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Ceramics International 39 (2013) S19–S23

CERAMICS INTERNATIONAL

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Dielectric properties and relaxor behavior of high Curie temperature $(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$–$Bi(Mg_{0.5}Ti_{0.5})O_3$ Lead-free ceramics

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Available online 16 October 2012

Abstract

The $(1-x)(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3-xBi(Mg_{0.5}Ti_{0.5})O_3$ [$(1-x)$BCZT–xBMT, $x=0.1$–0.7] lead-free solid solution ceramics were prepared by the conventional mixed oxide method. The phase structure was investigated by X-ray diffraction and results show that a single perovskite phase was obtained in all of these samples, suggesting that the added BMT diffused into BCZT to form a solid solution. Dense ceramics with relative densities $>95\%$ were obtained, and a small amount of BMT (≤ 50 mol%) acted as grain growth promoter, had an evident effect on grain size growth. Further increase of the BMT content inhibited the grain growth of BCZT samples. Temperature dependence of the dielectric properties showed that all the BCZT–BMT solid solution ceramics exhibited relaxor-like characteristics. With increasing BMT content, the Curie temperature was first increased and then decreased, giving a maximum value of 218 °C for the 0.4BCZT–0.6BMT composition. Furthermore, stable dielectric constants and low losses were obtained with $0.5 \leq x \leq 0.7$ in the wide temperature range, indicating that the system possess potential for high-temperature application.

Keywords: C. Electrical properties; C. Dielectric properties; D. $BaTiO_3$ and titanates

1. Introduction

Lead zirconate titanate (PZT) ceramics are the most widely used in piezoelectric materials due to the highest piezoelectric coefficients ($d_{33} \approx 200$–600 pC/N) and electromechanical coupling coefficients ($k_{33} \approx 0.6$–0.80) [1]. However, considering the lead oxide toxicity and growing demand of global environmental protection, there is an urgent need to develop a lead-free substitute that can compete with PZT [2]. Hence, lead-free piezoelectrics have attracted considerable attention in recent years and much effort has been made to develop highly piezoelectric lead-free materials. Recently, several notable Pb-free piezoelectric ceramics have been reported to exhibit promising piezoelectric properties [3], especially the (K, Na)NbO_3 based pseudo-ternary system and the BaTiO3 based pseudo-binary system.

$BaTiO_3$ is a famous material with tetragonal phase at room temperature and its piezoelectric constant d_{33} of 191 pC/N. In 2009, a Pb-free ferroelectric system $Ba(Zr_{0.2}Ti_{0.8})$–$x(Ba_{0.7}Ca_{0.3})TiO_3$(BCZT) has been reported [3], which is characterized by a phase boundary between R and T phases starting from a C–T–R triple point [2,3]. Generally speaking, there are two important parameters, i.e., piezoelectric constant (d) and Curie temperature (T_c) for actuator device application at off-resonance. However, its measured T_c was only 93 °C and this low T_c prevents its piezoelectric application in transducers. Therefore, it is urgent to increase the T_c to meet the practical application, especially in actuator device.

Eital et al. [4] proposed a guideline to search for new high Curie temperature piezoelectric ceramics of Bi- and Pb-perovskite relaxor solid solution with $PbTiO_3$. Recently, many solid solutions of $BaTiO_3$ with Bi-based compounds have attracted attention due to environmental protection issues and have been investigated, such as $BaTiO_3$–$BiScO_3$ [5,6] and $BiScO_3$–$Bi(Zn_{0.5}Ti_{0.5})O_3$–$BaTiO_3$[7] system. However, there is no report on the $(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$–$Bi(Mg_{0.5}Ti_{0.5})O_3$ solid solution ceramics. In this study, the

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http://dx.doi.org/10.1016/j.ceramint.2012.10.028

$(1-x)(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$–$xBi(Mg_{0.5}Ti_{0.5})O_3$ solid solution ceramics were designed and prepared. The structure, relaxor characteristics and temperature-dependent of dielectric properties have been investigated systematically.

2. Experimental

The $(1-x)(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$–$xBi(Mg_{0.5}Ti_{0.5})O_3$ solid solution ceramics with $x=0.1$–0.7 were prepared by conventional solid-state reaction route. The weighted raw materials of $BaCO_3$(99.8%), $CaCO_3$(99.95%), ZrO_2(99%), TiO_2(99.6%), Bi_2O_3 (99.975%) and MgO(99%) powders were mixed by planetary mill for 24 h. This mixture was dried at 100 °C for 12 h and then calcined at 1000 °C for 4 h. Thereafter, they were pressed into 12-mm-diameter pellets and sintered at various temperatures from 1050 °C to 1350 °C for 4 h in air.

The density was measured by the Archimedes method. The phase structure of the samples was examined by X-ray diffraction (XRD, Bruker D8 Advanced, Germany) with Cu K_α radiation. The microstructure of ceramic was characterized using a scanning electron microscopy (SEM) (JSM, EMP-800, Japan). In order to study their electrical properties, the samples were polished and painted with silver pastes on the two sides and then fired at 600 °C for 10 min. The temperature dependence of the dielectric constant and loss of the samples was measured with a high-precision LCR meter (Agilent E4980A) between 25 °C and 400 °C.

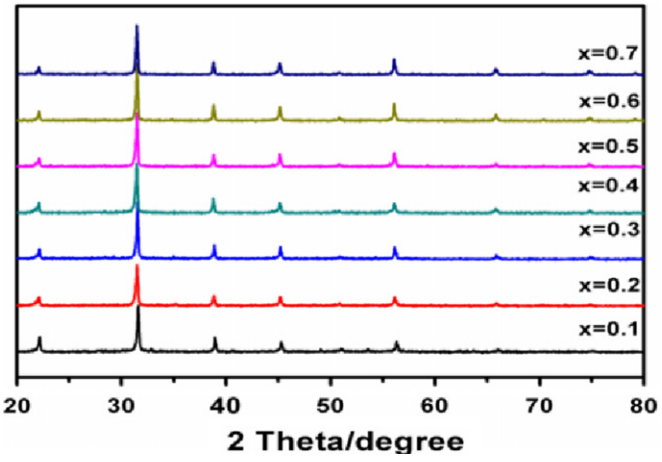

Fig. 1. XRD patterns of $(1-x)(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$–$xBi(Mg_{0.5}Ti_{0.5})O_3$ ($x=0.1$–0.7) solid solution ceramics measured at room temperature.

3. Results and discussion

Fig. 1 shows the XRD patterns of $(1-x)(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$–$xBi(Mg_{0.5}Ti_{0.5})O_3$ ($x=0.1$–0.7) solid solution ceramics measured at room temperature. It is evident that all samples crystallize with a perovskite structure and free of impurities, which demonstrated that $Bi(Mg_{0.5}Ti_{0.5})O_3$ had completely diffused into the lattice of $(Ba_{0.85}Ca_{0.15})(Zr_{0.1}Ti_{0.9})O_3$ and formed a solid solution. In addition, compared to BT–BZT and BT–BMT solid solution ceramics which were reported to be stable for BZT compositions below 50 mol% [8] and for BMT compositions below 60 mol% [9], the perovskite phase of BCZT–BMT is also stable with BMT composition below 70 mol%.

The SEM micrographs of the free surface of $(1-x)$BCZT–xBMT solid solution ceramics with different BMT contents are shown in Fig. 2. The sintering temperature was expected to decrease with increasing BMT contents and the optimum sintering temperature was

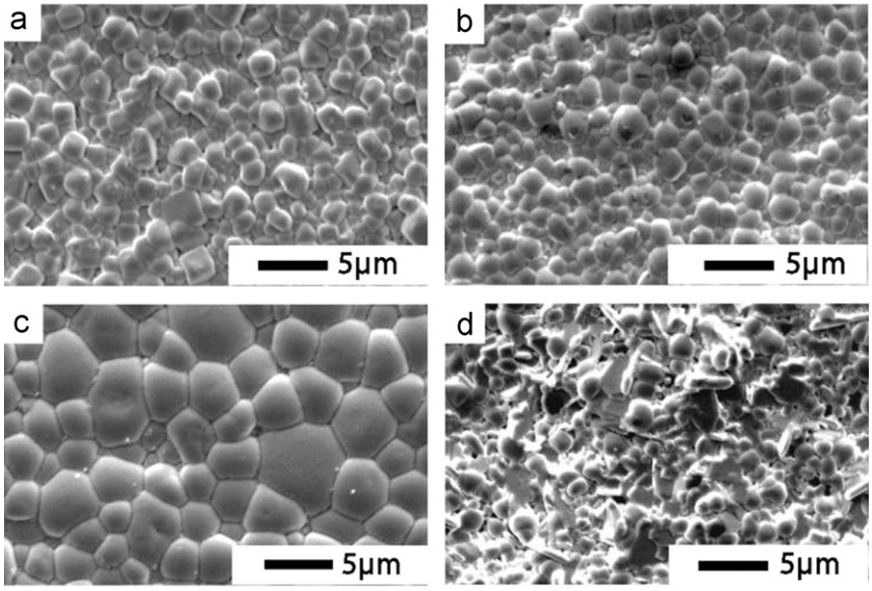

Fig. 2. SEM micrographs of the free surface of $(1-x)$BCZT–xBMT solid solution ceramics for (a) $x=0.1$, (b) $x=0.3$, (c) $x=0.5$ and (d) $x=0.7$.

initially determined based on the density and dielectric loss at room temperature. Dense and homogeneous microstructures were observed and the relative density of all studied samples was greater than 95%. It is clear that the average grain size increased with the addition of the BMT and then followed a sharp reduction when the BMT contents were over 50 mol%. As the addition reaches 50 mol%, the average grain size reaches approximately 4 μm. This suggested that a reasonable addition of BMT contents to BCZT solid solution ceramics can modify the grain size of the sample.

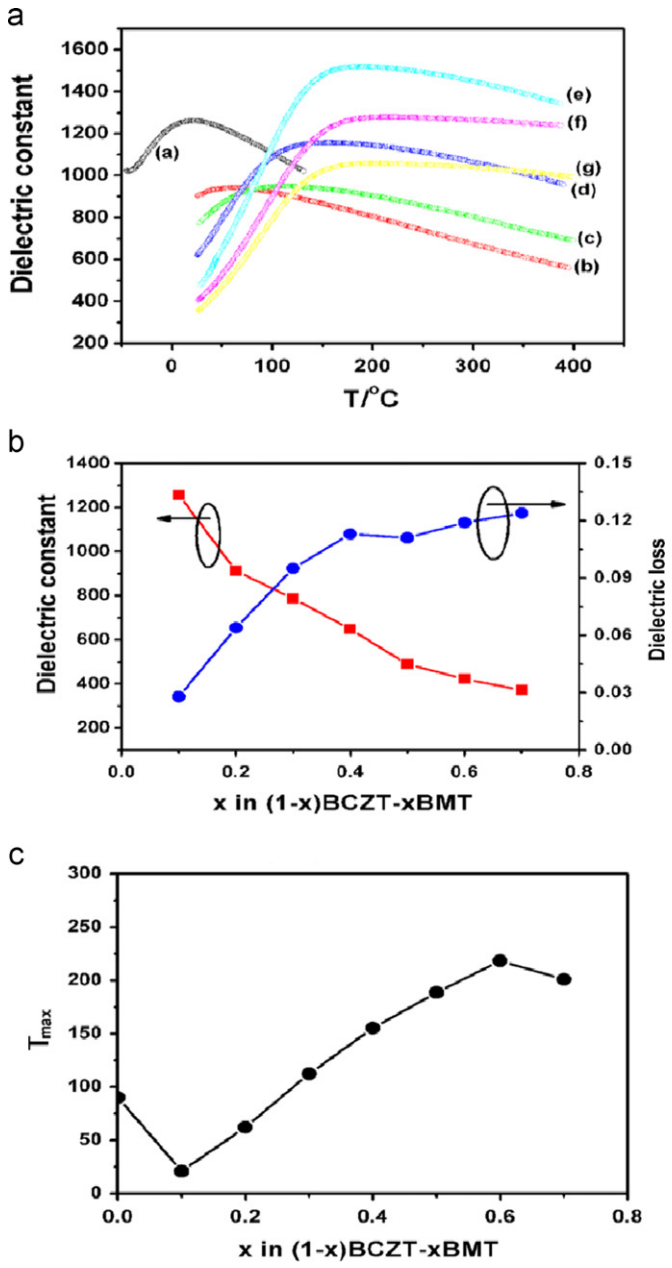

Fig. 3. (a) Temperature dependence of the dielectric constant of $(1-x)$BCZT–xBMT solid solution ceramics with different BMT contents measured at 100 kHz. (b) The variations of dielectric constant and loss measured at room temperature. (c) The T_{max} of $(1-x)$BCZT–xBMT solid solution ceramics as a function of BMT contents.

Fig. 3(a) displays the temperature dependence of the dielectric constant of $(1-x)$BCZT–xBMT solid solution with BMT content from $x=0.1$ to $x=0.7$ measured at 100 kHz. Obviously, one phase transition can be detected over a wide range of temperature, which is similar to other solid solution, such as BT–BLT [10], PT–BZN [11] and BT–BMT [9,12] system. According to Ren et al. [2], BCZT has two phase transition over a wide range of temperature. Considering the report in the BT–BS system [6] and BS–BZT–BT system [7], it can be implied that all the two phase transitions may be merged into a diffuse transition in the BCZT–BMT solid solution ceramics. The dielectric constant and loss for the $(1-x)$BCZT–xBMT solid solution measured at 100 kHz and room temperature are plotted in Fig. 3(b). The dielectric constant decreased monotonously from 1257 to 372 with the increase of BMT contents, while the corresponding dielectric loss increased monotonously from 2.8% to 12%, which is similar to the BT–BMT system [9,12] and BT–BZT system [8]. With respect to the high dielectric loss, it was proposed that a possible reason may be bismuth vacancies and other defects [9]. Fig. 3(c) illustrates the T_{max} of $(1-x)$BCZT–xBMT solid solution ceramics as a function of BMT contents measured at 100 kHz. The T_{max} exhibited a minimum of 20.9 °C with $x=0.1$. With the addition of BMT contents, the T_{max} increased and then exhibited a maximum of 218 °C with $x=0.6$, which is much higher than that of the pure BCZT ($T_{max}=93$ °C) and suggests a potential use of these ceramics for high T_c piezoelectric application. When the BMT content was over 60 mol%, the T_{max} decreased with further increase of the BMT contents. This abnormal phenomenon regarding the variation in T_{max} is similar to previous reports in the BT–BS binary system [6] and BS–BZT–BT ternary system [7]. Xiong et al. [13] proposed that in the BMT–BT system, the low level of BMT contents could lead to little interaction of Bi^{3+}, Mg^{2+} and Ti^{4+} ions, and is equal to Bi_2O_3, MgO, and TiO_2 oxide-doped in BT, respectively, which resulted in the depression of T_{max}. With the increase of BMT contents, the interaction of these ions was enhanced and the high T_{max} character of BMT prevailed.

The temperature dependence of dielectric constant and dielectric loss of $(1-x)$BCZT–xBMT ($x=0.4$–0.7) solid solution ceramics measured at various frequencies are shown in Fig. 4. The frequency dispersion of the dielectric constant and dielectric loss of $(1-x)$BCZT–xBMT solid solution ceramics could be obviously observed, suggesting a relaxation characterization, as presented in Fig. 4. Interestingly, a stable dielectric constant and dielectric loss with the addition of BMT contents from $x=0.5$ to $x=0.7$ could be observed when the temperature was over the Curie temperature. Moreover, for 0.4BCZT–0.6BMT solid solution ceramics, the dielectric constant is almost keep a constant and the dielectric loss was lower ($<1\%$) at 100 kHz and high temperature (200–350 °C). This result suggests that the lead-free relaxor $(1-x)$BCZT–xBMT solid solution ceramics possess potential for high-temperature application.

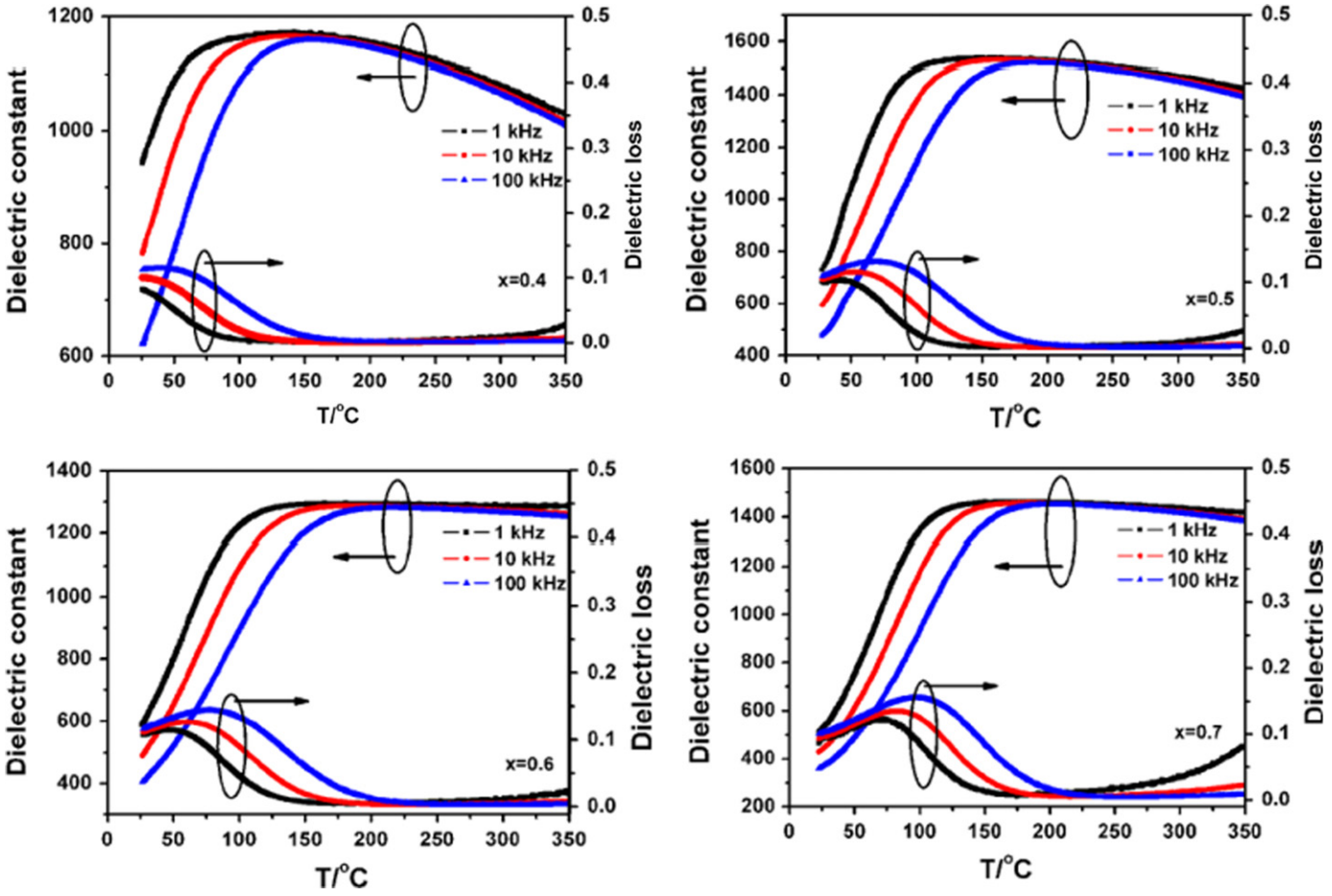

Fig. 4. Temperature dependence of dielectric constant and dielectric loss of $(1-x)$BCZT–xBMT ($x=0.4$–0.7) solid solution ceramics measured at various frequencies.

For the relaxor ferroelectrics, the diffuseness of the paraelectric–ferroelectric phase transition can be described by a modified Curie–Weiss law [14]:

$$\frac{1}{\varepsilon}-\frac{1}{\varepsilon_m}=\frac{(T-T_m)^{\gamma}}{C} \quad (1)$$

where C is the Curie temperature, and γ is called a diffusion coefficient, ranging from 1 for a normal ferroelectric and 2 for an ideal relaxor ferroelectric. To further investigate the effect of BMT content on diffuse phase transition behavior of $(1-x)$BCZT–xBMT solid solution ceramics, the plots of $\ln(1/\varepsilon-1/\varepsilon_m)$ as a function of $\ln(T-T_m)$ at 100 kHz are studied. The large γ values reveal the obvious relaxor behavior in $(1-x)$BCZT–xBMT solid solution ceramics, which is consist well with the BT–BMT system [9]. With respect to the relaxor behavior, Bokov et al. [15] proposed that the large difference in the valence between B′and B″ ions and small size of A-site cation would enhance the elastic drive towards ordering on the B-site in $A(B'\ B'')O_3$ system, which results in and highlight the diffuse phase transition with the addition of the B-cation ordering. When BMT was added into BCZT, Bi^{3+} and Mg^{2+} were introduce into A-sites and B-sites of ABO_3 perovskites structure, respectively, which leads to the off-center displacement due to the difference in the radius and result in the relaxor behavior in BCZT–BMT solid solution ceramics.

4. Conclusions

The $(1-x)$BCZT–xBMT lead-free solid solution ceramics were prepared as the new high T_c lead-free piezoelectric material. The stable perovskite structure could be obtained in all studied compositions. With the substitution of BMT, the Curie temperature was first increased and then decreased, giving a maximum value of 218 °C for the 0.4BCZT–0.6BMT composition. The temperature dependence of dielectric properties revealed that the all the BCZT–BMT solid solution ceramics exhibited relaxor-like characteristics. For the 0.4BCZT–0.6BMT solid solution ceramics, the dielectric constant is almost a constant and the dielectric loss was lower ($<1\%$) at 100 kHz and in the range of high temperature. Based on these results, the $(1-x)$BCZT–xBMT solid solution ceramics demonstrates potential in lead-free materials for high temperature application.

Acknowledgments

The authors would like to acknowledge the support from the National Natural Science Foundation of China under grant No. 50932007, 50972108.

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