Composition dependence of dielectric properties in $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3\text{--BaTiO}_3$ (PZN–PT–BT) relaxor ferroelectric ceramics

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Perovskite solid solution ceramics of PZN–PT–BT with several compositions were synthesized by solid-state reaction method. X-ray diffraction results indicate pure perovskite structures for all samples. Dielectric measurements show that the implicit $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BZN) composition could broaden the diffusion phase transition (DPT) peaks and lower the ϵ_{max} and T_{max} values. The observed dielectric properties may be caused by the increased cation disorder due to the substitution of barium onto the A-site and titanium onto the B-site.

Keywords: Relaxor ferroelectrics; dielectric properties; diffusion phase transition; cation disorder.

1. Introduction

Relaxor ferroelectrics have been widely investigated in the past several decades, due to their peculiar structure and properties. The disorder in the arrangement of different ions on the crystallographically equivalent sites is the common characteristic of relaxor ferroelectrics.¹ Relaxor ferroelectrics exhibit large saturated polarization (P_s), small remnant polarization (P_r), and slim hysteresis loop, which make them meet the requirements for energy storage application.² However, some typical relaxor ferroelectrics with $\text{Pb}(\text{B}'\text{B}'')\text{O}_3$ perovskite structure, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PMN) and $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (PZN), are not suitable for the energy storage application, due to their poor temperature stability.^{3–5} Recently, to meet the practical application in energy storage, many solid solutions of Bi-based perovskite compounds doped with BaTiO_3 (BT) have aroused much interest, such as $\text{BaTiO}_3\text{--BiScO}_3$ (BT–BS),^{6,7} and $\text{BaTiO}_3\text{--Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (BT–BMT),^{8,9} which possess good temperature stability. Compared with typical relaxor ferroelectrics, such as PMN, this new-type relaxor ferroelectric exhibits higher degree of diffuseness and stronger relaxation behavior, which may be caused by the increased cation disorder because of the substitution of Bi onto A-site. However, there is still controversy about whether they are different or similar qualitatively.^{10,11}

$\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{--PbTiO}_3\text{--BaTiO}_3$ (PZN–PT–BT) ceramics are a complicated system. Here, PZN is a typical relaxor ferroelectric with rhombohedral phase structure at room temperature.^{5,12} PT and BT are normal ferroelectric, where

they are usually used to stabilize phase structure. PZN–PT–BT, in which both A-site and B-site are occupied by two or more kinds of cations, like Bi-based relaxor ferroelectric mentioned above, may make this system even more complicated. In PZN-based binary solid solution, PZN–PT ceramics show peak shift ($\Delta T_C = 2^\circ\text{C}$ at most) with weak DPT behavior,¹³ whereas PZN–BT ceramics exhibit the strong relaxation behavior.¹⁴ Similar situation has also been observed in PMN–PT and PMN–BT systems. This phenomenon may indicate that the increased cation disorder in A-site can strengthen relaxation behavior. Moreover, Wang *et al.* reported that $\text{Ba}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (BZN)-rich paraelectric phase might be present in PZN–BT and PZN–PT–BT ceramics.^{15,16} In this work, we focused on the effect of BT content on the dielectric behavior of the PZN–PT–BT ceramics. The processing, microstructure and dielectric properties of the PZN–PT–BT system were systematically investigated.

2. Experimental Procedure

The compositions selected for this work including 0.75PZN–0.1PT–0.15BT, 0.7PZN–0.1PT–0.2BT, 0.75PZN–0.15PT–0.1BT, 0.7PZN–0.15PT–0.15BT, 0.75PZN–0.2PT–0.05BT and 0.7PZN–0.2PT–0.1BT (expressed as A1, B1, A2, B2, A3 and B3) ceramics were prepared by a two-step columbite reaction method, using the reagents of PbO (99.9%), ZnO (99.9%), Nb_2O_5 (99.9%), TiO_2 (99.9%) and BaCO_3 (99.9%) as starting raw materials (Sinopharm Chemical Reagent

Co. Ltd, Shanghai, China). First, ZnO and Nb₂O₅ were ball-milled using zirconia balls for 12 h, and calcined at 1000°C for 6 h. Then the precursor was mixed with PbO, TiO₂ and BaCO₃ in stoichiometric ratio and milled for 12 h. After drying, the mixture was pre-sintered at 900°C for 2 h in a sealed Al₂O₃ crucible. Next, the pre-sintered powders were ball-milled and dried again. The dried powders were well mixed with a 5 wt.% PVA as a binder and pressed into 12 mm in diameter and 1 mm in thickness pellets under a pressure of 150 MPa. The binder was burnt out at 600°C for 2 h in air. Finally, the samples were sintered at temperature range from 1190°C to 1250°C in a sealed Al₂O₃ crucible in case PbO evaporation from the pellets. For electric measurements, electrodes were fabricated on the parallel faces by using Silver paste.

Grinded powders of the sintering ceramics were used to identify the phase structure by means of X-ray diffractometer (XRD, Rigaku D/Max-2400, Tokyo, Japan) using CuK α radiation ($\lambda = 0.15406$ nm) operating at 40 kV and 100 mA. The microstructure of the ceramics samples was observed by using scanning electron microscopy (SEM, FEI Quanta 250 FEG, Hillsboro, OR). The dielectric temperature spectra were measured by a LCR meter (Agilent HP4284A, Santa Clara, CA, USA) with a frequency range from 100 Hz to 1 MHz.

3. Results and Discussion

Room temperature XRD patterns with a scanning angle from 20° to 70° for PZN-PT-BT samples with six

Fig. 1. (a) XRD patterns with a scanning angle from 20° to 70° and (b) enlarged XRD patterns from 40.0° to 50.0° for A1, B1, A2, B2, A3 and B3 ceramics samples.

Fig. 2. SEM images of surfaces of A1, B1, A2, B2, A3 and B3 samples, corresponding to (a)–(f).

Fig. 3. The dielectric constant and loss tangent as functions of temperature measured at 0.1, 1, 10, 100 and 1000 kHz for A1, B1, A2, B2, A3 and B3 ceramics samples, corresponding to (a)–(f). The heating rate is 3°C/min.

compositions are shown in Fig. 1(a). The single-phase diffraction patterns without any anomalous second phase have been observed for all the samples. Figure 1(b) shows the enlarged XRD patterns from 40° to 50° of PZN–PT–BT samples. A distinct peak splitting for the (200) peak, corresponding to a tetragonal symmetry, was detected for A2, B2, A3 and B3 samples. The XRD results suggest that the phase structure of A1 and B1 ceramics could be pseudocubic perovskite structure, whereas the phase structure of A2, B2, A3 and B3 ceramics could be tetragonal perovskite

structure. The above structure information is in accord with the phase diagram of PZN–PT–BT system.¹⁷

Figure 2 reveals the SEM micrographs from the surface of PZN–PT–BT samples. It is found that the sample is fully dense and has clear grain boundary. No significant differences can be found among these six images.

Figure 3 shows the dielectric constant and loss tangent measured at 0.1, 1, 10, 100 and 1000 kHz as functions of temperature from 30°C to 250°C. For A1, B1, A2 and B2 samples, the ceramics exhibit obvious DPT behavior.

Fig. 4. The dielectric constant as a function of temperature measured at 1 kHz for A1, B1, A2, B2, A3 and B3 ceramics samples.

Meanwhile, the dielectric dispersion of the dielectric permittivity and dielectric loss can be seen clearly, which demonstrates typical relaxor behavior. However, for A3 and B3 samples, sharp dielectric peaks, where ferroelectric state transformed towards paraelectric state, have been observed, which demonstrates normal ferroelectric-like behavior. In order to analysis the composition dependence of dielectric properties in PZN-PT-BT system qualitatively, the compositions can be separated into three parts, on the basis of the same content of PT: A1 and B1, A2 and B2, and A3 and B3. The temperature dependence of dielectric constant (at 1 kHz) for all studied compositions is shown in Fig. 4. For three parts of the compositions, as the PT content remains the same, the maximum permittivity ($\epsilon_{\max}$) and $T_{\max}$ values, at which the $\epsilon_{\max}$ was observed, decrease with the increase of BT content. But the effect of BT

compositions on DPT diffuseness (or the width) cannot be characterized distinctly.

To characterize the degree of DPT diffuseness quantitatively, two parameters have been introduced, $W2/3M-L$ and $W2/3M-H$ are defined as the difference between T_m and the temperature, where ϵ_r reaches 2/3 of the $\epsilon_{\max}$ from the low-temperature and high-temperature sides, respectively,¹⁸ as shown in Fig. 5(a). We chose $W2/3M-H$ instead of $W2/3M-L$ to evaluate the degree of diffuseness of DPT peaks, as the Curie-Weiss law only applies to the situation of the dielectric response above T_c .¹⁹ The diffuseness as a function of the compositions derived from $W2/3M-H$ measured at 1 kHz is shown in Fig. 5(a) and Table 1. Relation (1) has been introduced for further comparison of diffuseness by Smolenskii and Rolfe.^{20,21}

$$\frac{\epsilon_m}{\epsilon_r} = 1 + \left(\frac{T - T_m}{\delta_g} \right)^2 \quad (1)$$

where T_m , ϵ_m and δ_g are parameters. The value δ_g can be used to characterize the degree of DPT diffuseness. The results of fitting to the relation (1) are shown in Fig. 5(b) and Table 1. It can be seen that the diffuseness obtained by the above two methods are almost the same, as summarized in Table 1, indicating that the degree of diffuseness enhances with BT content.

The degree of DPT diffuseness may be explained by the assumption about BZN paraelectric nanoregions, which is suspected to be present in the PZN-PT-BT system.^{15,16} According to this assumption, as BT is introduced to PZN-PT, the four components (PZN, PT, BT and BZN) coexist, so that the apparent components (PZN, PT and BT) can be considered as the four-component PZN-PT-BT-BZN. The implicit components (PZN-PT-BT-BZN) can be calculated

Fig. 5. (a) ϵ_r/ϵ_m as a function of $T-T_m$ for PZN-PT-BT ceramics samples at 1 kHz, where $W2/3M-L$ and $W2/3M-H$, are the width of the temperature as the ϵ_r/ϵ_m becomes 2/3 height of the 1 from low-temperature and high-temperature sides, respectively. (b) ϵ_m/ϵ_r as a function of $T-T_m$ for PZN-PT-BT ceramics samples at 1 kHz (dot lines are raw data, solid lines are fitted by relation (1)).

Table 1. DPT width $W2/3M-H$ and δ_g for A1, B1, A2, B2, A3 and B3 ceramics samples.

Compositions	$W2/3M-H$ ($^{\circ}C$)	δ_g ($^{\circ}C$)
A1 (0.75PZN–0.1PT–0.15BT)	51	50
B1 (0.75PZN–0.1PT–0.2BT)	58	57
A2 (0.75PZN–0.15PT–0.1BT)	29	28
B2 (0.7PZN–0.15PT–0.15BT)	40	39
A3 (0.75PZN–0.2PT–0.05BT)	26	26
B3 (0.7PZN–0.2PT–0.1BT)	28	27

Fig. 6. The phase diagram of the implicit PZN–PT–BT–BZN system.

by the assumption that the crystallographically equivalent sites can be occupied randomly by different ions. Figure 6 shows the phase diagram of the implicit PZN–PT–BT–BZN system. In case of B1 sample, the phase diagram is divided into four parts: part 1, part 2, part 3 and part 4 corresponding to PT, BT, PZN and BZN, respectively. The area of each part is proportional to the corresponding implicit components. The implicit components for PZN–PT–BT system can be calculated by this method. The experimental compositions and the corresponding implicit components for all samples are summarized in Table 2. Figure 7 shows the variation of diffuseness temperature δ_g and $W2/3M-H$ as a function of

Table 2. Experimental compositions and the corresponding calculated implicit components for A1, B1, A2, B2, A3 and B3 ceramics samples.

Compositions	Experimental compositions (%)			Implicit components (%)			
	PZN	PT	BT	PZN	PT	BT	BZN
A1	0.75	0.10	0.15	0.6375	0.2125	0.0375	0.1125
B1	0.70	0.10	0.20	0.56	0.24	0.06	0.14
A2	0.75	0.15	0.10	0.675	0.225	0.025	0.075
B2	0.70	0.15	0.15	0.595	0.255	0.045	0.105
A3	0.75	0.20	0.05	0.7125	0.2375	0.0125	0.0375
B3	0.70	0.20	0.10	0.63	0.27	0.03	0.07

Fig. 7. The variation of diffuseness temperature δ_g and $W2/3M-H$ versus BZN component in the implicit PZN–PT–BT–BZN system.

BZN contents in the implicit PZN–PT–BT–BZN system. With the increase of BZN content, the δ_g and $W2/3M-H$ increases correspondingly, indicating that the degree of diffuseness enhances with BZN content. This phenomenon may demonstrate that the assumption about BZN paraelectric nanoregions, presented in PZN–PT–BT system, is reasonable. In addition, with the decrease of BZN content, the $T_{\max}$ becomes much higher, whereas the $T_{\max}$ values of B3 sample are higher than the $T_{\max}$ values of the A3 sample. More implicit BZN content can lead to the effect the T_m proposed by Wang *et al.*¹⁶ and in PZN–PT system, the T_m rises with increasing PT content.¹⁶ This exception may be caused by the fact that B3 sample possesses more implicit PT content.

It can be seen that compositions can affect the degree of diffuseness. A similar situation has also been observed in some Bi-based perovskite relaxor system.^{6–9,22} The change of the relaxor behavior caused by the addition of BT in the PZN–PT–BT ceramics may be explained by the increased cation disorder caused by the substitution of barium onto the A-site and titanium onto the B-site. To our understanding, the ferroelectricity of PZN–PT comes mainly from the ordering of electronic and ionic coupling between A-site and O-site (A–O coupling), whereas that of BT mainly comes from the B–O coupling.²³ As BT is introduced to PZN–PT, the A–O ordering may be disrupted by barium occupying A-site, leading to decreased T_m . The substitution of these cations creates the polar region of nanometer scale with randomly distributed directions of dipoles, leading to the diffuseness of DPT peaks.

4. Conclusions

In this work, perovskite solid solution of PZN–PT–BT with several compositions were studied. The dielectric properties vary significantly with compositions. Implicit BZN composition could broaden the diffuseness of DPT peaks and lower the $\varepsilon_{\max}$ and $T_{\max}$ values, which can be explained by

the increased cation disorder on the crystallographically equivalent sites.

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