Synthesis and Dielectric Characterization of Pyrochlore-Free $Pb_{1-x}Ba_x(Zn_{1/3}Nb_{2/3})O_3$ Ceramics

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Abstract. The dielectric properties and synthesis of pyrochlore-free lead zinc niobate ceramics with Ba substituting for Pb were investigated. Ba partial substitution for Pb was effective in stabilizing the perovskite structure in PZN ceramics, where the minimum amount of Ba substitution needed was about 20 mol%. The dielectric loss and the temperature coefficient of dielectric constant of PZN were reduced markedly with Ba substitution, while the dielectric constant was greater than 110. Good dielectric properties were obtained for the composition of $Pb_{0.3}Ba_{0.7}(Zn_{1/3}Nb_{2/3})O_3$: $\varepsilon = 133.5$, $\tan \delta = 0.0009$, $\tau_\varepsilon = -811$ ppm/$^\circ$C.

Keywords: synthesis, lead zinc niobate, perovskite structure, dielectric properties

1. Introduction

Modern wireless communication and microelectronics require the development of dielectric materials with high permittivity [1, 2]. Ferroelectric materials, which are different from the traditional paraelectric materials, have been extensively studied as microwave dielectrics because of their high permittivity [3–8]. Among them, lead based complex perovskite compositions are typical materials, such as $Pb(Mg_{1/3}Nb_{2/3})O_3$, $Pb(Fe_{1/2}Nb_{1/2})O_3$. Chen et al. [6, 8] reported the microwave dielectric properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$ modified by $CaTiO_3$, and obtained the materials with permittivity of more than 125 and the Qf value of 3100 GHz. However, to lower the temperature coefficient of dielectric constant remained a problem to be investigated. As another approach to obtain high-ε dielectrics and low dielectrics loss, we will discuss the possibility of PZN used as a dielectric ceramic.

$Pb(Zn_{1/3}Nb_{2/3})O_3$ with a partially disordered perovskite structure possesses the highest permittivity in the lead-based relaxor dielectric system, in which the value of ε_{max} reaches 22,000. Single crystals of PZN have been studied extensively for their excellent dielectric, optical and electrostrictive properties [9, 10]. The synthesis and dielectric properties of PZN ceramics stabilized by introducing $BaTiO_3$, $PbTiO_3$, and $SrTiO_3$ were also investigated [11, 12], but the dielectric properties of PZN ceramics at microwave frequencies have rarely been reported. Kato et al. [3] reported the dielectric properties of PZN ceramics modified by substituting Ca for Pb for possible use in microwave dielectrics. Their studies showed that the single-phase perovskite structure in PZN could not be obtained by substituting Ca for Pb with the amount varying from 25 mol% to 75 mol%, meanwhile the dielectric constant decreased from 95 to 55 and the temperature coefficient of resonance frequency was very high. The possible reason for not obtaining large dielectric constants and low temperature coefficients of resonance frequency was the formation of the pyrochlore phase in PZN.

It is well known that it is difficult to synthesize PZN ceramics with a perovskite single-phase structure by the conventional solid state reaction process. The relative ease of preparing the lead-based perovskites roughly follows the sequence $Pb(Zn_{1/3}Nb_{2/3})O_3 < Pb(Cd_{1/3}Nb_{2/3})O_3 < Pb(In_{1/2}Nb_{1/2})O_3 < Pb(Sc_{1/2}Nb_{1/2})O_3 < Pb(Ni_{1/3}Nb_{2/3})O_3 < Pb(Mg_{1/3}Nb_{2/3})O_3 < Pb(Fe_{1/2}Nb_{1/2})O_3 < Pb(Fe_{1/2}W_{1/2})O_3 < PbZrO_3 < PbTiO_3$ [13]. That means pure PZN is the most difficult to obtain, and the phase in PZN prepared by solid-state reaction at 1100°C is primarily a cubic pyrochlore

Table 1. The amount of additives needed to stabilize perovskite structure in PZN.

Additives	Minimum amount (mol%)	Reference
$PbTiO_3$	>25	[13, 15]
$SrTiO_3$	9~10	[11, 16]
$BaTiO_3$	6~7	[12, 17]
$PbZrO_3$	55~60	[12]
$Ba(Zn_{1/3}Nb_{2/3})O_3$	15	[18]
Substituting K for Pb	10	[19]

phase of $Pb_3Nb_4O_{13}$ which is detrimental to the dielectric properties. To suppress the formation of the pyrochlore phase, many approaches were proposed by using additives such as $PbTiO_3$ and $BaTiO_3$. These additives with the perovskite structure are helpful in forming the single-phase perovskite structure in PZN with good dielectric properties. Table 1 shows the amount of additive needed to stabilize the perovskite phase in PZN.

The synthesis of Ba-substituted PZN single crystals were investigated [14], but there were no reports on the dielectric properties of Ba-substituted PZN ceramics. In this paper, the modification of dielectric properties, especially the temperature coefficient of dielectric constant of PZN ceramics, by substituting Ba for Pb was investigated, and the mechanism and the formation of perovskite structure in PZN was also examined.

2. Experimental Procedure

The specimens were fabricated according to the formula $Pb_{1-x}Ba_x(Zn_{1/3}Nb_{2/3})O_3$, where $x = 0.0, 0.1, 0.2, 0.3, 0.5, 0.7, 0.9$. The columbite precursor method was used to prepare $ZnNb_2O_6$ [12] by calcining ZnO and NbO_5 mixtures in the proper ratio at 850~1000°C for 4 h. This precursor was then mixed in stoichiometric ratio with PbO and $BaCO_3$ powders by ball milling with ZrO_2 media in ethanol for 24 h and calcined at 850°C in air for 4 h. The synthesized powders were remilled and pressed into compacts of 12 mm diameter at a pressure of 98 MPa after adding PVA binder, then sintered at 1050°C to 1350°C in air for 1~2 h after binder burn out at 600°C for 1 h.

The microstructures were analyzed by scanning electron microscope (SEM) and powder X-ray diffraction using Cu Kα radiation. The dielectric constant and dielectric loss were measured using an HP4285A LCR meter at a frequency range of 100 kHz–10 Mkz.

Another HP4284A LCR meter, equipped with thermostat, was used to measure the temperature coefficient of dielectric constant τ_ε in the range from room-temperature to 85°C.

3. Results and Discussion

3.1. Microstructure and Phase Analysis

Unlike the phase $Pb_3Nb_4O_{13}$ obtained in previous investigations [11, 12, 20], the pyrochlore type cubic structure $Pb_{1.83}Nb_{1.71}Zn_{0.29}O_{6.39}$ was formed in present work for $x = 0.0$ (Fig. 1). Although the columibite method was used, it was not successful in preparing the single-phase perovskite structure without Ba substitution. Compared with the perfect pyrochlore phase $Pb_3Nb_4O_{13}$, the phase $Pb_{1.83}Nb_{1.71}Zn_{0.29}O_{6.39}$ was likely transformed from $ZnNb_2O_6$ with Pb substituting for Zn and Nb. With Ba substitution, the $Pb(Zn_{1/3}Nb_{2/3})O_3$ phase, with a rhombohedrally distorted perovskite structure, was the major phase in the compositions of $x = 0.1$ and 0.2. For the composition of $x = 0.3$~0.7, $Pb(Zn_{1/3}Nb_{2/3})O_3$
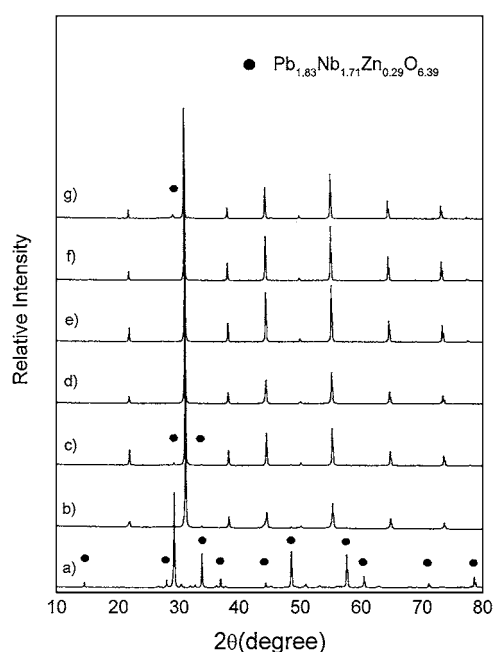

Fig. 1. XRD patterns of $Pb_{1-x}Ba_x(Zn_{1/3}Nb_{2/3})O_3$ ceramics: a) $x = 0.0$, 1050°C/1 h; b) $x = 0.1$, 1100°C/1 h; c) $x = 0.2$, 1100°C/1 h; d) $x = 0.3$, 1150°C/1 h; e) $x = 0.5$, 1150°C/1 h; f) $x = 0.7$, 1200°C/1 h; g) $x = 0.9$, 1350°C/1 h.

single-phase perovskite was obtained. For the compositions of $x = 0.1 \sim 0.9$, the lattice parameters of the PZN crystal cell increased from 4.06 Å to 4.09 Å with Ba substitution. Ba substitution was effective in stabilizing the perovskite structure in the PZN system.

The shape of the Pb^{2+} cation is not spherical with protuberances due to the presence of the $(6s)^2$ lone pair [13, 17, 20]. Effects of steric hindrance and mutual interactions between lone pairs and Zn^{2+} cations cause the instability of the perovskite structure in PZN. The reason that mutual interactions between lone pair of Pb^{2+} ion and Zn^{2+} ion exist but not between Pb^{2+} and Nb^{5+} is that the bond energy between high valence Nb^{5+} and O^{2-} is larger than that of low valence Zn^{2+} and O^{2-}. Furthermore, zinc is more volatile than other ions in PZN. Both lead to the formation of $Pb_{1.83}(Nb_{1.71}Zn_{0.29})O_{6.39}$ as shown in Fig. 1. If Pb^{2+} is partially substituted by Ba^{2+} with spherical shape, the effect of steric hindrance would disappear around the spherical cation. On the other hand, the diffusion of Ba^{2+} into $ZnNb_2O_6$ to form Ba-Nb clusters is a thermally activated process which is effective in stabilizing the perovskite structure [17]. Wakiya et al. calculated that the minimum content of substitution of spherical cations was 7.4 mol% [13] in PZN single crystals. The content needed to stabilize the PZN single crystal was 10 mol% for Ba in their work where their samples were heated in saturated PbO vapor, but Nomural et al. [18] reported that 15 mol% Ba substitution was needed to stabilized the PZN perovskite. In the present work about 20 mol% Ba substitution was needed to obtain single-phase perovskite PZN ceramics.

Besides the reasons mentioned above, there are two factors to influence the formation of perovskite structure in PZN: the tolerance factor t and the electronegativity difference between cations and anions. For the perovskite structure, t is given by $t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$, where r_A, r_B and r_O are the ionic radii of ions A, B and O, respectively, the electronegativity difference $e = (X_{A-O} + X_{B-O})/2$ can be calculated using Pauling's electronegativity [21]. The varieties of tolerance factor and electronegativity difference with Ba substitution for Pb are shown in Fig. 2. Both t and e increased with increasing Ba substitution and therefore are in favor of stabilizing the perovskite structure in the PZN system. For $x = 0.9$, however, the phase $Pb_{1.83}Nb_{1.71}Zn_{0.29}O_{6.39}$ appeared again. It possibly resulted from zinc vaporization at the high sintering temperature of 1350°C.
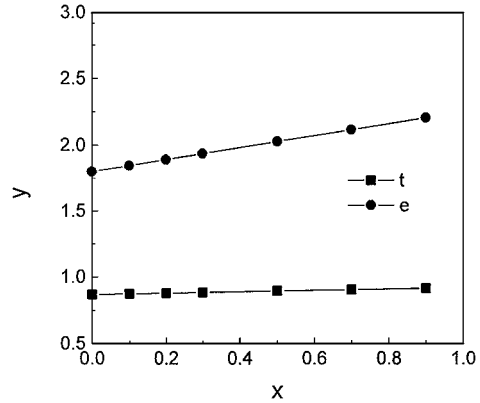

Fig. 2. The tolerance factor and electronegativity of $Pb_{1-x}Ba_x(Zn_{1/3}Nb_{2/3})O_3$ as functions of x.

The SEM micrographs of $Pb_{1-x}Ba_x(Zn_{1/3}Nb_{2/3})O_3$ ceramics sintered at 1050–1350°C for 1 h are shown in Fig. 3. All compositions had fine crystal structure. The grain size increased with increasing Ba content. But for $x = 0.9$, zinc vaporization resulted from the high sintering temperature lead to the formation of the pyrochlore phase $Pb_{1.83}(Nb_{1.71}Zn_{0.29})O_{6.39}$.

3.2. Dielectric Properties

Figure 4 illustrates the room temperature dielectric properties of PZN modified by Ba substitution. The dielectric loss of PZN was effectively decreased by the substitution of Ba for Pb, which reached the minimum value of 0.0004 at the composition of $x = 0.5$, then increased to 0.019 at $x = 0.9$ as a result of the formation of the $Pb_{1.83}(Nb_{1.71}Zn_{0.29})O_{6.39}$ pyrochlore phase. According to the micromechanism of structure formation in PZN, the substitution of Ba with spherical shape for nonspherical Pb ion on A-site leads to a more compact structure and subsequently to low dielectric loss. But in the composition of $x = 0.9$ with two phases coexisting, the dielectric loss rose again. With increasing x, the dielectric constant decreased from 5300 to 115, explained by Ba substitution for Pb.

The temperature coefficient of dielectric constant of $Pb_{1-x}Ba_x(Zn_{1/3}Nb_{2/3})O_3$ is shown in Fig. 5. Ba substitution for Pb on the A-site in PZN affected the configuration of the oxygen octahedron confining the movement of ions on the B-site, this decreased the variation of the dielectric constant with temperature significantly and improved the temperature coefficient of the
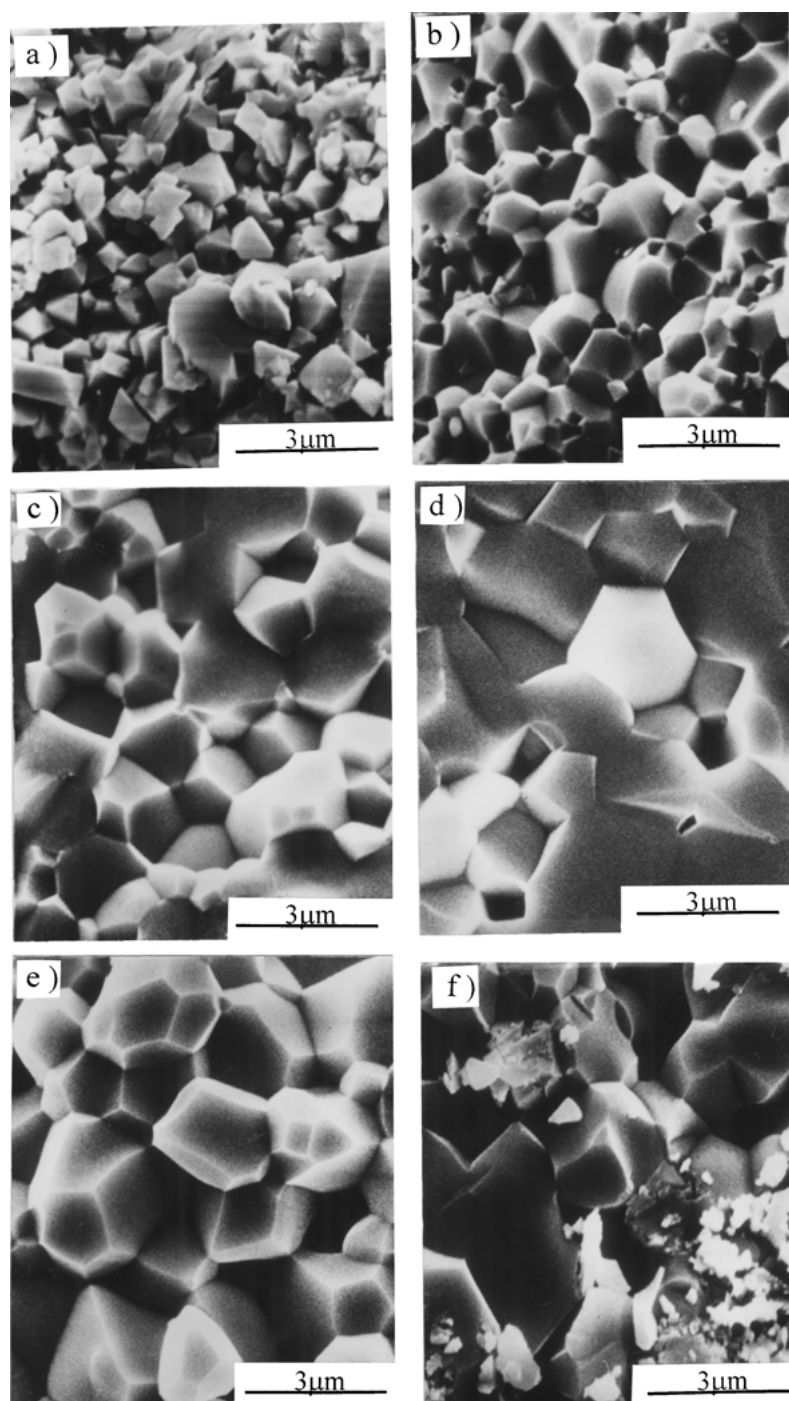
Fig. 3. SEM micrographs of $Pb_{1-x}Ba_x(Zn_{1/3}Nb_{2/3})O_3$ ceramics: a) $x = 0.0$, 1050°C/1 h; b) $x = 0.1$, 1100°C/1 h; c) $x = 0.3$, 1150°C/1 h; d) $x = 0.5$, 1150°C/1 h; e) $x = 0.7$, 1200°C/1 h; f) $x = 0.9$, 1350°C/1 h.
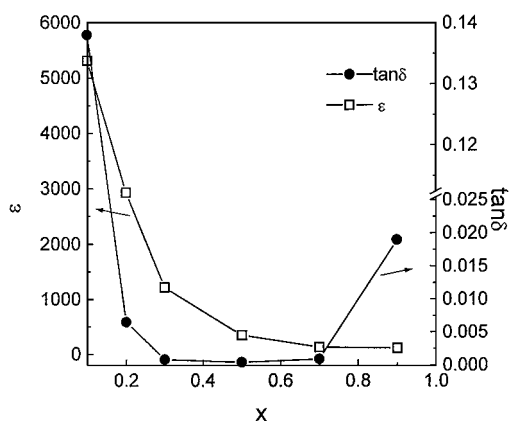
Fig. 4. Room-temperature dielectric properties of $Pb_{1-x}Ba_x(Zn_{1/3}Nb_{2/3})O_3$ ceramics as functions of x (at 1 MHz).

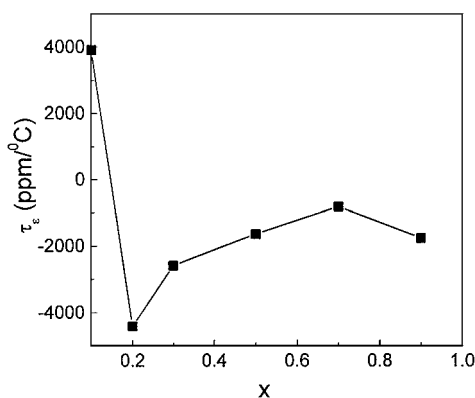*Fig. 5*. Temperature coefficient of dielectric constant of $Pb_{1-x}Ba_x(Zn_{1/3}Nb_{2/3})O_3$ ceramics as a function of x at 1 MHz.

dielectric constant τ_ε. As shown in Fig. 5, with increasing Ba substitution, τ_ε varied sharply from positive to negative at first, then the negative temperature coefficient became smaller with increasing x. For $x = 0.9$, the negative τ_ε increased slightly with formation of the pyrochlore phase. Good dielectric properties were obtained for the composition of $x = 0.7$: $\varepsilon = 133.5$, $\tan \delta = 0.0009$, $\tau_\varepsilon = -811$ ppm/°C at 1 MHz.

4. Conclusions

Ba substitution for Pb was effective in obtaining the rhombohedrally distorted perovskite structure in PZN. The minimum substitution amount needed to stabilize the provskite PZN ceramics was about 20 mol%. With Ba substitution, the dielectric loss and the temperature coefficient of dielectric constant reduced markedly, while the dielectric constant was greater than 110. Good dielectric properties were obtained in the composition of $Pb_{0.3}Ba_{0.7}(Zn_{1/3}Nb_{2/3})O_3$: $\varepsilon = 133.5$, $\tan \delta = 0.0009$, $\tau_\varepsilon = -811$ ppm/°C at 1 MHz. The present modified ceramics have great potential for microwave application if the temperature coefficient can be suppressed further.

Acknowledgments

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