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Journal of the European Ceramic Society 25 (2005) 2197–2200

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Fabrication and electric properties of PZN-based ceramics using modified columbite method

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Abstract

Complex $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN)-based ceramics have been prepared by three different columbite methods: conventional columbite (CC), B-site precursor columbite (BSPC) and A-site sequential mixing columbite (ASMC) method. The pyrochlore was not removed completely by IC and BSPC process for PZN-rich compositions. The transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) observation of the BSPC samples show that the BaO was segregated at triple junctions, implying that stabilization of the perovskite structure of the specimens was not completely achieved due to element segregation. On the other hand, full perovskite phase could be obtained by ASMC method for all compositions. Although the pyrochlore phase could mostly be removed by all three processes for specimens with PZN contents less than 50%, the dielectric behavior of PZN-based ceramics was markedly affected by the processing procedures.

Keywords: Electron microscopy; Ferroelectric; Dielectric properties; Perovskite; Sintering

1. Introduction

Lead zinc niobate, $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN), is a relaxor type of ferroelectric material.[1] The solid solution between PZN with rhombohedral symmetry and $PbTiO_3$ (PT) with tetragonal symmetry has a morphotropic phase boundary (MPB) near 10 mol% PT.[1] Single crystals with composition near MPB shows extremely large dielectric constant ($k \gg 22{,}000$) and piezoelectric coefficients $K_p \sim 92\%$, $d_{33} \sim 1500$pC/N.[2] However, it has been reported that perovskite PZN or 0.9PZN–0.1PT crystals are thermodynamically unstable over a wide range of temperatures (600–1400 °C) rapidly yielding a pyrochlore phase and PbO and ZnO as it decomposes.[3–5] To date, the most useful method to stabilize the perovskite structure includes additives such as $BaTiO_3$ (BT) and $SrTiO_3$ and so on.[6,7] The bond valence method was an effective way to estimate how many additives could stabilize the PZN perovskite structure.[8] However, formation of the pyrochlore phase has been frequently observed in lead-based $Pb(B_1,B_2)O_3$ type ferroelectric compounds which are supposed to possess perovskite structure. Yet the columbite method was effective in decreasing the pyrochlore phase in $Pb(B_1,B_2)O_3$ ceramics system. The columbite method can be employed to prepare pyrochlore free for the $Pb(Mg_{1/3}Nb_{2/3})O_3$ ceramic system, but it was difficult to use in a PZN ceramic system, indicating that atomic arrangement and phase formation in PZN ceramics may be correlated with preparation procedures or sequences, even if a columbite method was adopted.

In the present study, we attempted to find the best processing sequences to synthesize a perovskite PZN ceramic system. We believed that there are various reaction routes when one uses different processing procedures. Therefore we modified the mixing sequences during material processing, which were evaluated by the structural and microstructural analysis

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doi:10.1016/j.jeurceramsoc.2005.03.029

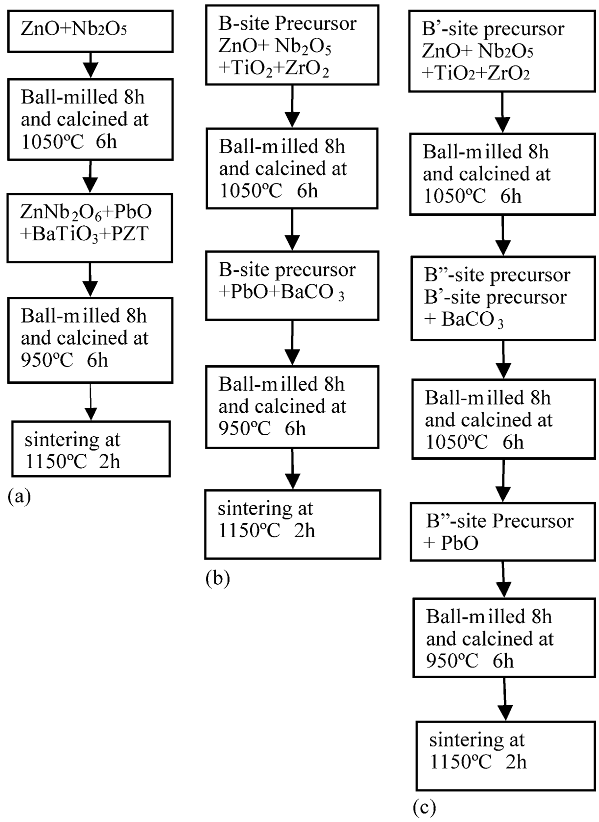

Fig. 1. Experimental processes (a) CC; (b) BSPC; and (c) ASMC.

carefully, in order to obtain PZN-based ceramics with appropriate electric properties.

2. Experimental procedures

According to the formulas $x(0.94\ \mathrm{Pb(Zn_{1/3}Nb_{2/3})O_3} + 0.06\ \mathrm{BaTiO_3}) + (1-x)((1-y)\mathrm{PbZrO_3} + y\mathrm{PbTiO_3})$ (PBZNZT), the specimens studied in this investigation were fabricated. The compounds were prepared using three preparation sequences: (a) conventional columbite (CC); (b) B-site precursor columbite (BSPC) and (c) A-site sequential mixing columbite (ASMC) method, as shown in Fig. 1.

The structure of samples was investigated by using powder X-ray diffraction (XRD). Percentage of the perovskite phase can be calculated from the X-ray peak intensities by using the following equation: % perovskite = $I_{\text{perovskite }(1\,1\,0)}/(I_{\text{perovskite }(1\,1\,0)} + I_{\text{pyrochlore }(2\,2\,2)})$. The microchemical homogeneity of the specimens was examined by using an energy dispersive X-ray spectrometer (EDS) on a field emission gun transmission electron microscope (FEG-TEM) (Philips Tecnai F30). The electron beam was contracted to 10 nm during EDS analysis of FEG-TEM.

After the pellets were polished, gold sputtered, painted with silver paste as electrodes, and fired at 600 °C for 30 min. Dielectric measurements were conducted to an HP4194A automatic system with a temperature controlled chamber to measure the dielectric constants of the specimens as a function of temperature between 100 Hz and 1 MHz. The samples were heated at a rate of 2 °C/min.

3. Results and discussion

Whether the PBZNZT ceramics form a stable perovskite phase can be forecasted by a bond valence method.[8] If the value of bond valence was greater than 1.74, the compound had a stable perovskite structure. The perovskite structure of the specimens of chosen compositions should be stable after fabrication. On the other hand, the PZT not only stabilize perovskite PZN, but also find a morphotropic phase boundary at $x = 0.6$ and $y = 0.48$.

The amount of perovskite phase of specimens, which was estimated by XRD, for various x values using different processes was shown in Fig. 2. Free pyrochlore phase can be eliminated only at $x = 0.5$ or below in the CC process and the amount of pyrochlore phase increased as x increased after sintering at 1150 °C for 2 h. After calcining the powders, both BSPC and ASMC processes could produce specimens with a full perovskite structure. But the amount of pyrochlore phase was increased as the PZN content increased for the BSPC process sintering samples, when x was greater than 0.7. However, it is clear that the BSPC method is more effective than that of CC method in reducing the pyrochlore phase. Whatever the BSPC method still could not remove the pyrochlore phase for all compositions after sintering.

Using EDS chemical composition analysis to investigate the atomic distribution of elements, the theoretical value of the Ba content was 1.5 at.%, but they were 0.34 and 3.62 at%, respectively in the grain and at triple junctions as shown in Fig. 3, implying that most of the $\mathrm{Ba^{2+}}$ ions had segregated at the grain boundaries. Furthermore, the free energy of PbO is lower than BaO,[9] so it was easier to form a perovskite structure with B-site precursor reacting by PbO. When all the A-sites were occupied by $\mathrm{Pb^{2+}}$ ions, the $\mathrm{Ba^{2+}}$ ions will segregate at the grain boundaries. When the dissolution of $\mathrm{Ba^{2+}}$ ions is not enough, the pyrochlore phase forms in sintering at 1150 °C. Thus the sintered samples with composi-

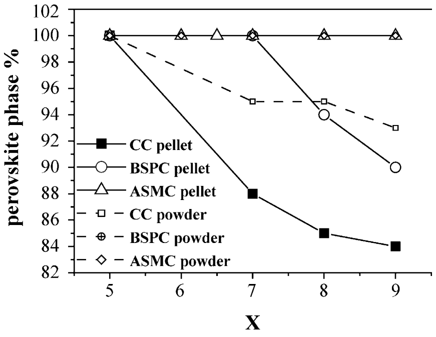

Fig. 2. The percentage of perovskite phase for various compositions of PBZNZT materials, which were calcined at 950 °C for 4 h and sintered at 1150 °C for 2 h, respectively.

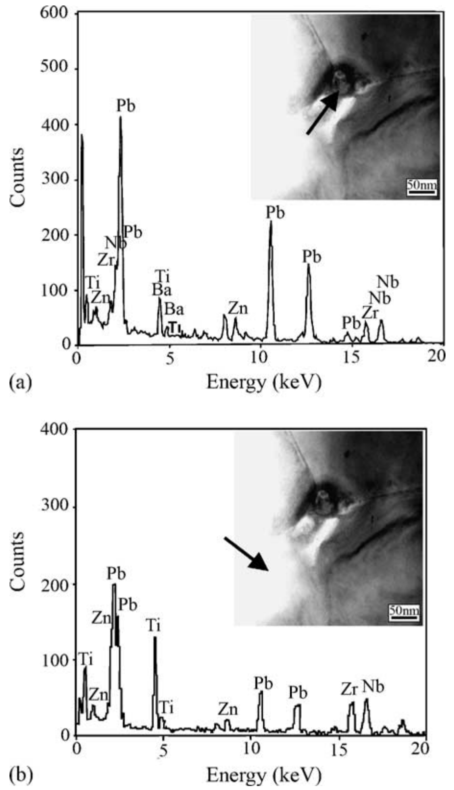

Fig. 3. EDS spectra of a PBZNZT specimen (a) at a triple junction and (b) in a grain for a $x = 0.5$ BSPC specimen. The Ba^{2+} is segregated to grain boundaries and triple junctions.

tions of $x > 0.7$ have a pyrochlore phase by using the BSPC process.

A new process by considering the mixing sequences of A-site elements, called "A-site elements sequential mixing columbite method (ASMC)" could solve this problem. All compositions of calcined powder and sintered samples could obtain the complete perovskite structure by the way of ASMC process, as shown in Fig. 2.

In this study, only the specimens of $x = 0.5$ for PBZNZT ceramic system can be synthesized to a complete perovskite phase by all three processes. However, there are differences to the lattice structures of the perovskite phase prepared by different methods. The XRD patterns display perovskite structures with two different sets of lattice parameters co-existing in a CC sample at composition of $x = 0.5$, as shown in Fig. 4. Whereas, ASMC samples clearly showed a single tetragonal perovskite structure in the XRD patterns. It had been studied that the micro-region heterogeneity would affect the phase structures and dielectric properties in PBZNZT ceramic system.[10,11] In the CC approach, the full perovskite phase of BT and PZT were used to synthesize a new perovskite PBZNZT phase. The large tolerance factor and electronegativity difference of BT and PZT would form more stable perovskite phase. Therefore, it was difficult to create a homogeneous composition through a solid state diffusion. Therefore, the phase of CC samples could not be defined clearly. The results indicated that composition homogeneity did not realize in CC specimens, and it neither improved the electric properties nor created a stable perovskite structure by the addition of BT.

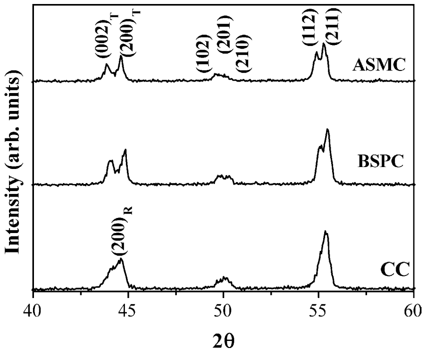

Fig. 4. Room-temperature XRD profiles for PBZNZT ($x = 0.5$, $y = 0.48$) materials with different processes.

The minimum temperature synthesizing BT with BaO and TiO_2 is 1100 °C or above[12] and PZT was difficult to synthesize a perovskite phase using an oxide-mixing method. However the powders through both BSPC and ASMC processes could form a single perovskite phase after calcined at 950 °C for 4 h, implying that synthesis of powders may pass through various chemical routes by different processes. All ions would be sequenced appropriately during a synthesis process to occupy the sites accurately. Therefore, A-site ions with higher chemical reactivity would dissolve late to the system. This concept was used in ASMC method so it was easier to synthesize perovskite for all compositions.

The dielectric constant and dielectric loss versus temperature curves of PBZNZT for $x = 0.5$ at 1 kHz was shown in Fig. 5. There was not clear difference between dielectric constant of BSPC and ASMC but the temperature for the peaks in the dielectric constant curve, T_m, was shifted by different processes. There were also differences between solid solution of Ba^{2+} ion for BSPC and ASMC process based upon EDS results. On the other hand, the dielectric constant of CC samples was obviously lower than those of BSPC and ASMC samples. This may be attributed to the heterogeneous composition of CC samples. The dielectric loss of BSPC samples was larger than that of ASMC sample. The Ba^{2+} ions did not dissolve in the grains of BSPC samples to stabilize

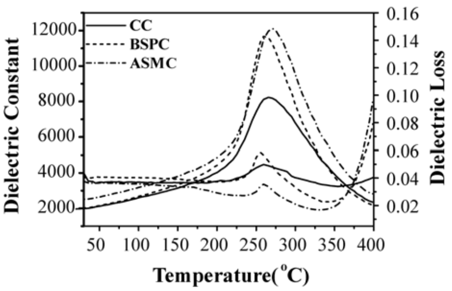

Fig. 5. The temperature dependence of dielectric constant and dielectric loss at 1 kHz for PBZNZT ($x = 0.5$, $y = 0.48$) materials with different processes.

the structure which may induce defects in the samples. The defects would decrease dielectric constant and increase dielectric loss.

4. Conclusions

There were various chemical reaction routes to synthesize ceramics of the PBZNZT system. The perovskite phases of BT and PZT were too stable to decompose and diffuse into the grain to suppress the pyrochlore phase in PZN ceramics. Therefore, the route of forming solid solution between $ZnNb_5O_6$ columbite with titania or zirconia before the addition of lead oxide or barium oxide is more beneficial to the suppressing of PZN pyrochlore phase. Hence the BSPC method was effective in synthesizing perovskite PBZNZT ceramics. However, the important issue in synthesis was not only the mixing of B-site cations but also the mixing A-site cations. In the study, reaction of barium oxide with other oxide ingredients was difficult since barium oxide was a refractory ingredient and its dissolution only occurs under high temperatures. Finally we conclude that the ASMC method was the best process to synthesize perovskite PBZNZT ceramics.

On the other hand, the phase of structure and dielectric properties were effected directly by processing sequence. The microcompositional homogeneity was improved by the ASMC process so that the dielectric constant and dielectric loss could be advanced.

Acknowledgments

Financial support from the National Science Council of Taiwan, Republic of China through project numbers NSC 90-2216-E-011-044 and NSC 91-2216-E-011-031 is gratefully acknowledged by the authors.

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