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# Stabilization of the perovskite phase in Pb($Zn_{1/3}$, $Nb_{2/3}$)$O_3$ ceramics modified by Ba($Zn_{1/3}$, $Nb_{2/3}$)$O_3$ and $BaTiO_3$

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Stabilization of the perovskite phase in PZN–BT–BZN ceramics prepared by solid-state sintering was investigated. With the addition of BT and/or BZN, the amounts of perovskite phase in PZN ceramics increased, but the amount of pyrochlore phase decreased. Optimum calcination conditions for this system, to obtain PZN ceramics with the minimum amount of the pyrochlore phase, are a temperature range between 950 and 1000 °C and a sintering time of 2–4 h. The perovskite phase of these systems could be 100% stabilized by the addition of more than 7 mol % BT, 8 and 10 mol % BTZN and BZN, respectively.

## 1. Introduction

Lead zinc niobate ceramic (PZN) is a ferroelectric material with the perovskite structure exhibiting a diffuse phase transition [1–3]. It has a rhombohedral structure at room temperature and undergoes a phase transition at 140 °C to a cubic structure. Single crystals of PZN showing excellent dielectric, optical, and electrostrictive properties have been studied extensively [4–7].

The solid solution between PZN with rhombohedral symmetry and $PbTiO_3$ (PT) with tetragonal symmetry has a morphotropic phase boundary (MPB) at room temperature for a composition with nearly 9 mol % PT [8]. Single crystals with a composition near the MPB usually show large dielectric and piezoelectric constants and higher electromechanical coupling coefficients (about 92%) than those of the PZT family ceramics. Single crystals of PZN–PT can also be grown by the flux method [9].

It is extremely difficult to prepare pure PZN or PZN–PT ceramics with the perovskite structure by conventional ceramic processing because the formation of stable lead-based pyrochlore-type phases invariably occurs [10–15]. The product obtained by solid-state sintering at about 1100 °C is largely a cubic pyrochlore phase of the $PbNb_2O_6$ type, which is detrimental to both dielectric and piezoelectric properties. Difficult in obtaining the stabilized perovskite phase in PZN ceramics is due to its thermodynamic instability [16].

The formation of the pyrochlore phase has been observed in a number of lead-based $Pb(B_1, B_2)O_3$ type ferroelectric compounds with the perovskite structure [13, 17]. The problem of pyrochlore formation has been studied in $Pb(Mg_{1/3}, Nb_{2/3})O_3$ (PMN) ceramics. By following a different processing scheme, Swartz *et al.* [10, 11] were able to stabilize the perovskite structure in PMN. The reaction sequence used by Swartz *et al.* was the columbite method. In this method, MgO is prereacted with NbO to form $MgNb_2O_6$ which has a columbite structure. The $MgNb_2O_6$ is then reacted with PbO to obtain 100% pure perovskite PMN ceramics. Because magnesium and zinc have the same charge and similar ionic radii, it seems plausible to prepare perovskite PZN ceramics by first preparing $ZnNb_2O_6$ with PbO. In the case of PZN, the reaction product obtained by this reaction sequence in pyrochlore [11], but the reasons are not clear.

Halliyal *et al.* [18] and Furukawa *et al.* [19] have reported that the formation of the pyrochlore phase in PZN can be suppressed by adding 15 mol % of either $BaTiO_3$ or $SrTiO_3$. These ceramics show a maximum dielectric constant of $\sim 5000$ which is much lower than that of PZN single crystals ($\sim 60\,000$). The ceramics in the $(1-x)$PZN–$x$PT system always yield a mixture of the perovskite and pyrochlore phase when $x < 0.75$. The perovskite structure in PZN–PT ceramics can be further stabilized by the addition of $Ba(Zn_{1/3}, Nb_{2/3})O_3$ (BZN), or by the partial substitution of PbO with $K_2O$. These additions, however, dilute the dielectric and piezoelectric properties.

In the present study, an attempt was made to stabilize the perovskite phase in PZN ceramics by adding only a small percentage of a second perovskite compound. If the perovskite phase can be stabilized using only a small amount of a second component, the properties of PZN probably will not be altered significantly. From previous work [18, 19], it is clear that the perovskite structure in PZN can be stabilized by the

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addition of a more ionic compound. Also, in the present work, an analysis of the stability of several compounds having the perovskite structure was conducted by considering the structure field map and ionic nature of the chemical bonds.

## 2. Experimental procedure

In the ternary system $(1-x-y)$PZN–$x$BT–$y$BZN, compacts were prepared by the conventional solid-state sintering technique. Near PZN, compositions were selected at 1 mol % intervals to determine the minimum amount of $BaTiO_3$ (BT), BTZN, and BZN needed to obtain ceramics with a 100% perovskite phase. For compositions with $x < 0.8$, reagent-grade powders of PbO, ZnO, $Nb_2O_3$, $TiO_2$ and $BaCO_3$ were used as starting materials. The constituents were dried prior to weighing. The mixtures were ball-milled in a polyethylene jar with ethanol for 12–16 h using a zirconia grinding medium. The slurry was dried and calcined for 1–10 h at temperatures ranging from 800–1150 °C. The calcined powder was ball-milled and dried again to obtain a homogeneous powder. Pellets, 12 mm diameter and 2–3 mm thick, were pressed with PVA binder, and the binder was burned out by slowly heating at 500 °C for 1 h. Compacts were sintered in a sealed alumina crucible at temperatures ranging from 900–1200 °C at a heating rate of 200 °C $h^{-1}$ in an SiC resistance furnace. To limit PbO loss from the compacts, a PbO-rich atmosphere was maintained by placing an equi-molar mixture of PbO and $ZrO_2$ inside the crucible.

For compositions with $0.8 < x < 1$, prereacted $ZnNb_2O_6$ and high-purity $BaTiO_3$ powder were used as precursor materials to increase the reactivity of the powders during calcination. First, reagent-grade ZnO and $Nb_2O_5$ were mixed by ball milling and calcined at 1000 °C for 4 h to obtain $ZnNb_3O_6$. Lead oxide, $ZnNb_2O_6$, and $BaTiO_3$ were then mixed and ball milled.

The relative amounts of the pyrochlore and perovskite phases were determined using powder X-ray diffraction patterns of the sintered bodies and measuring the major X-ray peak intensities for the perovskite and pyrochlore phases, for example, (1 0 0) and (2 2 2), respectively. The percentage of the perovskite phase was calculated from the X-ray peak intensities using the following equation [20]

$$\%\ \text{perovskite} = \frac{I_{\text{perovskite}\ (1\,1\,0)}}{I_{\text{perovskite}\ (1\,1\,0)} + I_{\text{pyrochlore}\ (2\,2\,2)}} \times 100 \qquad (1)$$

Powder X-ray diffractometry (PW 1700, Philips Electronic Co.) with Cu$K_\alpha$ radiation was also used. Theoretical densities were calculated from lattice parameter measurements, and bulk densities were geometically determined. The sintered microstructures were observed by scanning electron microscopy (Model 2000FX, Jeol). For the dielectric constant measurements, gold electrodes were sputtered and air-dry silver paint was applied over gold electrodes. The dielectric constant was measured by an automated system, in which a temperature control box and LCR (meters (HP4192A) were controlled by a desktop computer.

## 3. Results and discussion

### 3.1. The effects of calcination and sintering conditions on the stabilization of the perovskite phase

The calcination and sintering conditions, fired densities, and percentage of the perovskite phase for all the compositions of $(1-x)$PZN–$x$BTZN are given in Table I. To obtain highly densified compacts, calcination and sintering at a higher temperature were necessary for compositions containing a large fraction of $BaTiO_3$ and BZN. Compositions with $x$ in the range of $0.9 < x < 1$ could not be sintered to sufficiently high densities. Several compositions in the PZN systems with 2–20 mol % stabilizers were calcined at different temperatures for varing time intervals to examine the effects of the calcination condition on the amount of the perovskite phase formed. XRD patterns of separated mixtures which were calcined for 2 h at each calcination temperature, are shown in Fig. 1. The formation of the pyrochlore phase was suppressed by the addition of BTZN and, conversely, the degree of the perovskite-phase formation increased with increasing amount of BTZN.

Fig. 2 shows a plot of the percentage of the perovskite phase in each composition as a function of temperature. For all the composition, the amount of perovskite phase formed was less than 20% for the specimens calcined at temperatures lower than 850 °C. For the specimens calcined at temperatures higher than 850 °C, the amount of the perovskite phase increased sharply with temperature. Compositions with 8–10 mol % BTZN calcined at

TABLE I Calcination and sintering conditions, relative density and amount (%) of the perovskite phase $(1-x)$PZN–$x$BTZN

| $x$ | Calcination temp. (°C) | Sintering temp. (°C) | Sintering time (h) | Relative density (%) | Perovskite phase (%) |
|---|---|---|---|---|---|
| 0.00 | 900 | 1000 | 4 | – | 0 |
| 0.02 | 900 | 1000 | 2 | – | 30 |
| 0.04 | 900 | 1100 | 1 | 90–91 | 70 |
| 0.05 | 900 | 1100 | 1 | 94–95 | 80 |
| 0.07 | 900 | 1100 | 1 | 94–95 | 94 |
| 0.08 | 900 | 1100 | 1 | 95–95 | 100 |
| 0.09 | 900 | 1100 | 1 | 95–96 | 100 |
| 0.10 | 900 | 1100 | 1 | 95–96 | 100 |
| 0.12 | 900 | 1150 | 1 | 94–96 | 100 |
| 0.14 | 900 | 1150 | 1 | 92–94 | 100 |
| 0.15 | 900 | 1150 | 1 | 92–94 | 100 |
| 0.20 | 900 | 1150 | 1 | 92–94 | 100 |
| 0.25 | 900 | 1175 | 1 | 92–94 | 100 |
| 0.30 | 900 | 1175 | 1 | 91–94 | 100 |
| 0.40 | 900 | 1175 | 1 | 91–94 | 100 |
| 0.50 | 1000 | 1230 | 2 | 90–94 | 100 |
| 0.60 | 1000 | 1230 | 2 | 90–94 | 100 |
| 0.70 | 1000 | 1250 | 2 | 90–93 | 100 |
| 0.80 | 1000 | 1250 | 2 | 90–93 | 100 |
| 0.90 | 1100 | 1300 | 2 | 90–92 | 100 |
| 1.00 | 1100 | 1300 | 2 | 90–92 | 90 |

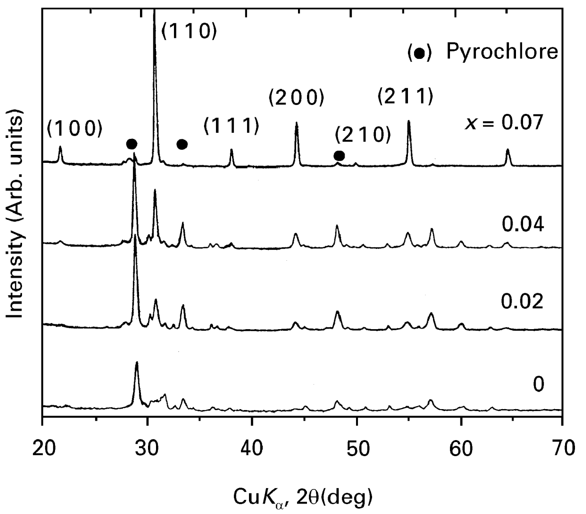

*Figure 1* X-ray diffraction patterns of $(1-x)$PZN–$x$BTZN powders calcined at 900 °C for 2 h.

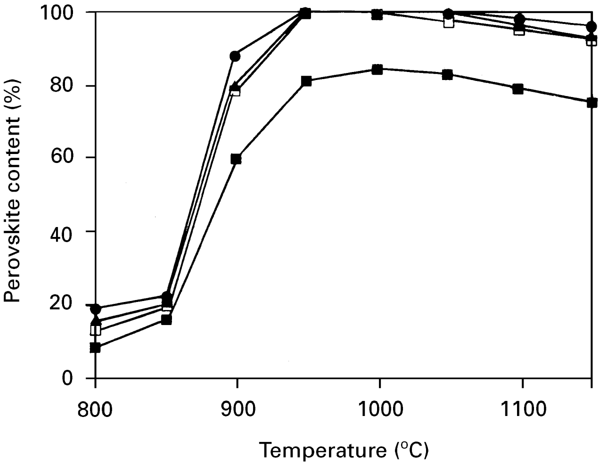

*Figure 2* Percentage of the perovskite phase at varying calcination temperatures in $(1-x)$PZN–$x$BTZN powders, calcined for 2 h: $x$ = (●) 0.10, (▲) 0.08, (□) 0.07, (■) 0.05.

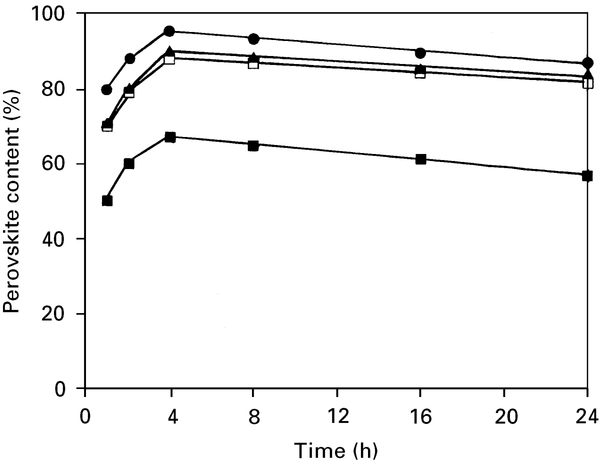

*Figure 3* Percentage of the perovskite phase at varying calcination times in $(1-x)$PZN–$x$BTZN powders, calcined at 900 °C. For key, see Fig. 2.

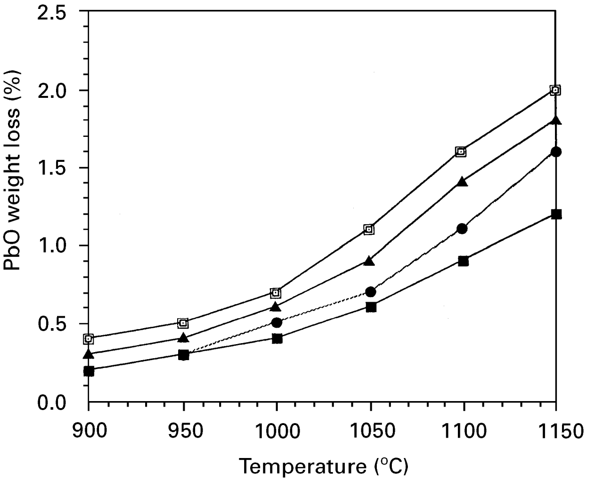

*Figure 4* Percentage of PbO weight loss at varying calcination temperatures in $(1-x)$PZN–$x$BTZN powders, calcined for 2 h: $x$ = (▣) 0.05, (▲) 0.07, (●) 0.08, (■) 0.10.

950–1050 °C showed 100% perovskite phase. In all the compositions, a small fraction of the pyrochlore phase was observed for calcinations above 1050 °C.

The effect of the calcination time on the amount of the perovskite phase is shown in Fig. 3. Initially, the amount of the perovskite phase increased sharply with calcination time and then decreased slowly for longer periods of time. This behaviour is supposed to relate to the evaporation of PbO during firing at high temperature. Fig. 4 shows a plot of the PbO evaporation during the calcination, supporting this assertion. It is known that the loss of PbO during firing favours the formation of pyrochlore phases in lead-based relaxor compounds, such as PMN [11]. A large weight loss during the sintering resulted in a PbO-deficient stoichiometry, which caused the degradation of the dielectric properties. From the results of the present work, the optimum calcination conditions to obtain PZN ceramics with the minimum amount of pyrochlore phase are a temperature in the range between 950 and 1000 °C and a sintering time of 2–4 h.

It should be noted that, for the calcination done at temperatures above 1050 °C, there is a slight formation of the pyrochlore phase. To depress the evaporation of PbO, it is important to select optimum sintering conditions, which is the primary factor for preparing the dense ceramics.

Lead zinc niobate ceramics without BT and/or BZN additives contained only the pyrochlore structure, but the percentage of the perovskite phase increased with the addition of $BaTiO_3$ and BZN, as shown in Table I. Compositions containing over the 7 mol % $BaTiO_3$ and 10 mol % BZN did not have any of the pyrochlore phase. It is clear that the formation of the pyrochlore phase in PZN can be completely avoided by adding 7 mol % $BaTiO_3$ or 10 mol % BZN. The results of the combined effects for the stabilization of the perovskite structure in PZN-BZN-BT system are shown in Fig. 5. The effects of the stabilization of the perovskite phase by the addition of BTZN and BZN can be explained from the view point of thermodynamics. The stability of the perovskite

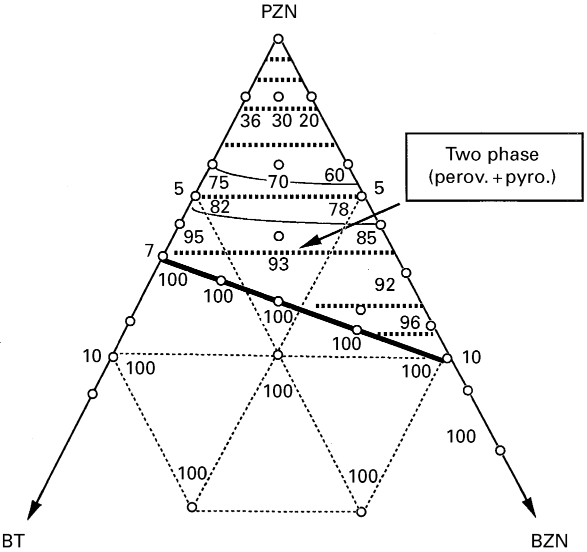

*Figure 5* Percentage of the perovskite phase in $(1-x-y)$PZN–$x$BZN–$y$BT ceramics sintered at 1100 °C for 2 h.

structure is dependent on the electronegativity difference between anions and cations, and the tolerance factor [2, 21]. From previous reports [18, 19], BT stabilized the perovskite structure in PZN due to its high electronegativity difference and tolerance factor. Similarly, we supposed that BT and BZN contributed to the stabilization of the perovskite phase in PZN by increasing both the electronegativity difference and tolerance factor.

## 3.2. Properties of the sintered body

Table II gives the grain size, which was calculated by a linear intercept technique from scanning electron micrographs, and density as a function of the sintering time for sintered bodies prepared from calcined powder at 900 °C. The average grain size was 1.2 and 6.4 μm at 1 and 32 h, respectively. The trend in the data in Table II indicates that an increase in the sintering time resulted in an increase in the grain size, but that density did not increase proportionally to the sintering time. In most dielectric ceramics, the dielectric constant depends on the grain size [22, 23]. The densities of the sintered bodies increased up to 4 h and then slowly decreased after 4 h, probably due to the loss of PbO. The percentage of the theoretical density was in the range 92%–96% for most of the compositions.

TABLE II Sintered density, grain size and dielectric constant of 0.86 PZN–0.14 BTZN sintered at 1100 °C at varying sintering times. The powder mixture was calcined at 900 °C for 2 h

| Sintering time (h) | Grain size (μm) | Sintered density (g cm$^{-3}$) | Dielectric constant (at 25 °C) |
|---|---|---|---|
| 1 | 1.2 | 7.53 | 9000 |
| 2 | 2.2 | 7.70 | 9200 |
| 4 | 3.3 | 7.78 | 9600 |
| 8 | 4.2 | 7.65 | 9900 |
| 16 | 5.3 | 7.60 | 10000 |
| 32 | 6.4 | 7.56 | 9900 |

In PZN–BTZN systems, the dielectric constants increased with both increasing sintering temperature and time, as shown in Table II. It should be stated, however, that the true grain-size effects of the dielectric constant cannot be resolved due to the difficulty in varying grain sizes without changing the density, PbO weight loss, microcracking, etc. The magnitude of the dielectric constant maximum increases with the addition of up to 7 mol % $BaTiO_3$, and decreases sharply with futher addition of $BaTiO_3$ with a maximum dielectric constant at 8 and 10 mol % of BTZN and BZN, respectively. The maximum room-temperature dielectric constants were observed: 7800 at 12 mol % BZN 10 000 at 14 mol % BTZN, and 9800 at 15 mol % BT.

## 4. Conclusion

Stabilization of the perovskite phase in PZN–BT–BZN ceramics prepared by solid-state sintering was investigated and the dielectric constants were measured. Lead zinc niobate ceramic without BT and/or BZN additives was shown to have a completely pyrochlore structure, but the percentage of the perovskite phase increased with the addition of $BaTiO_3$. Optimum calcination conditions to obtain PZN ceramics with a minimum amount of pyrochlore phase are a temperature range between 950 and 1000 °C and a sintering time of 2–4 h. The perovskite phase of these systems could be stabilized to 100% with the addition of more than 7 mol % $BaTiO_3$, 8 and 10 mol % of BTZN and BZN, respectively.

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