Effects of piezoelectric and dielectric properties of (Bi$_{0.5}$Na$_{0.5}$)Ti O$_3$-Ba (Ti, Zr) O$_3$ ceramics

Nan Ding$^{1,*}$, Hanxiang Cheng$^1$, Qiangqin Dai$^2$

$^1$ Guangzhou College of Technology and Business, Foshan 510008, China
$^2$ Guangzhou Automobile Group CO. LTD Automotive Engineering Institute, Guangzhou 510005, China

*Corresponding author e-mail: daiqiangqin@gacrnd.com

Abstract. Lead-free piezoelectric ceramics Zr and Mn-doped Ba (Zr$_{x}$Ti$_{1-x}$) O$_3$-0.5 mol% MnO$_2$ (BZT100-x-Mn, x=0.04, 0.045, 0.05, 0.055, 0.06 and 0.065) have been fabricated by the conventional solid-state reaction technique. The effects of Zr on the microstructure and electrical properties of the samples have been studied. The results revealed that the specimens exhibit the perovskite structure and a small amount of MnO$_2$ can improve effectively the densification and electrical insulation of the ceramics. Because of high densification, good electrical insulation the donor-and acceptor-doping effects of MnO$_2$, the piezoelectric and dielectric properties of ceramics are improved considerably. The ceramics shows an excellent piezoelectric strain constant $d_{33}$ as 213 pC/N. A distinct positive temperature coefficient of resistance (PTCR) effect over a wide temperature range has been observed in all samples. With the addition of 0.5 mol% MnO$_2$, the sample Ba(Zr$_{x}$Ti$_{1-x}$)O$_3$-0.5 mol% MnO$_2$ with x=0.06 (BZT6-Mn) ceramics display low $\rho$ values of $10^2$-10$^3$ near Curie Temperature.

Keywords: Ba (Zr, Ti) O$_3$; Mn-doped; ceramics; dielectrics; PTCR.

1. Introduction

Lead-free piezoelectric ceramics is a kind of new functional ceramic materials with satisfactory performance and good environmental compatibility. Sodium-Bismuth-Titanate (BNT) is a composite perovskite type ferroelectrics developed by Smolensky et al. In 1960. It belongs to the trigonal system at room temperature, and the Curie temperature is 320 ℃ [2]. BNT is considered to be one of the most attractive lead-free piezoelectric ceramic materials because of its strong ferroelectric property (residual polarization strength at room temperature $P_r = 38$ C / cm), large piezoelectric coefficient, lower dielectric constant, good acoustic performance and low sintering temperature. However, BNT has high coercivity ($E_c = 73$ kV / cm) and high conductivity in the ferroelectric phase region, so it is difficult to polarize. Therefore, it is necessary to dope or introduce other elements and structures on this basis. Barium-Zirconate-Titanate BZT is also an important lead-free piezoelectric ceramic. It has a high piezoelectric constant, up to 236 PC / N, but its Curie temperature is very low, about 100 ℃, which limits its application [4-6]. BNT-BZT ceramics are solid solutions formed by two phases of (BNT) and (BZT). The addition of BZT can improve the piezoelectric properties of BNT ceramics, and the addition
of BNT can increase the Curie temperature of BZT and reduce its sintering temperature, so as to obtain lead-free piezoelectric ceramics with good piezoelectric properties and meeting the use requirements [7]. At the same time, in BNT-BZT system, there is a quasi isomorphic phase boundary which transforms from a triangular phase to a tetragonal phase, and there is an excellent ferroelectric and dielectric property near the phase boundary [8-10]. The BNT-BZT formulation of \((1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{Ba} (\text{Ti}_{0.95}\text{Zr}_{0.05})\text{O}_3\) was studied, and its structure and electrical properties were analyzed.

2. Experiment

2.1. Preparation of pure BNT ceramics

According to the traditional ceramic preparation process, \((1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3, (x = 0, 0.04, 0.05, 0.06, 0.07)\) are respectively calculated as BNT, BNT4, BNT5, BNT6, BNT7. Using analytical pure BaCO\(_3\) (99%), TiO\(_2\) (99%) and Na\(_2\)CO\(_3\) (99%) as raw materials, the weighed mixed oxides were milled for 12 h, sieved and dried, pre fired at 1200 °C for 2 h, then grinded, pelletted, dried and sintered at 1480 °C for 2 h.

2.2. Preparation of BZT doped ceramics

The above BNT-BZT7 samples were synthesized by a secondary synthesis method, and the composition was \((1-x)(\text{Bi}_{0.5}\text{Na}_{0.5})\text{TiO}_3-x\text{Ba} (\text{Ti}_{0.95}\text{Zr}_{0.05})\text{O}_3 (x = 0, 0.04, 0.05, 0.06, 0.07)\). BZT was added according to the ratio, then milled twice, dried, pressed and sintered at 1400 °C / 2h. After polishing, the electrode was coated and its performance was measured. X-ray diffractometer (general XD-2 X-ray diffract meter) was used for phase analysis. The dielectric properties were measured by Agilent e4890 (USA) precision instrument. The piezoelectric coefficient d33 was measured by zj-6a quasi-static d33 / d31 instrument.

3. Results and Analysis

![Fig. 1 XRD of the same sample](image1.png) ![Fig. 2 XRD pattern at diffraction peak](image2.png)

Figure 1 shows the XRD spectrum of \((1-x)\) BNT-xBZT ceramics. It can be seen from the figure that there is no impurity peak when the ceramic sample is not doped (i.e. x=0). With the increase of BZT content x (0-0.05), the position of diffraction peak moves to low angle; however, when the content of BZT increases from 0.05 to 0.07, the position of diffraction peak moves to higher angle. This may be due to the change of lattice parameters due to the doping of BZT. Moreover, with the change of doping amount x, the lattice parameters also change, resulting in the shift of diffraction position [11]. In addition, as shown in the XRD pattern of the diffraction peak in Fig. 2, the phase spectrum of \((1-x)\) BNT-xBZT ceramics is between x = 0.06 and x = 0.07.
3.1. Microstructure

From the morphology and structure of each sample shown in Fig. 3, it can be seen that the sample without BZT has large grains, poor compactness and uneven grains. After doping, the grains grow with each other, and the compactness and uniformity are improved. Moreover, the ceramic has a square grain shape. Although the grain size is not obviously related to the BZT doping amount x, the grain size further decreases with the increase of BZT doping amount X. In addition, the grain size of 0.05 is the most suitable, because the density and uniformity are relatively well.

3.2. Measurement of dielectric constant

It can be seen from Fig. 4 that the addition of BZT will shift the dielectric peak value of the ceramics to low temperature, indicating that the Curie temperature has decreased [12]. In addition, the samples also have relaxation properties.

Fig. 5 shows the corresponding dielectric loss curve with temperature. The change of dielectric loss is related to the content of BZT [13], and with the increase of temperature, it first decreases and then increases. Moreover, the dielectric loss of the material at low temperature is low, but when the temperature rises to 350 °C, the dielectric loss of the material increases rapidly, which is mainly due to the increase of the conductivity of the material at high temperature [14]. In addition, it can be seen from the curve that under the same formula and sintering process, the same temperature resistance of the samples increases with the increase of BZT content. When the content of BZT reaches a certain value, the same temperature resistance will increase rapidly.
Fig. 5 shows the corresponding dielectric loss curve with temperature. The change of dielectric loss is related to the content of BZT [13], and with the increase of temperature, it first decreases and then increases. Moreover, the dielectric loss of the material at low temperature is low, but when the temperature rises to 350 °C, the dielectric loss of the material increases rapidly, which is mainly due to the increase of the conductivity of the material at high temperature [14]. In addition, it can be seen from the curve that under the same formula and sintering process, the same temperature resistance of the samples increases with the increase of BZT content. When the content of BZT reaches a certain value, the same temperature resistance will increase rapidly.

Table 1. Curie temperature Tm, dielectric constant M and dielectric loss of (1-x) BNT -xBZT ceramics at 1 kHz

| Samples | X=0 | X=0.04 | X=0.05 | X=0.06 | X=0.07 |
|---------|-----|--------|--------|--------|--------|
| Tm      | 356 | 326    | 336    | 338    | 344    |
| ε_m     | 1666.3 | 1865.6 | 1678.2 | 1846.6 | 1821.7 |
| ε″      | 207.4 | 237.6  | 248.3  | 235.0  | 220.0  |

3.3. Piezoelectric properties of (1-x) BNT -xBZT ceramics
In this experiment, the piezoelectric properties of each group of ceramic samples were tested by quasi-static tester produced by Institute of acoustics, Chinese Academy of Sciences. Proper amount of BZT solid solution into BNT can improve the high-voltage electrical properties [19]. The piezoelectric constant first increases with the increase of solid solution content. After the maximum value appears, the content of BZT continues to increase, and the value gradually decreases. Moreover, it has a certain degree with polarization electric field, polarization time and polarization temperature. In the process of the experiment, it may be due to the high polarization temperature (120 °C) or the insufficient polarization voltage. However, when the polarization voltage reaches 3.8kv, the ceramic will be broken down. The measurement results of each sample are very small, only about 10 PC / n.

3.4. Ferroelectric properties of (1-x) BNT-xBZT ceramics
In terms of the relationship with the ferroelectric properties of materials, both the residual polarization strength and the coercive electric field are important factors affecting the piezoelectric properties [20]. On the one hand, the high coercivity electric field makes the ferroelectric domain unable to fully turn in the polarization process, which is not conducive to improving the piezoelectric properties; on the other hand, the high residual polarization strength enhances the ferroelectricity, which is conducive to...
improving the piezoelectric properties [21]. Of course, the piezoelectric properties of piezoelectric ceramics are not only related to their ferroelectric properties, but also related to many factors such as the crystal structure of materials, the density of ceramics, grain size and polarization conditions [22]. However, for ferroelectric piezoelectric ceramics, it is necessary to improve and improve the piezoelectric properties of NBT based piezoelectric ceramics by fully reducing the coercive electric field and increasing the residual polarization strength [23].

Figure 6 shows the hysteresis loop of the sample at room temperature. It can be seen from the figure that there is no linear change of polarization intensity P with the applied electric field intensity E in the four hysteresis loops. It shows that the domain orientation is not complete under the maximum electric field strength in this test. Due to many factors, the possibility of breakdown is high.

![Hysteresis loops of (1-x) BNT-xBZT ceramics at room temperature](image)

Fig. 6 Hysteresis loops of (1-x) BNT-xBZT ceramics at room temperature

Table 2. Residual polarization strength (Pr) and coercive field (Ec) of (1-x) BNT -xBZT ceramic samples

| Samples | X=0 | X=0.04 | X=0.05 | X=0.06 | X=0.07 |
|---------|-----|--------|--------|--------|--------|
| Pr(μm/cm²) | 5.5 | 5.2 | 4.7 | 4.2 | 2.8 |
| Ec(kV/cm) | 4.1 | 3.8 | 3.5 | 3.0 | 1.8 |

The remanent polarization strength (PR) and coercivity field (EC) of each sample are listed in Table 2.

1. It can be clearly seen from table 2 that the residual polarization strength (PR) and coercivity field (EC) decrease linearly with the increase of BZT content. Therefore, the addition of BZT can effectively improve the high coercivity of NBT ceramics.

Disadvantages:

2. Compared with the other four samples, the hysteresis loop of sample x = 0.07 shows incomplete polarization.

3. It can be seen that with the increase of BZT content, the area of hysteresis loops of the four samples decreases gradually, which indicates that the polarization loss of the samples decreases with the increase of BZT amount.
4. Conclusion
BNT-BZT ceramics with different content of BZT were prepared by solid state method. The effects of different content of BZT and preparation process on the phase structure, microstructure, dielectric properties, piezoelectric properties and ferroelectric properties of BNT-BZT ceramics were studied.

(1) With the increase of BZT content, the phase structure of the ceramics transits from the triangular phase to the tetragonal phase. When the content of BZT is between 0.06 and 0.07, there is a quasi isomorphic phase boundary.

(2) With the increase of BZT content, the ceramic grain distribution is uniform, and the ceramics with relatively dense and good uniformity are obtained at x = 0.05.

(3) Through the study of the dielectric properties of the ceramics, there are two dielectric peaks. With the increase of temperature, TT moves to the low temperature direction, while TM moves to the high temperature direction. According to Curie Weiss law, all ceramics are relaxor ferroelectrics.

(4) For PTC effect, it shows a "U-shaped rule", that is, with the increase of BZT content, the resistance r first decreases and then increases. When the temperature is low, the resistance range is 500-1000 Ω.

(5) For ferroelectric properties, BNT-BZT is a kind of relaxor ferroelectric materials.

References
[1] Z.G. Lu, G. Calvarin, Frequency dependence of the complex dielectric permittivity of ferroelectric relaxors, Phys. Rev. B. 1995, 51(5): 2694-2702.
[2] S. Anwar, P.R. Sagdeo, N.P. Lalla, Ferroelectric relaxor behavior in hafnium doped barium titanate ceramic, Solid State Commun. 2006, 138(7): 331-336.
[3] Y. Zhi, A. Chen, R.Y. Guo, A.S. Bhalla, Dielectric properties of Ba(Ti,Zr1-x)O3 solid solutions, Mater. Lett. 2007, 61(2): 326-329.
[4] S. B. Reddy, K. P. Rao, M.S. R. Rao, Structural and dielectric characterization of Sr substituted Ba(Zr,Ti)O3 based functional materials, Appl. Phys A. 2007, 89(4): 1011-1015.
[5] E. Antonelli, M. Letonturier, J.C. M’Peko, A.C. Hernandes, Microstructural, structural and dielectric properties of Er3+-modified BaTi0.85Zr0.15O3 ceramics, J. Eur. Ceram. Soc. 2009, 29(8): 1449-1455.
[6] M. Kumar, A. Garg, R. Kumar, M.C. Bhatnagar, Structural, dielectric and ferroelectric study of Ba0.8Sr0.2Zr,Ti1−xO3 ceramics prepared by the sol–gel method, Phys. B. 2007, 403(10-11): 1819-1823.
[7] H.Y. Tian, Y. Wang, J. Miao, H.L.W. Chan, C.L. Choy, Preparation and characterization of hafnium doped barium titanate ceramics, J. Alloys Compd. 2007, 431(1-2): 197-202.
[8] Y. Zhi, A. Chen, R.Y.Guo, A.S. Bhalla, Piezoelectric and strain properties of Ba(Ti1−xZrx)O3 ceramics. J.Appl Phys. 2002, 92(3): 1489-1493.
[9] W.Q. Cao, J.W. Xiong, J.P. Sun, Dielectric behavior of Nb-doped Ba(Zr,Ti1−x)O3, Mater. Chem. Phys. 2007, 106(2-3): 338-342.
[10] Y.L. Wang, L.T. Li, J.Q. Qi, Z.L. Gui, Ferroelectric characteristics of ytterbium-doped barium zirconium titanate ceramics, Ceram. Int. 2002, 28(6): 657-661.
[11] F. Moura, A.Z. Simões, B.D. Stojanovic, M.A. Zaghete, E. Longo, J.A. Varela, Dielectric and ferroelectric characteristics of barium zirconate titanate ceramics prepared from mixed oxide method, J. Alloys Comp., 2008, 462(1-2): 129-134.
[12] M. Kuwabara, Positive temperature coefficient of resistivity effect in undoped barium titanate ceramics, J.Appl.Phys., 1994, 76(2) 1326-1328.
[13] S.W. Ding, G. Jia, J.Wang, Z.Y. He, Electrical properties of Y-and Mn-doped BaTiO3-based PTC ceramics, 2008, 34(8): 2007-2010.
[14] S.S. Jida, T.Suematsu, T. Miki, Effect of microwave heating on BaTiO3: Nb ceramics with positive temperature coefficient of resistivity, J. Appl. Phys., 1999, 86(4): 2089-2091.
[15] F. Moura, A.Z. Simoes, L.S. Cavalcante, M.A. Zaghete, J.A. Varela, E. Longo, Ferroelectric and dielectric properties of vanadium-doped Ba(Ti0.90Zr0.10)O3 ceramics, J. Alloys Comp., 2008,
[16] K. Park, Characteristics of porous BaTiO3-based PTC thermistors fabricated by adding graphite powders, Mater. Sci. Eng. B. 2004, 107(1-2):9-14.

[17] N. Nanakorn, P. Jalupoom, N. Vaneesorn, A. Thanaboonsombut, Dielectric and ferroelectric properties of Ba(Zr,Ti1-x)O3 ceramics, Ceram. Int., 2008, 34(4):779-782.

[18] H. Takeda, W. Aoto, T. Shiosaki, BaTiO3–Bi1/2Na1/2TiO3 solid-solution semi-conducting ceramics with Tc>130 °C, Appl. Phys. Lett., 2005, 87(10): 102104.

[19] C. Hofer, R. Meyer, U. Bottger, R. Waser, Characterization of Ba(Ti, Zr)O3, ceramics sintered under reducing conditions, J. Eur Ceram Soc. 2004, 24(6): 1473-1477.

[20] S.J. Kuang, X.G. Tang, T.D. Cheng, N. Ding, and Q.X. Liu, Dielectric properties of high Tc ceramics based on BaTiO3 with (111) texture characteristics, Phys. Status Solidi A, 2009, 206(4): 745-749.

[21] S.J. Kuang, X.G. Tang, L.Y. Li, Y.P. Jiang, Q.X. Liu, Influence of Zr dopant on the dielectric properties and Curie temperature of Ba(Zr,Ti1-x)O3 (0≤x≤0.12) ceramics, Scripta Mater., 2009, 61(1): 68-71.

[22] X.G. Tang, J. Wang, X.X. Wang, H.L.W. Chan, Effects of grain size on the dielectric properties and tunabilities of sol-gel derived Ba(Zr0.2Ti0.8)O3 ceramics, Solid State Commun., 2004, 131(3-4): 163-168.

[23] W.J. Merz, Double hysteresis loop of BaTiO3 at the Curie point, Phys. Rev. 1953, 91(3):513-517.

[24] L. Affleck, J. Seaton, C. Leach, Characterisation of the R–T response of BaTiO3 thermistors on three different length scales, J. Eur Ceram Soc., 2007, 27(12): 3439-3444.

[25] W. Heywang, Bariumtitanat als sperrschichthalbleiter, Solid-State Electron. 1961, 3(1): 51-58.