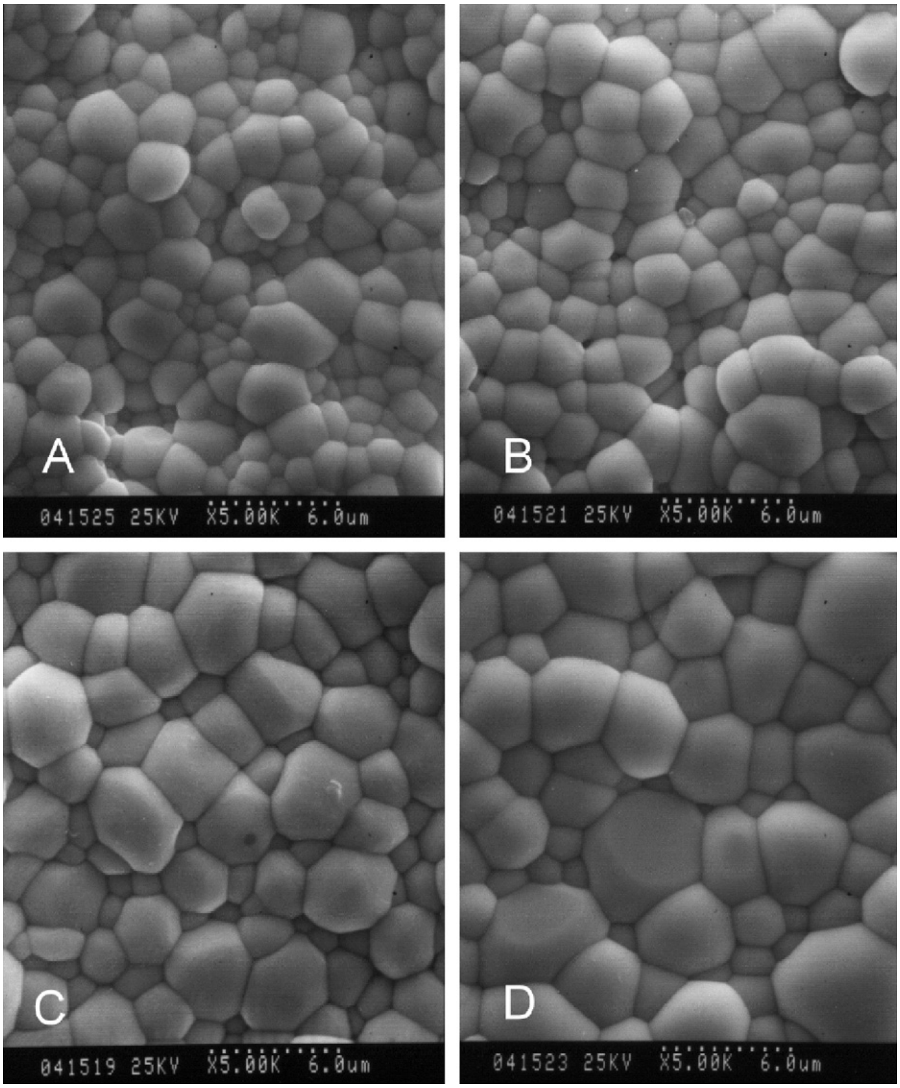

Fig. 5. SEM photographs of as-fired 10BPZN ceramics sintered at (A) 1080 °C, (B) 1100 °C, (C) 1120 °C and (D) 1150 °C for 2 h.

grains formed at higher sintering temperature. Similar results were also observed in PFN ceramics prepared using reaction-sintering process. Abnormal grains larger than 8 μm appear in 1120 °C/2 h and 1150 °C/2 h sintered pellets. In these pellets, most grains are smaller than 4 μm. As in the pellets sintered at 1180 °C/2 h and 1210 °C/2 h, more uniform grains are formed. At temperatures below 1150 °C, reaction is not completed during the heating up period before sintering temperature. Parts of the mixed powder were reacted and grew first, therefore, abnormal large grains formed. Reaction is completed for those pellets heated up to 1180 °C and 1210 °C. More uniform grains grow during the soak time [14]. Grain size increased slightly at sintering temperatures below 1100 °C for 8BPZN in Fig. 4. Larger grains could be found easily at temperatures above 1120 °C. This means 1120 °C is high enough for 8BPZN grains to grow. Fig. 5 shows the SEM photographs of as-fired 10BPZN ceramics sintered at 1080–1150 °C for 2 h. Grains are smaller than those in 8BPZN after sintered at 1080–1120 °C. This is reasonable since the sintering temperature for $Ba(Zn_{1/3}Nb_{2/3})O_3$ is higher than $Pb(Zn_{1/3}Nb_{2/3})O_3$. In previous studies, sintering temperatures > 1300 °C were needed for $Ba(Zn_{1/3}Nb_{2/3})O_3$ [19,20]. As more $Ba(Zn_{1/3}Nb_{2/3})O_3$ is contained in 10BPZN, higher sintering temperature is needed for a same grain size.

The dielectric constant at 1 kHz of BPZN ceramics at room temperature (K_{RT}) are listed in Table 1. It increased with sintering temperature. As all of the samples are pyrochlore-free, this was resulted from the density value and grain size. In the study of Lee and co-workers, K_{RT} is only 4300 for 8BPZN ceramics prepared via the conventional solid state and sintered at 1100 °C for 2 h [21]. In 8BPZN ceramics prepared via the B-site precursor route, K_{RT} reached 9500 [9]. K_{RT} of 12,600 was obtained in 8BPZN after sintered at 1100 °C in this study. Properties for BPZN ceramics prepared using B-site precursor route and reaction-sintering process are listed in Table 2. Higher dielectric constants were obtained in BPZN ceramics via reaction-sintering process due to higher perovskite content and density. K_{max} of 13,500 (at 75 °C), 19,600 (at 50 °C) and 14,800 (at 28 °C) at 1 kHz could be obtained in 6BPZN, 8BPZN and 10BPZN, respectively. It is also noted that dielectric maximum temperature (T_{max}) in BPZN ceramics via reaction-sintering process is lower than BPZN ceramics prepared via B-site precursor route. Similar results were also found in PMN and 0.6PMN–0.4PFN ceramics prepared via reaction-sintering process. In PMN via reaction-sintering process, T_{max} at −11 °C or −12 °C was measured at 1 kHz [13]. T_{max} at −5 °C in PMN via B-site precursor route was measured at 1 kHz [22]. While in 0.6PMN–0.4PFN ceramics, T_{max} at 40 °C was measured at 10 kHz via reaction-sintering process [23] and at 45 °C via B-site precursor route [22]. From the results above, reaction-sintering process is proven more effective than conventional and B-site precursor routes in preparing BPZN ceramics with high dielectric constant.

4. Conclusions

Pyrochlore-free BPZN perovskite ceramics could be produced using a simple and effective reaction-sintering process successfully. Highly dense BPZN ceramics with a density higher than 98.5% of theoretical density could be obtained. Higher dielectric constants were obtained in BPZN ceramics via reaction-sintering process than via B-site precursor route. K_{max} of 13,500 (at 75 °C), 19,600 (at 50 °C) and 14,800 (at 28 °C) at 1 kHz could be obtained in 6BPZN, 8BPZN and 10BPZN, respectively. Dielectric maximum temperature (T_{max}) in BPZN ceramics via reaction-sintering process is lower than BPZN ceramics prepared via B-site precursor route.

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