Key Engineering Materials
ISSN: 1662-9795, Vol. 492, pp 194-197
doi:10.4028/www.scientific.net/KEM.492.194

Online: 2011-09-27

Dielectric and Piezoelectric Properties of Lead Free $(1-x-y)Na_{1/2}Bi_{1/2}TiO_3$-$xBaTiO_3$-$yBiFeO_3$ Piezoelectric Ceramics

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Keywords: Piezoelectric; Dielectric.

Abstract. Lead-free $(1-x-y)Na_{1/2}Bi_{1/2}TiO_3$-$xBaTiO_3$-$yBiFeO_3$ ceramics were synthesized by ordinary sintering technique. The compositional dependence of phase structure and electrical properties of the ceramics was systematically investigated. All samples possessed pure perovskite structure. The dielectric and piezoelectric properties of ceramics were investigated with the amount of different $BiFeO_3$ substitutions. The addition of $BiFeO_3$ can not only decrease E_c and P_r but also lead to a significant degradation of the dielectric loss tanδ.

Introduction

For more than half a century, $(1-x)PbZrO_3$-$xPbTiO_3$ (PZT) ceramics are the most important and most widely used piezoelectric materials because of their excellent performance. However, PZT ceramics contain more than 60 wt% lead, the evaporation of lead caused serious environmental pollution. Thus, numerous investigators have developed alternative lead-free materials to PZT ceramics. Bismuth sodium titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (abbreviated to BNT), first discovered by Smolenshii et al. in 1960 [1], is an attractive lead-free A-site complex-perovskite due to its relatively large remanent polarization (P_r = 38 μC/cm^2) and high Curie temperature (T_c =320.8°C) [2-4]. However, high conductivity and high coercive field E_c can cause problems in the poling process, and thus limit its application. To deal with the problems, the solid solutions of BNT with other compounds and the combination of multiple additives have been widely investigated, such as BNT-$BaTiO_3$ [5], $(Na_{1/2}Bi_{1/2})TiO_3$-$NaNbO_3$ [6], $(Bi_{1/2}Na_{1/2})TiO_3$-$(Bi_{1/2}Li_{1/2})TiO_3$-$(Bi_{1/2}K_{1/2})TiO_3$ [7], BNT-$Bi_{1/2}K_{1/2}TO_3$-$BaTiO_3$ [8], $(Bi_{1/2}Na_{1/2})TiO_3$-$(Bi_{1/2}Li_{1/2})TiO_3$-$BaTiO_3$ [9], $(Bi_{1/2}Na_{1/2})TiO_3$-$(Bi_{1/2}K_{1/2})TiO_3$-$BiFeO_3$ [10] and so on. Among these, $0.94Na_{1/2}Bi_{1/2}TiO_3$-$0.06BaTiO_3$ has the excellent piezoelectric property.

In this study, Fe_2O_3 were added to $0.94Na_{1/2}Bi_{1/2}TiO_3$-$0.06BaTiO_3$ (abbreviated as BNBT6) ceramics by forming a new solid solution to promote sintering and get better electrical properties. The effects of additives on the phase transition behavior and electrical properties have been studied.

Experimental

$(1-x-y)Na_{1/2}Bi_{1/2}TiO_3$-$xBaTiO_3$-$yBiFeO_3$ (x = 0.06, y=0, 0.01, 0.02, 0.03) were prepared using analytical grades of Na_2CO_3 (99.8%), and Bi_2O_3 (99.64%), Fe_2O_3 (99.0%), $BaCO_3$ (99.9%) and TiO_2 (99.0%). The powders were mixed in a nylon bottle for 12 h using ZrO_2 milling media in anhydrous ethanol. The dried powders were pressed into disks at 70 MPa prior to reaction at 880°C for 4 h to form the desired perovskite phase. The crushed calcined pellets were again ball milled for 12 h, followed by the addition of 5 wt% PVA binder and pressed into 15mm diameter disks with 1.5mm thickness at 200 MPa. After burning out the PVA binder at 650°C for 3 h, the disks were sintered at 1180°C for 3 h. Densities of the samples were determined using the Archimedes method. To measure the electrical properties, silver electrodes were made on both surfaces of the sintered disks.

The microstructure of the sample surfaces was analyzed by scanning electron microscopy (SEM) (JSM-5380, Japan) and the phase was analyzed by X-ray diffraction (XRD) using Cu Kα radiation (λ = 1.54178 Å) in the 2θ range of 20°-80° (D8 Advance, Bruker incorporation, Germany). P–E hysteresis loops were recorded at room temperature using an aix-ACT TF 2000FE-HV ferroelectric test unit (Trek610D). Polarization was carried out in silicon oil at 30 kV/cm field for 20 min and the piezoelectric coefficient d_{33} was measured using a quasi-static d_{33} meter (Sznocera Piezotronics INC). The dielectric properties were determined using an Agilent 4294A precision Impedance Analyzer in the temperature range from 25°C to 450°C. The electromechanical coupling factor k_p was determined by the resonance and antiresonance method according to IEEE standards using an impedance analyzer (Agilent4294A).

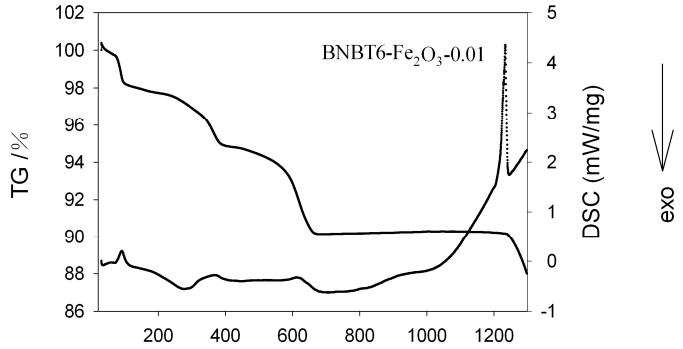

Fig. 1. TG-DSC patterns of the BNBT6-yBiFeO$_3$ ceramics powder

Results and Discussion

Analysis of thermal properties of powders. According to the TG-DSC results shown in Fig.1, there was a rapid decrease in the powers weight at approximately 100, 400 and 600°C under flowing dry air conditions. Since the reaction temperature for a large batch would be higher than that observed under TG conditions, 850°C were chosen as the holding temperatures for the step treatment. By holding at these temperatures, there was sufficient time to enhance the decomposition of carbonate and formation of BNBT6-yBiFeO$_3$ ceramics. What is more, from the TG/DSC patterns of the ceramic powders we can see the temperature of the reaction and the sintering.

Structural and microstructural studies. The XRD patterns of the samples are shown in Fig.2. All patterns exhibit a single perovskite phase, no secondary phase can be detected, which means that Ba^{2+} and Fe^{3+} have diffused into the lattice to form a solid solution.

Fig. 3 shows the cross-section morphological features of BNBT6-yBiFeO$_3$ ceramics modified with different concentrations of BiFeO$_3$ sintered at 1180°C for 3 h. From the SEM images, it can be seen that the grains have regular crystal shape and the crystalline boundaries are clearly observed in all samples .It can be observed that all samples have dense microstructures .The addition of BiFeO$_3$ has a little influence on the growth of BNBT6-yBiFeO$_3$ ceramics. It is evidently from Fig. 3 that the grain size of the specimens with the increasing of BiFeO$_3$ content is increased.

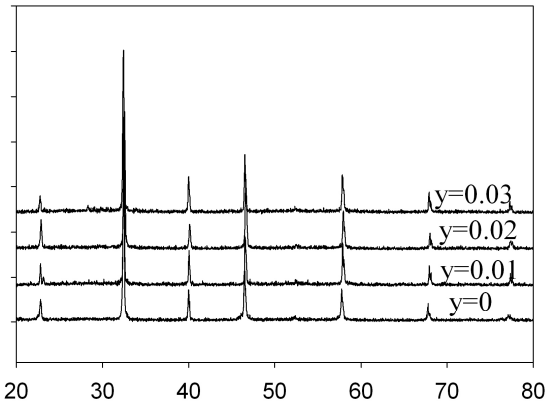

Fig.2 XRD patterns of the BNBT6-yBiFeO$_3$ ceramics sintered at 1180°C

Ferroelectric and piezoelectric studies. The P-E measurements for specimens are summarized in Fig.4. It is shown that the remnant polarization P_r of the BNBT6-yBiFeO$_3$ ceramics decrease from 37 to 25μC/mm^2 while the coercive field E_c also decrease as y varies from 0 to 0.03. The optimum ferroelectric

properties (P_r=25μC/cm^2, E_c=3.25kV/cm) of the ceramics is obtained at y=0.02. As mentioned above, pure BNBT6 ceramics have a remnant polarization P_r of 37μC/cm^2 and relatively high coercive field E_c of 4.0 kV/cm. Comparing with pure BNBT6 ceramics, BNBT6-y$BiFeO_3$ ceramics possess a lower P_r as well as a lower E_c. It is well known that low E_c makes the ceramics easily poled and lower P_r is beneficial to the piezoelectric properties. These results lead to the conclusion that the addition of $BiFeO_3$ can decrease E_c and P_r.

Table 1 gives the dielectric, piezoelectric, and physical properties of BNBT6-y$BiFeO_3$ ceramics. From table 1 we can see that the least dielectric loss tanδ, and piezoelectric constant appear at y=0.02. And what is more all doped sample present lower dielectric loss tanδ with respect to those of the non-doped samples [8].

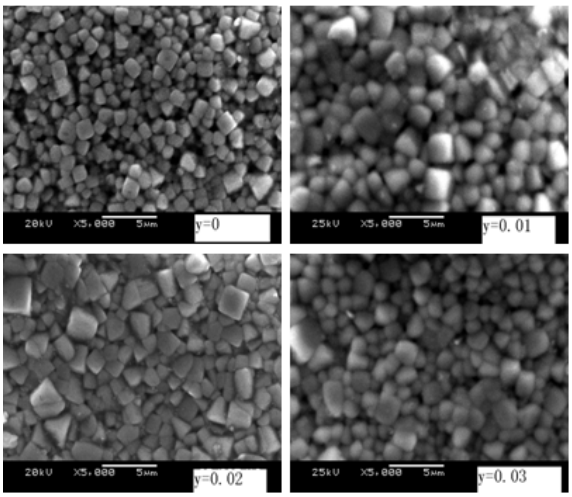

Fig.3 SEM micrograph of the (1-x-y)$Na_{1/2}Bi_{1/2}TiO_3$-x$BaTiO_3$-y$BiFeO_3$ ceramics

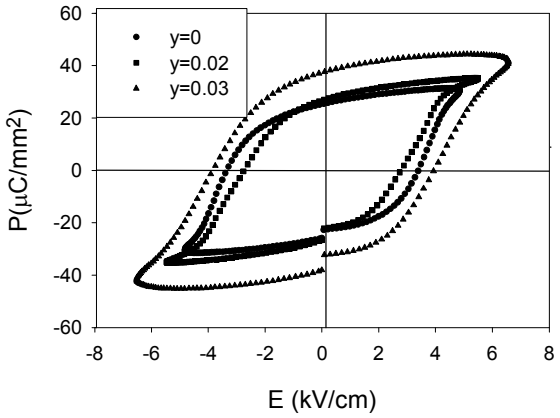

Fig. 4. P-E hysteresis loops of (1-x-y)$Na_{1/2}Bi_{1/2}TiO_3$-x$BaTiO_3$-y$BiFeO_3$.

Table 1 Physical constants of BNBT6-y$BiFeO_3$ ceramics for different $BiFeO_3$ doping amounts.

Compositions	0	0.01	0.02	0.03
d_{33}	122	131	141	112
K_p	0.158	0.142	0.249	0.156
Q_m	171	138	147	118
*Tan*δ (10kHz)	0.615	0.3119	0.3285	0.4167
ρ(g/cm^2)	5.86	5.45	5.5	5.40

Dielectric studies. Fig.5 shows the temperature dependence of dielectric constants ε_r of (1-x-y)$Na_{1/2}Bi_{1/2}TiO_3$-x$BaTiO_3$-y$BiFeO_3$ ceramics as a function of x at 1, 10 and 100kHz. Similar to the BNT ceramics, two abnormal dielectric peaks were observed for all samples, which originate from the phase transition from ferroelectric to anti-ferroelectric (T_d) and anti-ferroelectric to paraelectric phase(T_m), respectively. It can be observed that ε_r for all ceramics show frequency dependence. ε_r for all ceramics decreases with the increasing of frequency. The T_d and T_m also exhibit obvious dependence on the frequency. With increasing frequency, both T_d and T_m move to higher temperatures.

Summary

BNBT6 ceramics spatially substituted with $BiFeO_3$ were prepared by ordinary sintering technique, and their structure and electrical properties were studied. Results showed that the ceramics $BiFeO_3$ have diffused into the lattice to form a solid solution. And with the increase of $BiFeO_3$ can not only decrease E_c and P_r but also lead to a significant degradation of the dielectric loss tanδ.

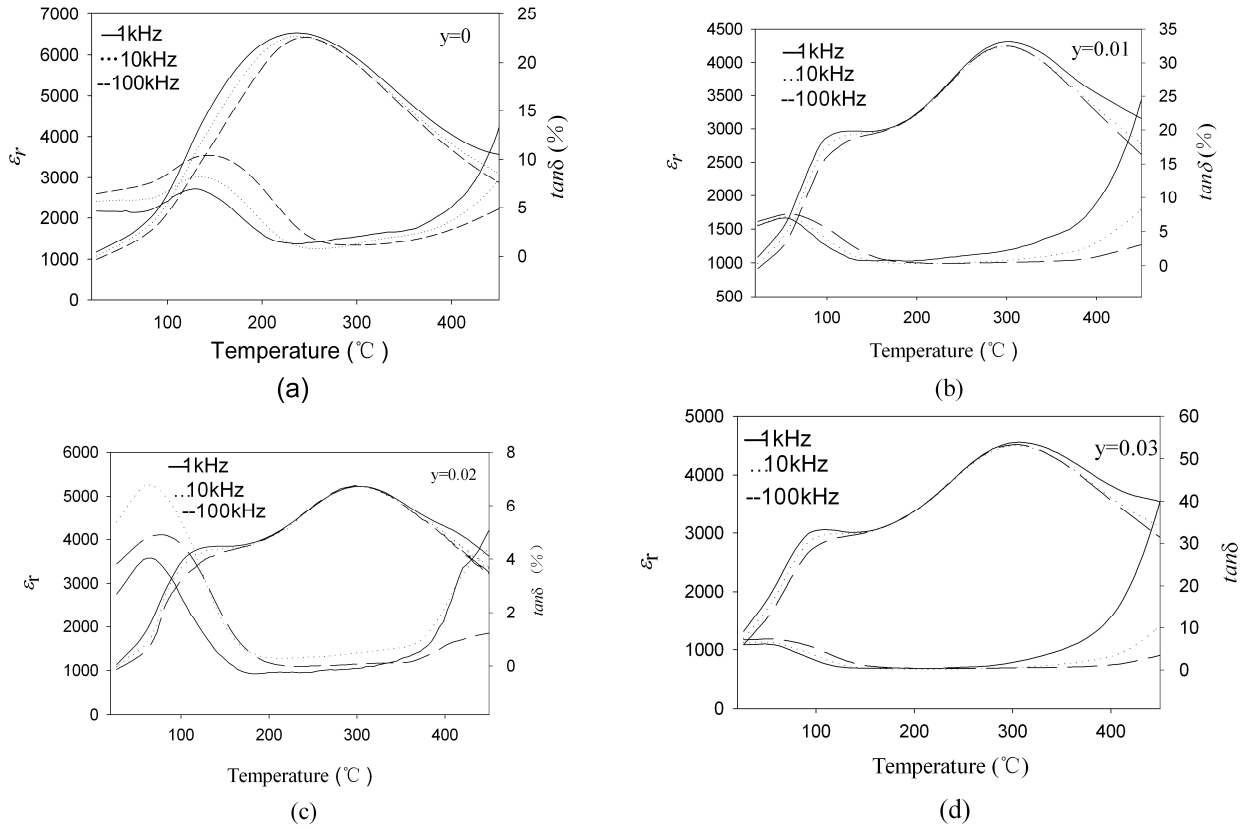

Fig. 5 Temperature dependence of dielectric constants ε_r and dielectric loss *tan*δ of BNBT6- y$BiFeO_3$ ceramics as a function of y at different frequency: (a) y = 0, (b) y = 0.01, (c) y = 0.02, (d) y = 0.03

Acknowledgements

This work was Supported by the technology research Foundation of Shandong province (No. 2008GG10003011), the Doctor Foundation of Shandong province (Grant No. 2007BS04047), the Sciences Innovation Foundation of Shandong province (Grant No. 2007ZZ42) and the Science key project Foundation of Ministry of Education (No. 208075).

References

[1] G. Smolenskii, V. Isupov, A. Agranovskaya, et al.: Sov. Phys. Sol. Sta. Vol. 11 (1961), p. 2651.

[2] T. Takenaka, K. Maruyama and K. Sakata:Appl. Phys. Vol. 30 (1991), p.2230.

[3] T. Takenaka, K. Sakata: Ferroelectrics Vol. 95 [1] (1989), p.153.

[4] Q.B. Yang, X.Z. Jing Y.X. Li, et al: Electronic Components and Materials. Vol. 23 (2004).

[5] Q. Xu, S.J. Wu, S. T. Chen, et al: Materials Research Bulletin. Vol. 40[2] (2005), p. 373.

[6] Y.M. Li, W. Chen, J. Zhou, et al: Materials Science and Engineering B Vol. 112 [1] (2004), p.5.

[7] Z.p. Yang, Y.T. Hou, H. Pan, et al: Journal of Alloy and Compounds Vol.480 (2009),p.246.

[8] X. Y. Wang, C. L. Wang, M. L. Zhao, etal: Materials Letters Vol.61 (2007),p.3847.

[9] P.Jarupoom, K.Pengpat, N.Pisitpipathsin, et al: Current Applied Physics Vol.8 (2008),p.253.

[10] C.R. Zhou, X.Y. Liu,W. Z. Li, et al: Mater. Chem. Phys.Vol.114 [2-3] (2009),p.832 .