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Phase structure and electrical properties of $(0.8-x)$ $BaTiO_3$–$0.2Bi_{0.5}Na_{0.5}TiO_3$–$x$$BaZrO_3$ lead-free piezoceramics

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ABSTRACT

Lead-free piezoelectric ceramics $(0.8-x)BaTiO_3$–$0.2Bi_{0.5}Na_{0.5}TiO_3$–$xBaZrO_3$ (BT–BNT–xBZ, $0 \leq x \leq 0.08$) doped with 0.3 wt% Li_2CO_3 were prepared by conventional solid-state reaction method. With the Li_2CO_3 doping, all the ceramics can be well sintered at 1170–1210 °C. The phase structure, dielectric, ferroelectric and piezoelectric properties of the ceramics were investigated. Results show that a morphotropic phase boundary (MPB) between tetragonal and pseudocubic phases exists at $x = 0.03$–0.04. The addition of Zr can improve the piezoelectric properties of BT–BNT ceramics. Furthermore, a relaxor behavior is induced and the tetragonal–cubic phase transition shifts towards lower temperatures after the addition of Zr. The ceramics with $x = 0.03$ possess the optimum electrical properties: $d_{33} = 72$ pC/N, $k_p = 15.4\%$, $\varepsilon_r = 661$, $P_r = 18.5\ \mu C/cm^2$, $E_c = 34.1$ kV/cm, $T_c = 150\ °C$.

1. Introduction

$BaTiO_3$ (BT) is a well known lead-free ferroelectric material with perovskite structure, which possesses good piezoelectric and dielectric properties. However, BT has a relatively low Curie temperature ($T_c \sim 120\ °C$), along with the orthorhombic–tetragonal (O–T) phase transition at about 5 °C, leading to poor temperature stability of the electrical properties [1]. For use of BT based lead-free piezoelectric ceramics, it is necessary to increase the T_c and shift the O–T phase transition away from the application temperature range.

$Bi_{0.5}Na_{0.5}TiO_3$ (BNT) is a perovskite ferroelectric ceramics which has a high T_c of 320 °C [2]. It was reported that the introduction of BNT could increase the T_c of the BT ceramics [3,4]. Furthermore, the phase transition at about 5 °C shifted to lower temperatures and gradually disappeared with increasing amount of BNT. In particular, a relatively high T_c of 146 °C and stable dielectric properties were obtained for the 0.8BT–0.2BNT ceramics [5]. However, the piezoelectric and ferroelectric properties of the 0.8BT–0.2BNT ceramics are still low ($d_{33} = 56$ pC/N, $P_r = 6.8\ \mu C/cm^2$) [5,6].

Yu et al. reported that Zr-doped BT ceramics show promising piezoelectric properties. A high d_{33} (236 pC/N) and a large remanent polarization ($P_r = 13.3\ \mu C/cm^2$) were obtained for the $Ba(Zr_{0.05}Ti_{0.95})O_3$ ceramics [7]. The main purpose of this work is to investigate the effect of Zr content on the phase structure and electrical properties of the $(0.8-x)BaTiO_3$–$0.2Bi_{0.5}Na_{0.5}TiO_3$–$xBaZrO_3$ (abbreviated as BT–BNT–xBZ) ceramics. A small amount (~0.3 wt%) of Li_2CO_3 was added in order to decrease the sintering temperature of the BT–BNT–xBZ ceramics, because the low melting point of Li compounds can promote the formation of a transitory liquid phase during sintering [8,9].

2. Experimental

A conventional ceramic fabrication technique was used to prepare Li_2CO_3 (0.3 wt%) doped BT–BNT–xBZ ($0 \leq x \leq 0.08$) ceramics. The oxide or carbonate powders of Bi_2O_3 (99%), TiO_2 (98%), $BaCO_3$ (99%), Na_2CO_3 (99.8%), Li_2CO_3 (97%) and ZrO_2 (99%) were selected as starting materials. The powders in stoichiometric ratio of the compositions were mixed in ethanol with agate balls by ball milling for 8 h. The dried powders were calcined at 900–1000 °C for 2–4 h in air. The synthesized powders were again ball milled, granulated, and pressed into discs by dry pressuring with diameter of 10 mm and thickness of 1 mm. The compacted disks were sintered in air between 1170 and 1210 °C for 2 h. Silver slurry was coated on both sides of the discs and then treated at 700 °C for 10 min as electrodes. The specimens were poled in silicone oil at room temperature under 4 kV/mm for 30 min.

X-ray diffraction (XRD) patterns of the ceramics was performed using Cu Kα radiation in the θ–2θ scan mode (X' Pert PRO). The microstructures were observed using scanning electron microscopy (SEM, S440). The remanent polarization (P_r) and coercive field (E_c) were determined from polarization versus electric field (P–E) hysteresis loops measured by a Radiant Precision Workstation (USA). The dielectric constant (ε_r) and dielectric loss (tan δ) of the samples were measured using an impedance analyzer (HP 4278A). The electromechanical coupling factor k_p was measured using an impedance analyzer (HP 4294A). The piezoelectric constant was measured using a piezo-d_{33} meter (ZJ-3A). The bulk densities of the sintered samples were measured by Archimedes' method.

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3. Results and discussion

For the BT–BNT–*x*BZ ceramics without Li_2CO_3 doping, the sintering temperature is about 1270–1320 °C. It was found that all of the samples had low densities and were difficult to be polarized due to the large leakage current. After the doping of 0.3 wt% Li_2CO_3, all the ceramics can be well sintered at relatively lower temperatures (1170–1210 °C). The sintering temperature of the ceramics increases with increasing *x*. Fig. 1 shows the SEM images of BT–BNT–*x*BZ ceramics doped with 0.3 wt% Li_2CO_3. It can be observed in Fig. 1 that the grain boundary is clear and almost no visible pores are found in both samples. The grain size is about 2–3 and 3–5 μm for the ceramics with $x = 0$ and $x = 0.03$, respectively. When $x \leq 0.04$, the samples have high bulk density around 5.56–5.70 g/cm^3, which are 93.2%–95.1% of the theoretical values. However, the bulk density decreases to 5.34 g/cm^3 at $x = 0.08$, which may be due to the volatilization of Bi and Na at higher sintering temperature (~1210 °C).

Fig. 2 shows the XRD patterns of the BT–BNT–*x*BZ ceramics as a function of *x*. The BT–BNT–*x*BZ ceramics possess a pure perovskite phase when $x \leq 0.05$, indicating that Zr^{4+} has diffused into the BT–BNT lattices to form a solid solution. In addition to the perovskite phase, trace of secondary phase is found in the sample with $x = 0.08$, which can be assigned to $BaZrO_3$ (PDF# 06-0399). It can be observed in Fig. 2 that the ceramics with $x \leq 0.03$ possess a tetragonal phase, which is characterized by a (0 0 2)/(2 0 0) peak splitting at about 46° (Fig. 2(b)). When $x \geq 0.05$, the two diffraction peaks (0 0 2) and (2 0 0) have merged into a single peak of (2 0 0). It is found that the lattice anisotropy *c*/*a* of the 0.8BT–0.2BNT ceramics is about 1.0145. The tetragonality of the BT–BNT–*x*BZ ceramics decreases with increasing *x*. When $x = 0.05$, the lattice anisotropy decreases to about 1.0017. It seems that the crystal structures of the samples with $x \geq 0.05$ transform to pseudocubic symmetry. A MPB between tetragonal and pseudocubic phases may exist at $x = 0.03$–0.04. This is similar to the results in our previous report for $(1 - x)$BNBT12–*x*ALN10 ceramics [10].

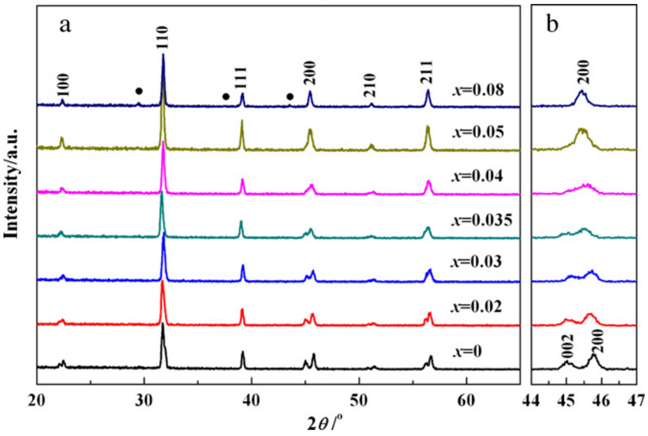

Fig. 2. XRD patterns of BT–BNT–*x*BZ ceramics in the 2θ range: (a) 20–70° and (b) 44–47°.

Fig. 3(a) shows the *P*–*E* hysteresis loops of the BT–BNT–*x*BZ ceramics, while the variations of E_c and P_r as a function of *x* are shown in Fig. 3(b). Normal *P*–*E* hysteresis loops are observed when $x \leq 0.05$. For the sample with $x = 0.08$, the loop becomes slim. As shown in the Fig. 3(b), the E_c decreases significantly from 43.7 to 12.5 kV/cm as *x* increases from 0 to 0.08. The P_r increases slightly

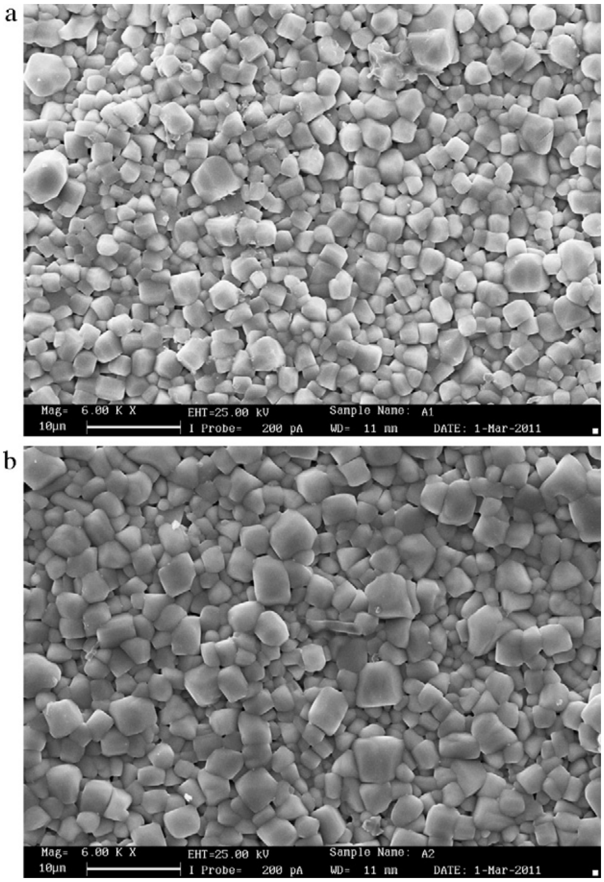

Fig. 1. SEM micrographs of BT–BNT–*x*BZ ceramics with (a) $x = 0$, sintered at 1170 °C for 2 h, and (b) $x = 0.03$, sintered at 1190 °C for 2 h.

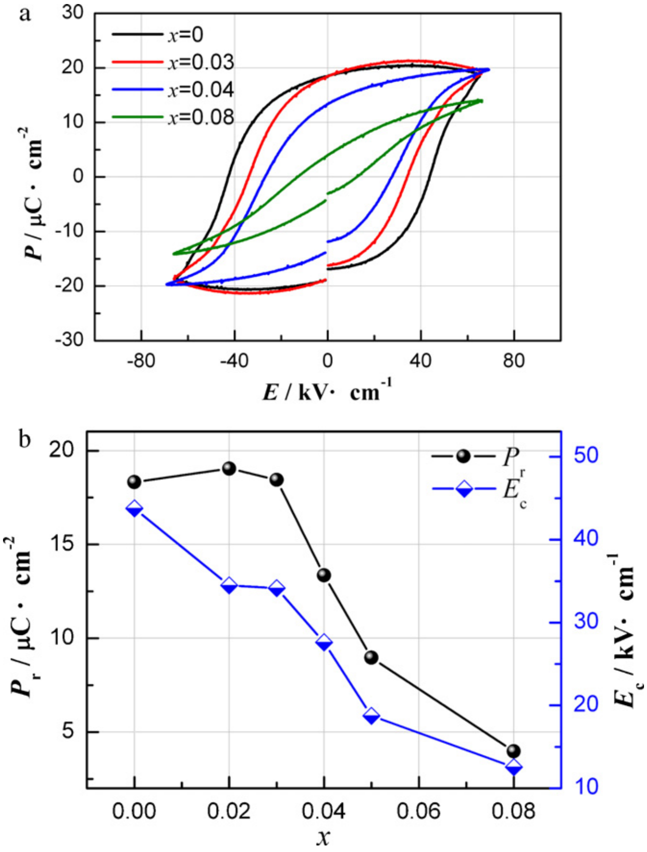

Fig. 3. (a) *P*–*E* hysteresis loops of the BT–BNT–*x*BZ ceramics with $x = 0$, 0.03, 0.04, and 0.08; (b) the variation of P_r and E_c of the samples as a function of *x*.

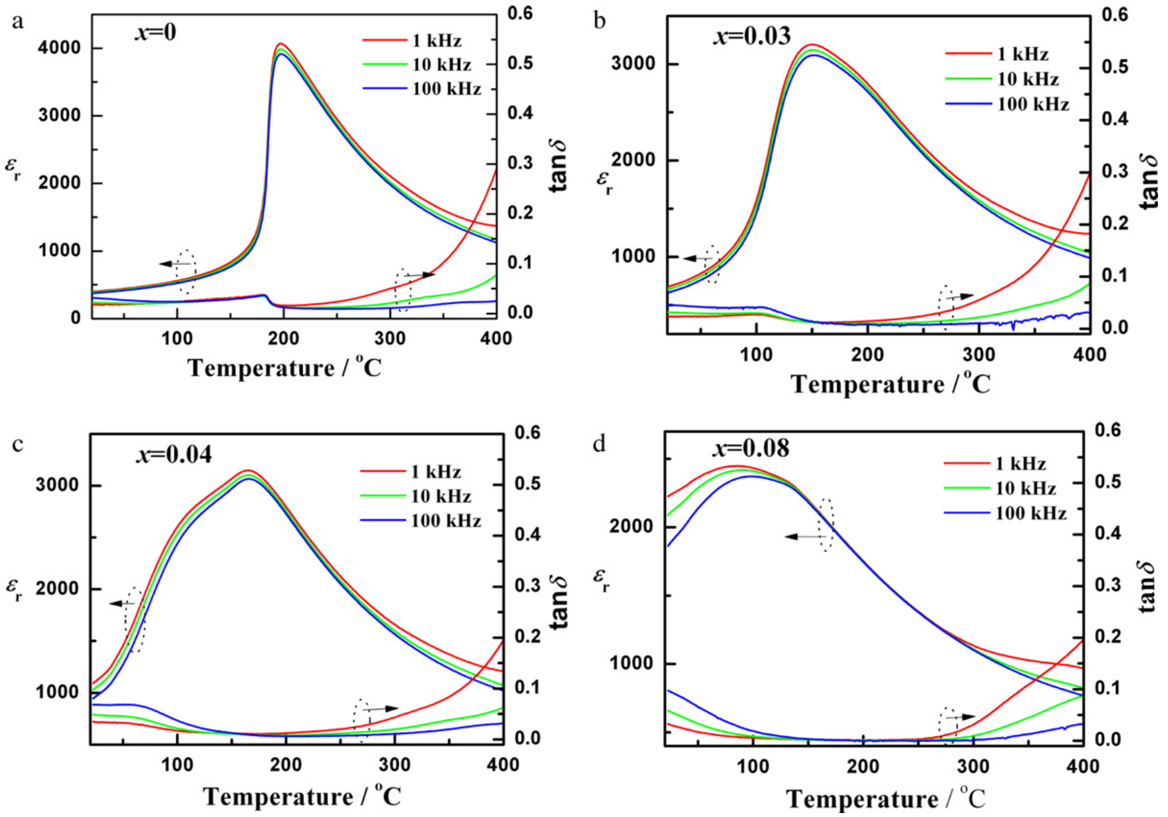

Fig. 4. Temperature dependence of ε_r and tan δ of poled BT–BNT–*x*BZ ceramics at different frequencies ranging from 1 to 100 kHz: (a) $x = 0$; (b) $x = 0.03$; (c) $x = 0.04$; (d) $x = 0.08$.

when $x \leq 0.03$, and then decreases linearly with further increasing *x*. The P_r and E_c of the ceramics with $x = 0.08$ are 3.97 μC/cm^2 and 12.5 kV/cm, respectively. On the other hand, these results also confirm that the crystal structures of the samples with $x \geq 0.05$ are not true cubic symmetry but a pseudocubic structure because pervoskite material with cubic symmetry has no spontaneous polarization.

The piezoelectric and dielectric properties of BT–BNT–*x*BZ ceramics are listed in Table 1. When $x = 0$, the piezoelectric constant is 56 pC/N. This result is in agreement with the previous work by Huang et al. [5]. With increasing *x*, the d_{33} and k_p reach the maximum values of 72 pC/N and 16.1% at $x = 0.03$ and 0.04, respectively. When $x = 0.08$, the d_{33} decreases to only about 14 pC/N. The dielectric constant ε_r increases from 388 to 2224 as *x* increases from 0 to 0.08. These results indicate that the piezoelectric properties of the 0.8BT–0.2BNT ceramics can be improved by the addition of a proper amount of Zr. In general, piezoelectric ceramics with higher remnant polarization P_r and lower coercive field E_c possess higher piezoelectric properties. Because higher P_r indicates higher oriented degree of ferroelectric domain, and lower E_c can facilitate the domain movement. The improvement of piezoelectric properties of the BT–BNT–*x*BZ ceramics can mainly be attributed to the decrease of E_c. Although the sample with $x = 0.08$ has the lowest E_c (~12.5 kV/cm), the P_r is so small (~3.97 μC/cm^2) that the piezoelectricity is very weak ($d_{33} \sim 14$ pC/N). Furthermore, for the compositions ($x = 0.03$–0.04) near the MPB, it is thought that the improved symmetry can reduce the internal stress of domain reorientation and make the domain transition more easily in poling process, which can also increase the piezoelectric properties [11].

Fig. 4(a)–(d) shows the temperature dependence of ε_r and tan δ of poled BT–BNT–*x*BZ ceramics with $x = 0$, 0.03, 0.04 and 0.08, respectively, at different frequencies ranging from 1 to 100 kHz. A relatively sharp peak is observed at 200 °C when $x = 0$, which corresponds to the cubic–tetragonal phase transition temperature (T_c). This is consistent with the results reported by Suchanicz et al. [3]. After the addition of BZ, the relaxor-like behavior becomes more obvious. The T_c shifts towards lower temperatures with increasing *x*. At $x = 0.03$, the T_c decreases to 150 °C. However, the T_c of the sample with $x = 0.08$ cannot be determined accurately due to the broadening phase transition peak. The temperature (T_m) at which ε_r reaches the maximum value decreases to about 75 °C.

The diffuseness of phase transition of BT–BNT–*x*BZ ceramics were determined by a modified Curie–Weiss law, $1/\varepsilon_r - 1/\varepsilon_m = C^{-1}(T - T_m)^\gamma$ [12], where ε_m is the maximum value

Table 1
Piezoelectric and dielectric properties of BT–BNT–*x*BZ ceramics.

BBNTZ*x*	$x = 0$	$x = 0.02$	$x = 0.03$	$x = 0.04$	$x = 0.05$	$x = 0.08$
d_{33} (pC/N)	56	64	72	71	60	14
k_p (%)	14.8	15.2	15.4	16.1	14.2	–
ε_r (1 kHz)	388	533	661	1020	1279	2224
tanδ (1 kHz)	0.048	0.062	0.066	0.049	0.071	0.054
P_r (μC/cm^2)	18.3	19.0	18.5	13.3	8.90	3.90
E_c (kV/cm)	43.7	34.5	34.1	27.6	18.7	12.5

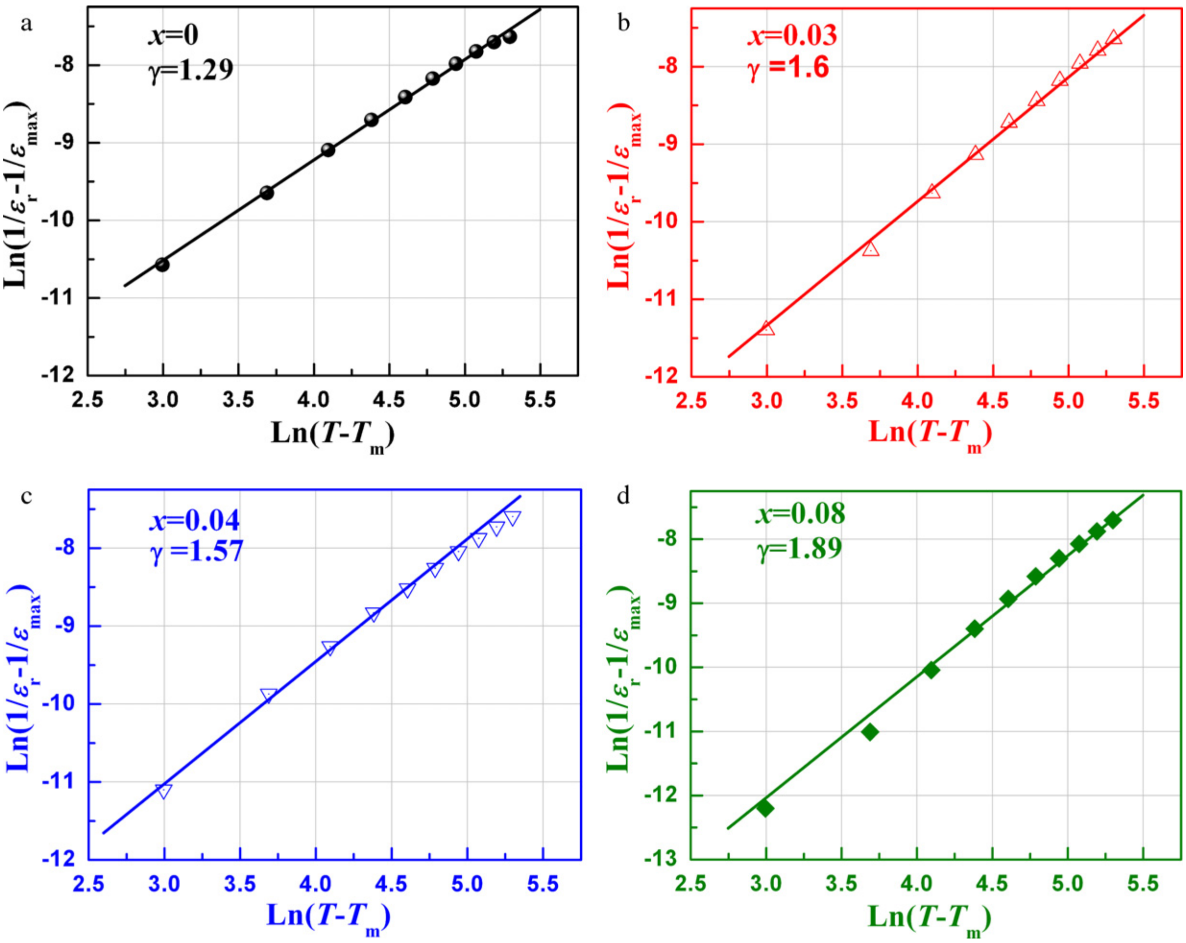

Fig. 5. Plots of $\ln(1/\varepsilon_r - 1/\varepsilon_m)$ vs $\ln(T - T_m)$ of BT–BNT–xBZ ceramics at 10 kHz.

of ε_r at the phase transition temperature T_m, γ is the degree of diffuseness, and C is the Curie-like constant. γ can have a value ranging from 1 for a normal ferroelectric to 2 for an ideal relaxor ferroelectric. Fig. 5(a)–(d) shows the plots of $\ln(1/\varepsilon_r - 1/\varepsilon_m)$ vs $\ln(T - T_m)$ for the samples with $x = 0$, 0.03, 0.04, 0.08, respectively. All the samples exhibit a linear relationship. It is known that BT is a normal ferroelectric with a γ value of 1.06 [13]. It can be observed in Fig. 5(a) that the γ of the sample with $x = 0$ is 1.29, indicating that the degree of diffuseness of the phase transition increases when incorporating 20 mol% of BNT into BT. It is also found that the γ of the ceramics increases with increasing x. When $x = 0.08$, the γ of the sample increases to 1.89. This result indicates that the ceramics transform to a relaxor ferroelectric, implying a composition-induced diffuse transition. Generally, relaxor behavior in a mixed-oxide system is caused by randomly distributed electrical field or strain field [14,15]. In perovskite-type compounds, the relaxor behavior appears when at least two cations occupy the same crystallographic site A or B. This phenomenon has been observed in the BNT and $Pb(Mg_{1/3}Nb_{2/3})O_3$–$PbTiO_3$ system. For the BT–BNT–xBZ ceramics, it is thought that Zr^{4+} in B-site behaves as a destabilizer against normal ferroelectrics and induces paraelectric behavior due to its larger ionic diameter (0.79 Å) and lower polarization [13]. Thus, the relaxor behavior occurs with the incorporation of Zr into BT–BNT. For the ceramics with high concentration of Zr (e.g. $x = 0.08$), the sample possesses the pseudocubic phase and shows a strong dielectric relaxation, which may be attributed to the coexistence of ferroelectric domains and nonpiezoactive (paraelectric) regions around T_m [16].

4. Conclusions

The BT–BNT–xBZ ($0 \le x \le 0.08$) ceramics doped with 0.3 wt% Li_2CO_3 were prepared by conventional solid-state reaction method. With the Li_2CO_3 doping, all the ceramics can be well sintered at 1170–1210 °C and exhibit a dense microstructure. A MPB between tetragonal and pseudocubic phases exists at $x = 0.03$–0.04. Furthermore, a relaxor behavior is induced after the addition of Zr. When $x = 0.08$, the γ of the sample is about 1.89. The temperature dependence of dielectric properties shows that T_c shifts towards lower temperatures with increasing x. Near the MPB, the ceramics with $x = 0.03$ show the optimum electrical properties: $d_{33} = 72$ pC/N, $k_p = 15.4\%$, $P_r = 18.5\ \mu C/cm^2$, $E_c = 34.1$ kV/cm, $\varepsilon_r = 661$ and $T_c = 150$ °C.

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