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Ceramics International 39 (2013) 6707–6712

CERAMICS INTERNATIONAL

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$Bi(Zn_{1/2}Ti_{1/2})O_3$ modified $BiFeO_3$–$BaTiO_3$ lead-free piezoelectric ceramics with high temperature stability

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Received 1 January 2013; received in revised form 29 January 2013; accepted 30 January 2013
Available online 8 February 2013

Abstract

Lead-free high-temperature ceramics with compositions of $0.71BiFe_{1-x}(Zn_{1/2}Ti_{1/2})_xO_3$–$0.29BaTiO_3$ (BFZTx–BT, $x=0$–0.05 mol fraction) were fabricated by a conventional solid state reaction method. The effect of $Bi(Zn_{1/2}Ti_{1/2})O_3$ (BZT) addition on the microstructure, electrical properties, relaxor behavior, and temperature stability has been studied. XRD patterns revealed that all compositions formed a single perovskite phase of pseudo-cubic crystal structure. The grain size was slightly affected by BZT addition. The diffuse phase transition and strong frequency dispersion of dielectric permittivity are observed for BZT modified ceramics. The addition of BZT into BFZTx–BT was also found to affect the piezoelectric properties and temperature stability of the ceramics with maximum values observed for $x=0.5\%$ and 1% BFZTx–BT compositions, respectively. The optimum piezoelectric properties with $d_{33}=163$ pC/N, together with high-temperature stability with a depolarization temperature $T_d \sim 380$ °C, reveal the BFZTx–BT ceramics to be promising high-temperature Pb-free piezoelectric materials.

Keywords: C. Electrical properties; Lead-free piezoelectric ceramic; Temperature stability; Electroceramics

1. Introduction

It is well known that lead zirconate titanate (PZT) ceramics have been widely used because of the excellent properties in morphotropic phase boundary (MPB) where rhombohedral and tetragonal phases coexist [1]. Nevertheless, the use of lead based ceramics not only brings serious environmental problems but also makes the composition percentage wrong because the high sintering temperature evaporated the lead oxide. Most importantly, the undoped PZT ceramics have a T_c of only 386 °C which limits their applications in high temperature sensors such as space exploration and electric aircraft [1–6]. Therefore, seeking an environment friendly, high Curie temperature and high performance piezoelectric ceramic has been becoming more and more important.

Recently, the research for high temperature ceramics has focused on the $BiMeO_3$–$BaTiO_3$ binary system due to high Curie temperature at MPB [7–14]. In these systems, Me represents a generic, suitably sized cation with a valence 3+ or a mixture of cations with an average valence of 3+ (Sc, Fe, $Mg_{1/2}Ti_{1/2}$, $Ni_{1/2}Ti_{1/2}$, etc.). Among the available compositions of $BiMeO_3$–$BaTiO_3$, $(1-x)BiFeO_3$–$xBaTiO_3$ is one of the most promising applications for high temperature due to the high T_c (619 °C at $x=0.25$), reasonable piezoelectric property (e.g., $d_{33}=116$ pC/N) and low cost [15]. Therefore, the $BiFeO_3$–$BaTiO_3$ system has been widely studied. Lee et al. [16] found that the piezoelectric constant (d_{33}) and planar electromechanical coupling factor (k_p) of the $0.75BiFeO_3$–$0.25BaTiO_3$ ceramic sintered at 980 °C were 134 pC/N and 0.322, respectively. In our previous study, $(1-x)BiFeO_3$–$xBaTiO_3$ ceramic exhibited optimal electrical properties $d_{33}=136$ pC/N, $k_p=0.312$, $T_c=485$–434 °C, and $T_d=420$–320 °C at the MPB composition $x=0.275$–0.30 [17]. Recently, Yang et al. [18] reported that Mn- and Cu-modified $(1-x)BiFeO_3$–$xBaTiO_3$ ($x=0.29$) ceramic simultaneously exhibited improved electrical properties of $d_{33}=170$ pC/N, $k_p=0.342$, and temperature stability with $T_c=485$ °C and $T_d=480$ °C. In addition,

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http://dx.doi.org/10.1016/j.ceramint.2013.01.110

the B-site complex Bi-based ferroelectrics of $Bi(Mg_{1/2}Ti_{1/2})O_3$ and $Bi(Ni_{1/2}Ti_{1/2})O_3$ modified $(1-x)BiFeO_3$–$xBaTiO_3$ ceramics were studied systematically by Zhou and Fujii [19–21].

Although the ferroelectric and piezoelectric properties of many $BiMeO_3$–$BaTiO_3$ materials have been reported at room temperature, only select piezoelectric properties of a few systems have been demonstrated at high temperature. In addition, $Bi(Zn_{1/2}Ti_{1/2})O_3$ (BZT) is another important Bi based perovskite structure compound which has the largest calculated ionic polarization of over 150 μC/cm^2 [22]. It is tetragonal and has the highest c/a ratio of 1.211. It has been reported that the addition of BZT can obviously improve the properties of $PbZrO_3$, $BaTiO_3$, and BNT–BKT ceramics [23–25].

In this contribution, therefore, the structure, electrical properties and temperature stability of $Bi(Zn_{1/2}Ti_{1/2})O_3$ modified $BiFeO_3$–$BaTiO_3$ are evaluated and discussed in detail.

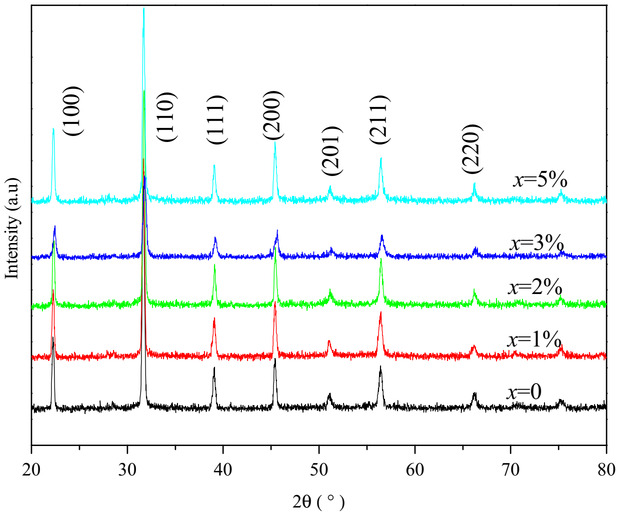

Fig. 1. Room temperature XRD patterns of BFZTx–BT ceramics.

2. Experimental procedure

$0.71BiFe_{(1-x)}(Zn_{1/2}Ti_{1/2})_xO_3$–$0.29BaTiO_3$ (BFZTx–BT)+ 0.6 wt% MnO_2 (used as a donor to reduce oxygen vacancies formed during calcination and sintering) ceramic samples were made by the conventional solid-state sintering method. The fully dry materials Bi_2O_3 (99.9%), TiO_2 (99.9%), ZnO (99.9%), Fe_2O_3 (99.9%), and $BaCO_3$ (99.8%) were weighted and ball-milled together with ethyl alcohol for 24 h. The compounds were dried and calcined at 850 °C for 4 h and then mixed with 5% PVA. The powders were pressed into disks with a pressure of 100 MPa. Then they were sintered at 990 °C for 2 h. Silver paste was screen-printed on the surfaces as electrodes and then fired at 600 °C for 10 min. X-ray diffraction (XRD, D8-2-Advanced, Bruker AXS, Germany) was used to detect the phase transformation in the range of 20–80°. Scanning electron microscopy (SEM, JSM-5610LV, JEOL, Japan) was used to examine the surface microstructure. An impedance analyzer (Agilent 4294A, Agilent Technologies, America) was used to measure k_p, the capacitance and the loss ($Cp-D$). A Berlincourt d_{33} meter (ZJ-3A, China) was used to measure the direct piezoelectric coefficient (d_{33}). Room-temperature polarization versus electric field (P–E) hysteresis loops were measured by a ferroelectric tester (Radiant Precision Workstation, America).

3. Results and discussions

The XRD patterns of the BFZTx–BT piezoelectric ceramics are shown in Fig. 1. The doping of BZT did not change the crystal structure of the ceramics and all the samples show pseudo-cubic structure. As some articles reported, the BF–BT system with BT content <33 mol% is expected to have rhombohedral distorted perovskite structure [15]. But for the present samples, pseudo-cubic was the only pattern which could be seen in the XRD. Previous work reported the crystalline structure, ferroelectric loop and the dielectric anomaly around Curie temperature of $0.65BiFeO_3$–$0.35BaTiO_3$ ceramics, and found the ceramics have pseudo-cubic symmetry and high Curie temperature [26]. Therefore, small rhombohedral phase distortion, or the coexistence of rhombohedral and cubic phases should be the reason for the XRD patterns of the BFZTx–BT piezoelectric ceramics.

The surface microstructure of BFZTx–BT ceramics sintered at 990 °C for 2 h are shown in Fig. 2. The grain size tends to increase slightly up to 3% BZT addition with the average grain size about 8.0 μm. However, the grain size decreases evidently with further doping of BZT. When the doping amount was raised to 5%, the grain size decreased to ~3 μm. Therefore, a small amount of BZT doping increased the grain size of the BF–BT system, but further doping of BZT may stockpile in the grain boundary and suppress the growth of grain size.

Fig. 3 shows the temperature dependence of dielectric constant ε_r of BFZTx–BT ceramics at frequencies of 1 kHz, 10 kHz and 100 kHz. As seen in figure, with the increasing amount of doping BZT, Curie temperature (T_c) shifts slightly to a lower temperature for $x \leq 3\%$ compositions. When x exceeds 3%, Curie temperature begins to decrease obviously, which is indicated in Fig. 3. At the same time, with the increasing amount of BZT, the dielectric constant ε_m of BFZTx–BT ceramics at Curie temperature decreases. As shown in Fig. 3, relaxor characteristics are clearly evident in the temperature dependence of dielectric permittivity at different frequencies. A pronounced broadening of the dielectric response, indicating the features of diffuse phase transition, occurs, and the diffuse phase transition characteristics are more obvious with the increasing BZT content. The main relaxor characteristics, $\Delta T_m = T_m(100\ kHz) - T_m(1\ kHz)$, are presented in Fig. 4. It can be seen that the main relaxor characteristics increase evidently with x. It is commonly

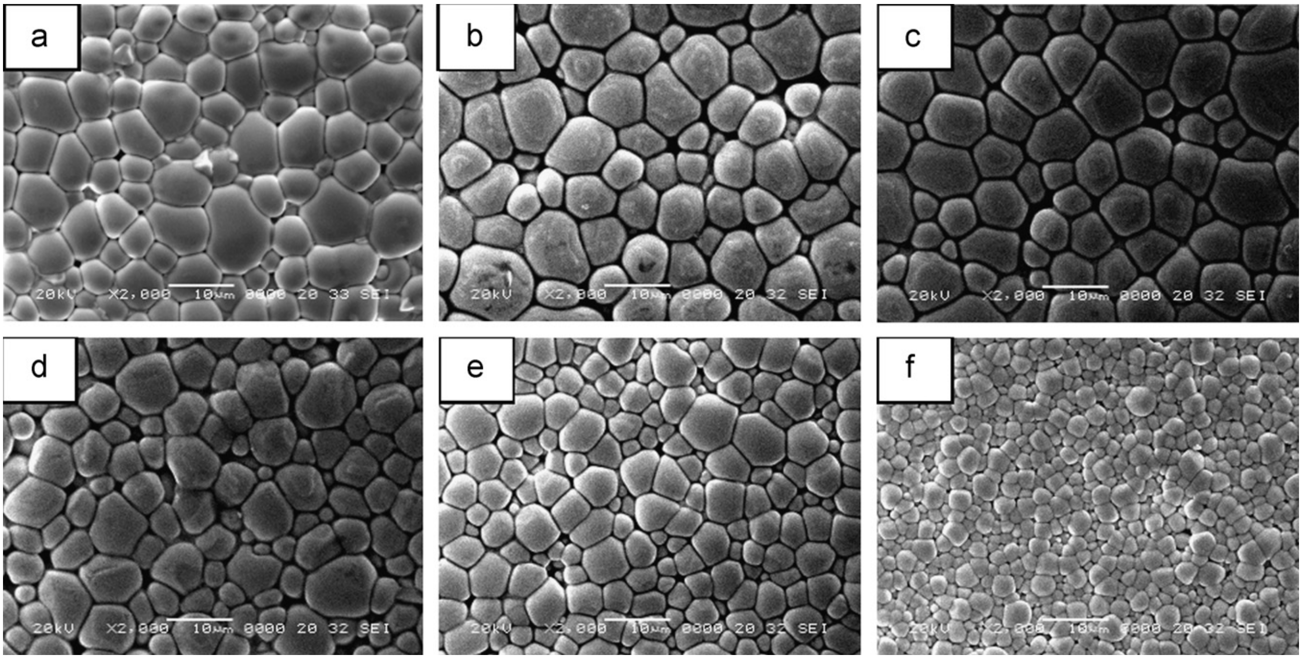

Fig. 2. SEM images of BFZTx–BT ceramics: (a) $x=0$, (b) $x=0.5\%$, (c) $x=1\%$, (d) $x=2\%$, (e) $x=3\%$, and (f) $x=5\%$.

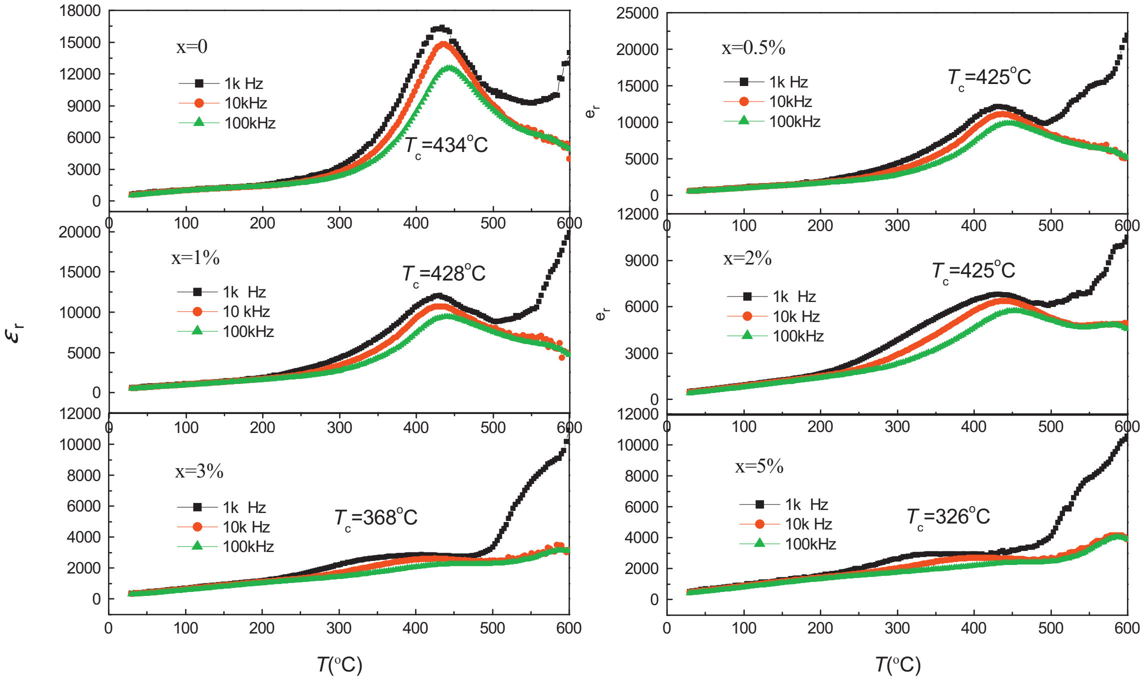

Fig. 3. Temperature dependence of dielectric constant ε_r of BFZTx–BT ceramics at frequencies of 1 kHz, 10 kHz and 100 kHz.

known that the dielectric behavior of relaxor ferroelectrics is generally explained in the literature in terms of small regions of local spontaneous polarization (so called polar-regions) with a nanometer scale size [27,28]. Origin of the polar-regions is caused by the structural disorder. For BZT modified BFZTx–BT ceramics with the perovskite structure (ABO_3), the B-site ionic radii of $(Zn_{1/2}Ti_{1/2})^{3+}$ (0.673 nm, 6CN) is close to that of Fe^{3+} (0.645 nm, 6CN) and Ti^{4+} (0.605 nm, 6CN) [29]. Therefore, $(Zn_{1/2}Ti_{1/2})^{3+}$ ions would enter B-site and substitute Fe^{3+} or Ti^{4+} ions. Thus, more different ions in B-site with a fluctuating composition could lead to a local disorder at B-site and disruption of long-range order, which could be a possible explanation for the more significant relaxor characteristics in the high level doping of BZT ceramics. Furthermore, another small dielectric anomaly for $x \geq 2\%$

samples is apparent at ~580 °C, of the origin which at this stage is still unknown.

Fig. 5 shows the piezoelectric coefficient d_{33} and planar mode electromechanical coupling coefficient k_p of the BFZTx–BT ceramics as a function of composition x. It can be seen from Fig. 5, with the increasing amount of BZT, the piezoelectric constant d_{33} increases slowly up to a maximum value 163 pC/N at $x=1\%$. The planar coupling factor k_p increases from 0.298 to a maximum value 0.321 with x increasing from 0% to 0.5%, then decreasing sharply with further increase of BZT. The piezoelectric properties of BFZTx–BT ceramics were superior to those of $(1-x)$BiFeO$_3$–xBaTiO$_3$ ceramics reported by Lee and Leontsev [15,16], and Bi(Mg$_{1/2}$Ti$_{1/2}$)O$_3$, Bi(Ni$_{1/2}$Ti$_{1/2}$)O$_3$ modified $(1-x)$BiFeO$_3$–xBaTiO$_3$ ceramics reported by Zhou and Fujii et al. [19–21]. It is reported that the piezoelectric properties in ferroelectric polycrystalline materials are caused not only by the intrinsic effect in connection with the change of the polarization magnitude, but also by the extrinsic contribution [30,31]. The extrinsic contribution is dominated by densification/porosity, the secondary phases, grain size and defects. The low doping of BZT can promote slightly the grain growth of the ceramics, which facilitates the domain movement and thus causes the improvement of piezoelectric properties. In contrast, fine-grained ceramics with high doping level of BZT will limit the domain variants and lower the polarization and piezoelectric response. On the other hand, the intrinsic effect originates from the ionic displacement and polarization. In Pb-based and Bi-based perovskite solid solutions, the B-cation displacement and ferroelectric activity of Mg, In, Sc, W, Zr, Fe, Nb, Zn, and Ti ions were reported [32]. The results indicated that the B-cation displacement and ferroelectric activity of Zn and Ti ions are larger than those of Fe ions. The results may also be applied to BFZTx–BT ceramics as they have a perovskite-type structure similar to that of the BFZTx–BT system. The substitution of (Zn$_{1/2}$Ti$_{1/2}$)$^{3+}$ ions for Fe^{3+} ions would cause the increase of ferroelectric activity and polarization, and thus the improvement of piezoelectric properties for BFZTx–BT ceramics. The increase of ferroelectric activity and polarization of BFZTx–BT ceramics is shown in Fig. 6(a), which indicates the P–E hysteresis loops measured under the electric field of 5 kV/mm, and

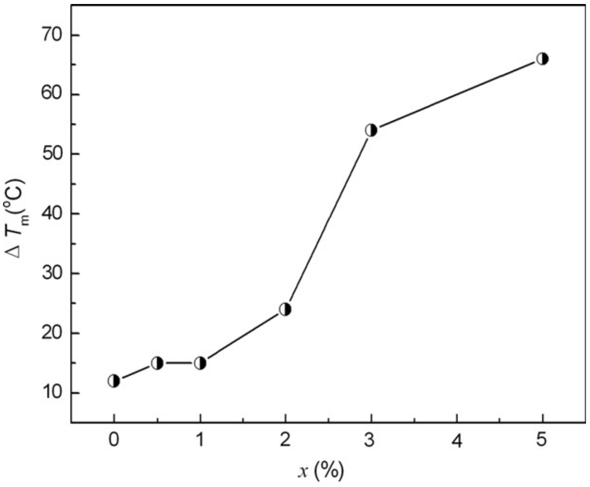

Fig. 4. Main relaxor characteristics, $\Delta T_m = T_m$ (100 kHz) − T_m (1 kHz) as a function of BZT content x.

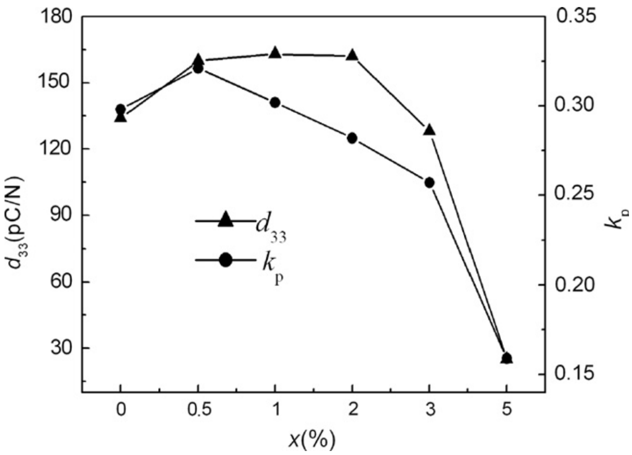

Fig. 5. Piezoelectric constant d_{33} and planar electromechanical coefficient k_p of BFZTx–BT ceramics.

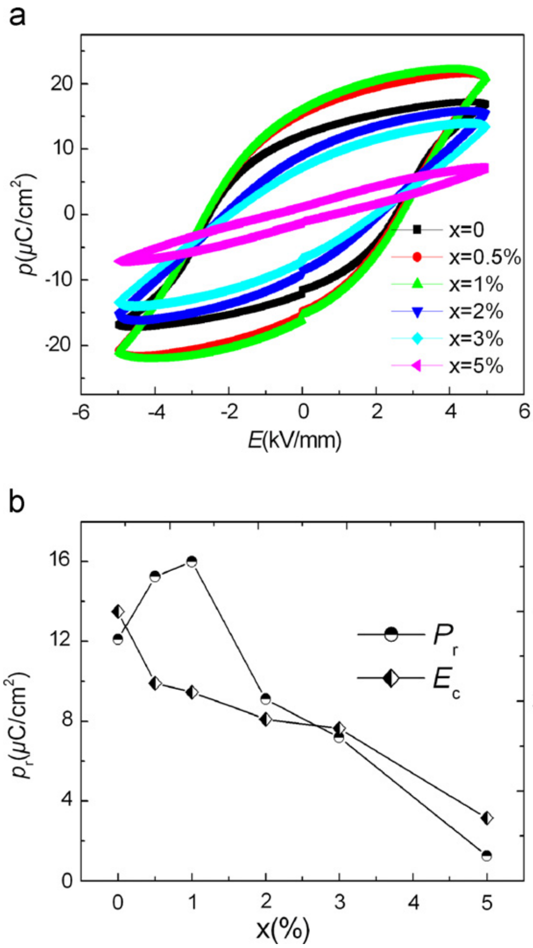

Fig. 6. P–E hysteresis loops, remnant polarization P_r and coercive field E_c for BFZTx–BT ceramics: (a) P–E hysteresis loops, (b) P_r and E_c.

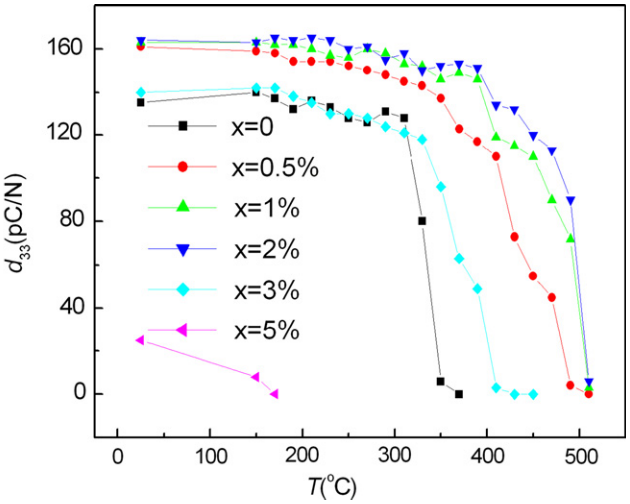

Fig. 7. Temperature of piezoelectric constant d_{33} of poled BFZTx–BT ceramics measured *ex-situ*.

Fig. 5(b) shows the change of the remnant polarization P_r and coercive field E_c of BFZTx–BT ceramics. With the doping of BZT, the remnant polarization first increased from 12.4 μc/cm^2 to 16.2 μc/cm^2 with x from 0 to 1%, and then reduced rapidly with further increasing of x. The coercive field E_c was continuing to drop with the increase of x.

The depolarization temperature is very important and plays an important role in device applications. Temperature dependence of d_{33} of BFZTx–BT ceramics as a function of BZT content is shown in Fig. 7. All samples were measured at room temperature after they were short-circuited and annealed at various temperatures for 1 h. The piezoelectric constant slightly decreases up to a critical temperature and then drops dramatically. In general, the critical temperature is called depolarization temperature (T_d). It is observed that, as the BZT content increases, T_d first increases and then reach a maximum value of ~380 °C at $x=1\%$ and 2%, and in the it end decreases with further increase of x. The high depolarization temperature of BFZTx–BT ceramics indicates that the BFZTx–BT system is very suitable for high temperature applications.

4. Conclusions

Bi(Zn$_{1/2}$Ti$_{1/2}$)O$_3$ modified BiFeO$_3$–BaTiO$_3$ (BFZTx–BT) lead-free piezoelectric ceramics were successfully synthesized by the conventional solid-state sintering method. Their crystal structure, microstructure, relaxor characteristics, piezoelectric properties, and depolarization temperature (T_d) have been studied systematically. X-ray diffraction patterns show that the addition of BZT did not change the crystal structure of the ceramics and all the ceramics formed pure perovskite structure. As the BZT content increases, the relaxor characteristics were more obvious. At the same time, the piezoelectric coefficient d_{33}, planar mode electromechanical coupling coefficient k_p and depolarization temperature T_d first increased and then decreased, and reached maximum values of $d_{33}=163$ pC/N, $k_p=0.321$, and $T_d=380$ °C with 0.5%, 1% and 2% BZT addition, respectively. The results show that the BFZTx–BT system in high temperature ceramic has a very good application prospect.

Acknowledgements

This work was supported by the National Nature Science Foundation of China (61261012), Guangxi Science Foundation (2010GXNSFD013007 and 2010GXNSFB013010), Guangxi Education Department Foundation (201012MS083) and Guangxi Key Laboratory of Information Materials (1110908-09-Z).

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