Asian Journal of Chemistry; Vol. 26, No. 6 (2014), 1698-1700

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2014.17328

Structure and Electrical Properties of Lead-free Piezoelectric Ceramics $Bi_{0.5}Na_{0.5}TiO_3$-$Ba_{0.94}Sr_{0.06}(Sn_{0.08}Ti_{0.92})O_3$†

QIYI YIN[1,2], ZHAOQI SUN[1,*], SHIWEI SHI[1], JIE YANG[2], CHANGAN TIAN[2] and MEILING BAO[2]

[1]School of Physics and Material Science, Anhui University, Hefei 230601, P.R. China
[2]Department of Chemistry and Material Engineering, Hefei University, Hefei 230601, P.R. China

*Corresponding author: E-mail: szq@ahu.edu.cn

Published online: 10 March 2014; AJC-14869

New lead-free piezoelectric ceramics BNBSST-100x have been prepared by the traditional solid state sintering technique and systematically studied. The results of XRD confirm that all ceramics samples possess pure perovskite structure, showing that the morphotropic phase boundary between rhombohedral and tetragonal phase of the ceramics locates in the range of $0.02 < x < 0.06$. The BNBSST-4 ceramic samples near the morphotropic phase boundary exhibits improved properties, which are d_{33} = 203pC/N, k_p = 41 %, ε_r = 1128, tan θ = 2.6 %, P_r = 35.6 μC/cm^2 and E_C = 3.51 kV/mm, suggesting that the ceramics are suitable for future application.

Keywords: Lead-free, Piezoelectric ceramics, SnO_2, Ferroelectricity.

INTRODUCTION

All kinds of piezoelectric ceramics have been extensively studied and widely used in different related devices due to discovery of piezoelectric effect in 1880 by J. and P. Curie[1]. Particularly, lead-based piezoelectric ceramics based on lead zirconate titanate (PZT) are universally used for various actuator, sensor applications as well as microelectronic devices result from their excellent piezoelectric properties. In recent years, the search for alternative piezoelectric materials is a very active research topic and a great deal of attention has been focused on different types of lead-free piezoelectric ceramics, which because the use of the lead-based ceramics can cause serious lead pollution to man and environmental due to the high toxicity of lead oxide and a high volatility even at low temperatures[2,3]. Thus, it is urgent to develop environment-friendly materials which can replace lead zirconate titanate-based ceramics. Bismuth sodium titanate (BNT) discovered by Smolenskii and Aganovskaya[4] is one of the most important lead-free piezoelectric materials because of its excellent piezoelectric and ferroelectric properties as well as the lack of lead pollution during the preparation process[4]. However, the electrical properties of pure bismuth sodium titanate is quite poor due to its relatively high conductivity and large coercive field. As a result of these, a lot of important work is focused on the modification and preparation technology of the bismuth sodium titanate-based ceramics so that their electrical properties are improved[5,6].

In this work, lead-free piezoelectric ceramics (1-x) $Bi_{0.5}Na_{0.5}TiO_3$-$xBa_{0.94}Sr_{0.06}(Sn_{0.08}Ti_{0.92})O_3$ (BNBSST) were synthesized by the traditional solid-state reaction processes at 1140 ºC. Their phase composition, microstructure, electrical properties were also investigated.

EXPERIMENTAL

The piezoelectric ceramics $(1-x)Bi_{0.5}Na_{0.5}TiO_3$-$xBa_{0.94}Sr_{0.06}(Sn_{0.08}Ti_{0.92})O_3$ (x = 0.00, 0.02, 0.04, 0.06, 0.08) (abbreviated as BNBSST-100x) were prepared by a conventional ceramic process using high purity oxides or carbonate powders of Bi_2O_3 (99.97 %), TiO_2 (99.9 %), SnO_2 (99.98 %), Na_2CO_3 (99.9 %), $BaCO_3$ (99.9 %) and $SrCO_3$ (99.9 %) as starting raw materials. Firstly, these powders were weighed and mixed fully in the appropriate stoichiometry in ethanol by ball-milling which medium is agate ball for 24 h and calcined at 900 ºC for 2 h. After calcining, the calcined powders were milled again for 10 h and mixed thoroughly with a PVA binder solution and then pressed uniaxially into disk samples of 1.2 cm in diameter and 1.0 mm in thickness. These disk samples were sintered at 1140 ºC for 2 h in atmospheric air. Silver electrodes were fired on both sides of the samples at

†Presented at The 7th International Conference on Multi-functional Materials and Applications, held on 22-24 November 2013, Anhui University of Science & Technology, Huainan, Anhui Province, P.R. China

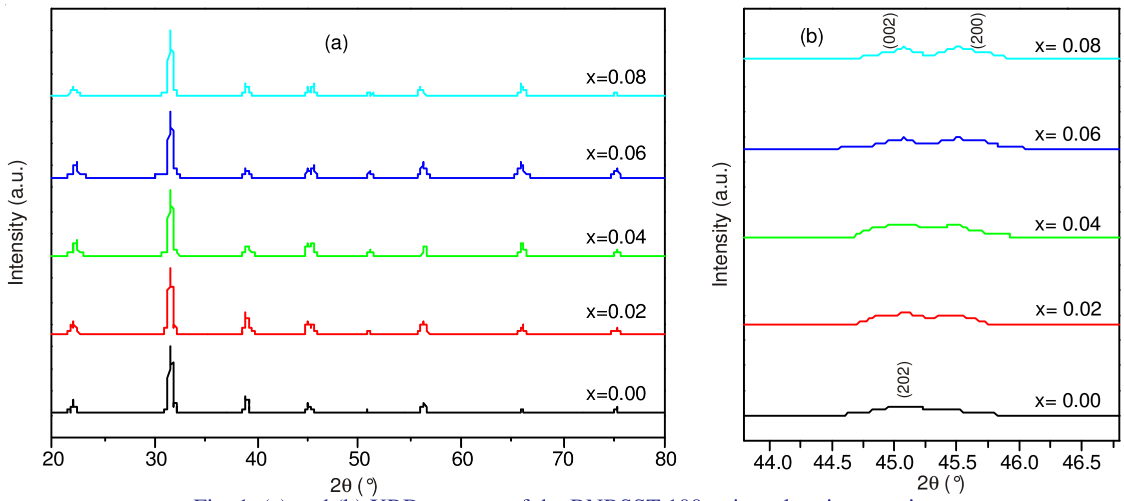


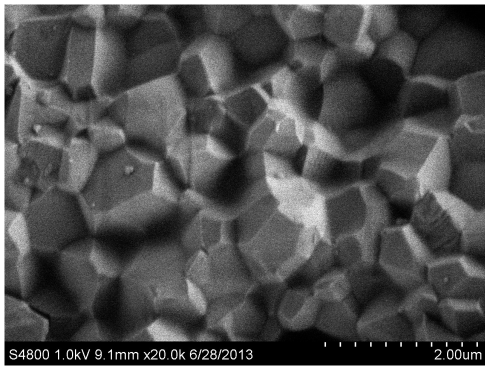
Fig. 1. (a) and (b) XRD patterns of the BNBSST-100x piezoelectric ceramics

500 ºC for 0.5 h in order to the subsequent poling and electrical measurements. The samples were poled in 70 ºC silicon oil bath using a DC electric field of 3-5 kV/mm for 0.5 h. The crystalline structure of the sintered samples was examined using an X-ray diffraction (XRD) with CuK$_\alpha$ radiation (Rigaku, Tokyo, Japan). The microstructure of the ceramics was studied by scanning electron microscope (SEM) (S-4800, Hitachi, Japan). The piezoelectric constant d_{33} was measured using a piezo-d_{33} meter (ZJ-3A, China). The electromechanical coupling factor k_p was determined by the resonance method using an impedance analyzer (Agilent 4294A). The relative permittivity ε_r and loss tangent tan δ of the ceramics at 10 kHz were measured using an impedance analyzer (Agilent 4192A). Ferroelectric hysteresis loops were measured at room temperature using a ferroelectric tester (Trek 609B, Radiant Technologies, Inc., Albuquerque, NM).

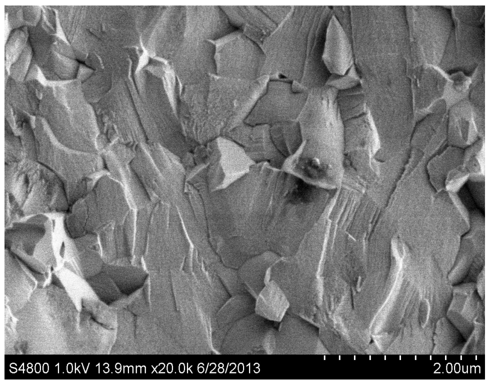
RESULTS AND DISCUSSION

The XRD patterns of the BNBSST-100x ceramics sintered at 1140 ºC are shown in Fig. 1. As shown in Fig. 1(a), all the ceramics possess a pure perovskite structure and no second phases are detected, indicating that Ba^{2+}, Sr^{2+}, Sn^{4+} and Ti^{4+} have completely diffused into the bismuth sodium titanate lattices to form a series of continuous solid solutions. Similar to pure bismuth sodium titanate ceramics, it is obvious that only the (202) characteristic peaks are shown when $x \leq 0.02$, implying that the BNBSST-100x ceramics have a rhombohedral perovskite structure. However, with x increasing from 0.02 to 0.06, the crystal structure of the BNBSST-100x ceramics transforms featured with the splitting of (202) diffraction peak into (002) and (200) peaks at 44-47 ºC and the intensities of the two peaks change with the increasing of tetragonal phase and at $x \geq 0.06$, the ceramics exhibit the single tetragonal phase, which are presented in Fig. 1(b). These results reveals that the morphotropic phase boundary (MPB) between rhombohedral and tetragonal structures is formed in the BNBSST-100x ceramics with $0.02 < x < 0.06$. Similar results have been obtained in the other bismuth sodium titanate-based ceramics reported[7].

Fig. 2 shows the SEM micrographs of the BNBSST-4 ceramics sintered at 1140 ºC for 2 h. As can be seen from Fig. 2(a), almost no pores are found on the surface and grains boundary is very clear. Fig. 2(b) exhibits the SEM micrographs of a transect of the BNBSST-4 ceramics, there are a few small pores and a stain which might be caused during the preparation in the body of the ceramics, the fracture behaviour of the ceramics is penetrating grain fracture, indicating the existence of good mechanics properties. From the both pictures of Fig. 2, the observations of SEM micrographs affirm that this ceramic is densely sintered and 1140 ºC is an appropriate sintering temperature.



(b)



(a)

Fig. 2. SEM micrographs of the BNBSST-100x (x = 0.04) ceramic at 1140 ºC for 2 h. (a) External; (b) transect

The piezoelectric and dielectric properties (d_{33}, k_p, ε_r and tan δ) of the BNBSST-100x ceramics as a function of $Ba_{0.94}Sr_{0.06}(Sn_{0.08}Ti_{0.92})O_3$ (BSST) concentration were measured are shown in Fig. 3. As can be seen from Fig. 3(a), the piezoelectric constant d_{33} and the planar electromechanical coupling factor k_p of BNBSST-100x ceramics increase with increasing BSST fraction up to 0.04 and then decrease with further increase in x value in BNBSST-100x ceramics. The maximum values of d_{33} = 203pC/N and k_p = 41 % are obtained at x = 0.04. As for Fig. 3(b), it can been observed that the variation tendency of ε_r with increasing BSST content is similar to the change law of piezoelectric properties and ε_r reachs the maximum value of 1128 at x = 0.04, but tan δ change is just opposite comparing with ε_r and reaches a minimum value of 2.6 % at x = 0.04. The results indicate that an optimal piezoelectric and dielectric properties can be gained at the composition x = 0.04 near the morphotropic phase boundary.

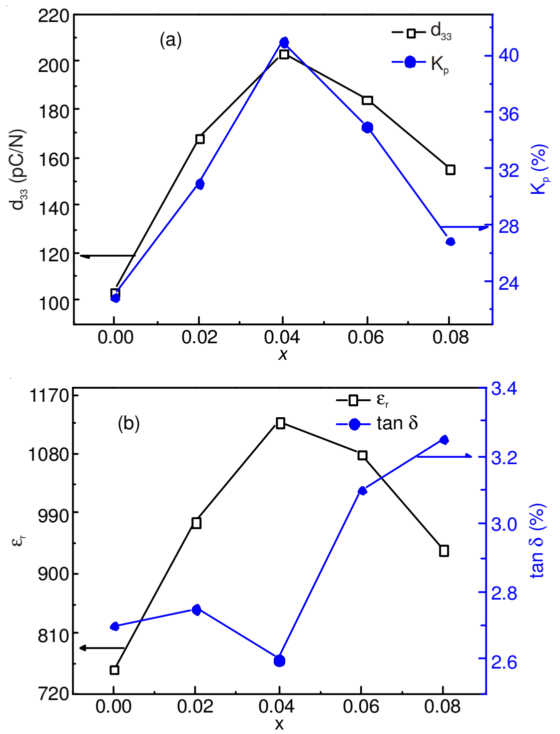


Fig. 3. Variations of (a) Piezoelectric and (b) dielectric properties (at 10 kHz) with x for the BNBSST-100x ceramics

Fig. 4(a) shows the P-E curves of the BNBSST-100x (x = 0.00, 0.02, 0.04, 0.06, 0.08) ceramics at room temperature. All these ceramics samples exhibit a typical P-E loops of ferroelectrics with square like shape, a relatively steep P-E slope, especially the BNBSST-100x (x = 0.04, 0.06) ceramics exhibit strong ferroelectric properties. Fig. 4(b) presents the remnant polarization P_r and coercive field E_C as a function of x. It is exhibited that P_r and E_C of the BNBSST-100x ceramics increases with x increasing , reaching a maximum value of 35.6 μC/cm² and 3.51 kV/mm at x = 0.04, then P_r and E_C decreases when x further increasing, which indicating that the strongest ferroelectricity of BNBSST-4 ceramic in all the samples is inseparable from excellent piezoelectric properties at x = 0.04.

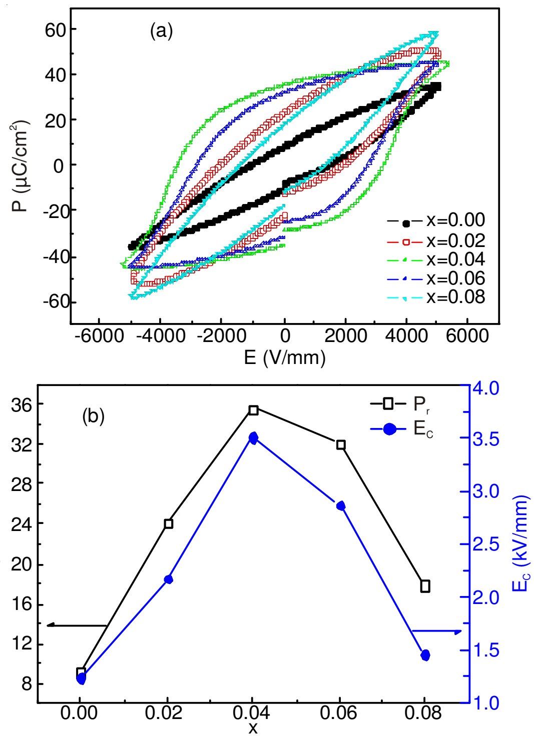


Fig. 4. (a) P-E curves and (b) P_r , E_C as a function of x for the BNBSST-100x ceramics at room temperature

Conclusion

New lead-free piezoelectric ceramics BNBSST-100x have been prepared by the conventional solid state sintering method. The crystal structures, microstructure, dielectric, piezoelectric and ferroelectric properties of the ceramics have been studied. X-ray diffraction confirms that a series of successive solid solution featured with a pure perovskite structure have been formed and morphotropic phase boundary of the ceramics exists at 0.02 < x < 0.06. The BNBSST-100x ceramics compared with pure bismuth sodium titanate ceramic show a relatively large P_r and low E_C and the piezoelectric properties of the ceramics also are significantly improved, which due to the morphotropic phase boundary. The BNBSST-4 ceramic sample near the morphotropic phase boundary shows excellent electrical properties, the optimum values of d_{33}, k_p, ε_r, tan δ, P_r and E_C are, respectively 203 pC/N, 41, 1128 and 2.6 %, 35.6 μC/cm² and 3.51 kV/mm, which suggests that the ceramics are very promising lead-free piezoelectric materials.

ACKNOWLEDGEMENTS

This work was supported by the National Natural Science Foundation of China (No. 51272001, 51072001, 51102073 and 61290301), the National Science Research Foundation of Education Ministry of China for Scholars Return from Overseas, the Natural Science Foundation of Education Department of Anhui Province (No. KJ2013B229).

REFERENCES

1. S. Katzir, *Arch. Hist. Exact Sci.*, **57**, 61 (2003).
2. T. Takenaka, K.- Maruyama and K. Sakata, *Jpn. J. Appl. Phys.*, **30**, 2236 (1991).
3. C.R. Zhou and X.Y. Liu, *J. Mater. Sci.*, **43**, 1016 (2008).
4. G.A. Smolenski and A.I. Aganovskaya, *Sov. Phys. Solid State*, **1**, 1429 (1960).
5. D. Lin, D. Xiao, J. Zhu and P. Yu, *J. Eur. Ceram. Soc.*, **26**, 3247 (2006).
6. G. Fan, W. Lu, X. Wang and F. Liang, *Appl. Phys. Lett.*, **91**, 202908 (2007).
7. Y.J. Dai, J.S. Pan and X.W. Zhang, *Key Eng. Mater.*, **336-338**, 206 (2007).