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Morphotropic phase boundary and electrical properties of lead-free bismuth sodium lanthanum titanate—barium titanate ceramics

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Abstract The important properties of lead-free piezoelectric ceramics have been investigated from Bismuth Sodium Lanthanum Titanate and Barium Titanate system: $(1-y)(Bi_{0.5}Na_{0.5})_{(1-1.5x)}La_xTiO_3$(BNLT)—$y$BaTiO$_3$(BT) where $x = 0.017$ and $y = 0 - 0.2$, respectively. The morphotropic phase boundary (MPB) was found to be around $y = 0.1$ by the x-ray diffraction and dielectric measurement at various amount of BT. The temperature dependence of dielectric constant (ε_r) at various value of y showed the diffuse phase transition exhibiting the relaxor type ferroelectrics. The degree of diffuseness increased at a high doping content of about $y = 0.15$ where the second phase transition (T_2) of the ferroelectric to antiferroelectric phase disappeared. Moreover, this sample had the maximum piezoelectric coefficient (d_{33}) of about 112 pC/N with relatively low dielectric constant. The optimum sintering temperatures and the microstructures of the dense BNLT-BT ceramics were also examined.

Keywords BNLT · BT · Lead -free piezoelectric ceramic · Conventional ceramic method

1 Introduction

Bismuth Sodium Titanate $(Bi_{0.5}Na_{0.5})TiO_3$, as abbreviated to BNT, is a perovskite ferroelectric relaxor-type material discovered by Smolenskii et al [1]. At room temperature, BNT is strongly ferroelectric and has the Curie temperature $T_c = 320°C$, remanent polarization $P_r = 38\ \mu C/cm^2$ and coercive field $E_c = 73$ kV/cm. This material has been studied continually by several researchers [2, 3]. It has phase transitions which are the rhombohedral to tetragonal phase at about $200^\circ C$ (T_2). The tetragonal-rhombohedral transition corresponds to a transformation from an antiferroelectric state to a ferroelectric state.

Recently, BNT-based ceramic materials are of interest as a new candidate for lead-free piezoelectric materials to replace the widely used lead-based perovskite materials, because of the free control of sintering atmosphere and the release of lead pollution during the preparation process of BNT. However, the electrical properties of the BNT ceramic are quite poor comparing to those found in Lead-based piezoelectric ceramics. To improve its properties, several solid solutions of BNT based materials, such as BNT-PbTiO$_3$[4], BNT-SrTiO$_3$[5, 6], BNT-CaTiO$_3$[7], BNT-Ba(Ti,Zr)O$_3$[8] and BNT-BaTiO$_3$[6, 9] have been studied. Among those the $(1-x)(Bi_{0.5}Na_{0.5})TiO_3{-}x$BaTiO$_3$ ceramics, studied by Takenaka, [9] had relatively good piezoelectric properties especially at the morphotropic phase boundary (MPB) where x is close to 0.06 mole [10–13]. Another way to improve the electrical properties of BNT is by the addition of a modifier element such as Nb^{5+}, Co^{3+}[12], Fe^{3+}[14] and La^{3+}[15] etc. Aree Harabut and Ahmad Safari [15] reported the effect of La additive on piezoelectric properties of $(Bi_{0.5}Na_{0.5})_{(1-1.5x)}La_xTiO_3$:BNLT ceramics. It was found that the dielectric constant (ε_r) and a piezoelectric charge constant (d_{33}) increased up to 550 and 91 pC/N respectively, where the La doping content was 1.72 at.%.

Consequently, those two previous works of a solid solution method ($(1-x)(Bi_{0.5}Na_{0.5})TiO_3{-}x$BaTiO$_3$) and the rare earth additive of La^{3+} brought about the idea of this project which was aimed at producing the ceramics from

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$(Bi_{0.5}Na_{0.5})_{(1-1.5x)}La_xTiO_3$(BNLT) $-y$$BaTiO_3$(BT) system where the optimum values of x have been chosen from the work done by Aree Harabut and Ahmad Safari and y have been varied between 0 and 0.20. The effect of BT content and also sintering condition on the physical, dielectric and piezoelectric properties of BNLT-BT ceramics were investigated. The microstructures of the ceramics in this system were also examined.

2 Experimental procedure

The starting chemicals for producing $(Bi_{0.5}Na_{0.5})_{(1-1.5x)}La_xTiO_3$(BNLT) $-y$$BaTiO_3$(BT) ceramics, where $x = 0.017$ and $y = 0$, 0.06, 0.10, 0.15 and 0.2, were the reagent grade bismuth oxide (Bi_2O_3), sodium carbonate (Na_2CO_3), Lanthanum oxide(La_2O_3), titanium oxide (TiO_2) and barium carbonate ($BaCO_3$). The batch compositions of BNLT and BT were weighed and mixed via vibro-milling method for 30 min. Then both mixtures of BNLT and BT were dried and calcined at 950°C (for pure perovskite) and 1200°C respectively. Both powders were then again mixed corresponding to the above ratio by vibro-milling method for 30 min with acetone as a milling media. After drying and sieving the mixture, the resulting powder was made into pellets of 15 mm in diameter with thickness of about 2 mm using uniaxial pressing in stainless steel mold. The pellets were then sintered between 1100°C and 1175°C in an electric furnace and air atmosphere under controlled heating/cooling rates of 3°C/min with 2 h dwell time. The phase identification and density of sintered ceramic composite samples were investigated using the X-ray diffraction technique (XRD: Siemen D−500) and Archimedes's method respectively. The microstructures of the sintered ceramics were observed using scanning electron microscope (SEM: JSM-6335F). The sintering pellets were polished and then sliver paste was applied on to both surfaces for electrical contact. The dielectric constant (ε_r) of the selected ceramics was carried out between room temperature and 450°C at various frequencies from 100Hz, 1kHz and 10kHz using an LCZ-meter (HP4192A). The samples were poled at 80°C in silicone oil bath with DC field of 25–30 kV/cm for 30 min before piezoelectric measurement. The piezoelectric charge coefficient (d_{33}) of the samples was measured using a piezoelectric-d_{33}-meter (PM3001, KFC TECH).

3 Results and discussion

The maximum density of the ceramics from $(1-y)$BNLT-yBT system where $y = 0.06 - 0.2$ was obtained at the same sintering temperature of about 1150°C as can be seen in Fig. 1. A single-phase perovskite could be obtained in this system with rhombohedral, tetragonal symmetry or mixing of both symmetries in each XRD pattern at various BT content which can be distinguished by the splitting of XRD peak at 2θ range between 45° and 47° as shown in Fig. 2. The structural symmetry of BNLT ($y = 0.0$) sample is rhombohedral which is corresponding to the single peak at about 46.8° in its XRD pattern. The splitting of the peak starts to appear at $y = 0.1$ and becomes stronger with increasing amount of BT. The mixing of tetragonal and rhombohedral symmetries indicating the MPB of this system, was found at around $y = 0.10$. This may be confirmed by the maximum dielectric constant (ε_r) at room temperature of $y = 0.1$ sample as illustrated in Fig. 3. The MPB of this system is different from that of Takenaka [9] who reported the MPB of around $x = 0.06$ in (1-x)BNT-xBT system. It may be assumed that the addition of La^{3+} of about 1.7 at.% in our system shifted the MPB to the higher content of BT of about $y = 0.1$. This may be caused by the lattice distortion of La-doped BNT or BNLT powder before the addition of BT powder. How-

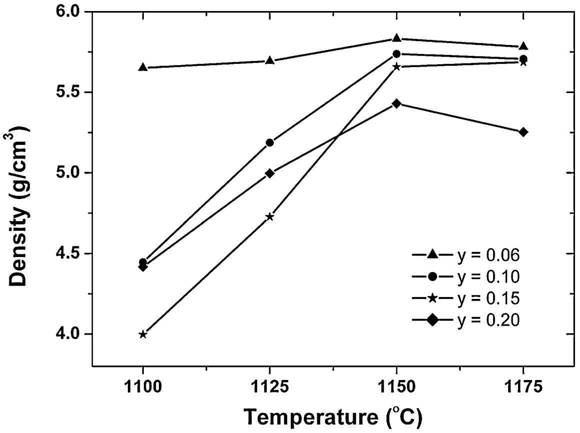

Fig. 1 The density of the ceramics from $(1-y)$BNLT - yBT system versus sintering temperature at various value of y

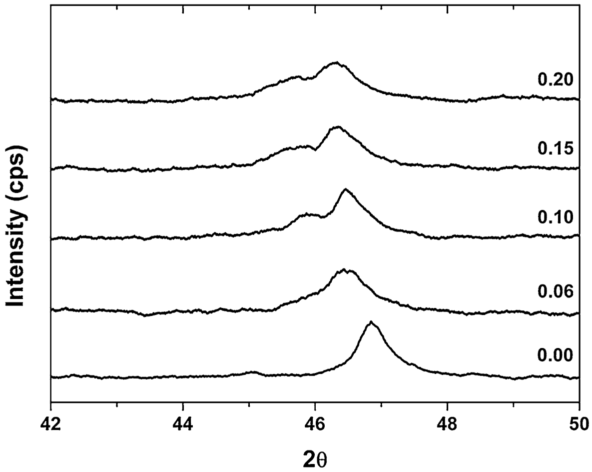

Fig. 2 X-ray diffraction patterns of $(1-y)$BNLT$-y$BT ceramics at various value of y at 2θ between 42° and 45°

Table 1 The two phase transitions: T_2 and T_C in this work and others

Sample	BT (mol%)	La (at%)	T_2 (˚C)	T_C (˚C)
0.94BNLT−0.06BT[a]	6	1.7	156	314
0.90BNLT−0.10BT[a]	1	1.7	142	303
0.85BNLT−0.15BT[a]	1.5	1.7	–	269
BNT [16]	0	0	200	320
BNBT−6+1 at.% La [12]	6	1	125	275

[a] Samples prepared in this work

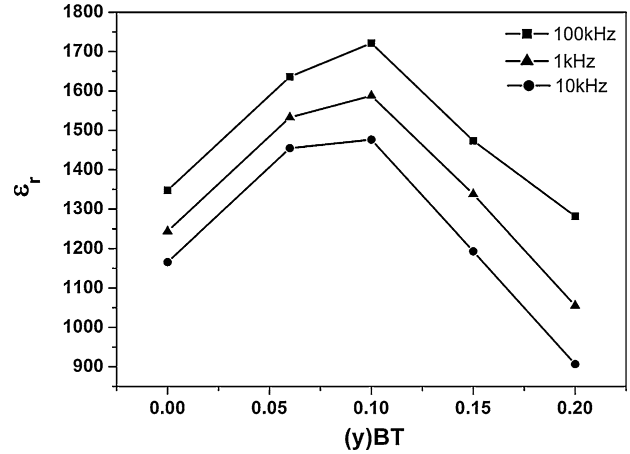

Fig. 3 The dielectric constant (ε_r) at room temperature versus composition of BT $(1-y)$BNLT $-y$BT ceramics: $y = 0 - 0.2$ mole, at various frequencies

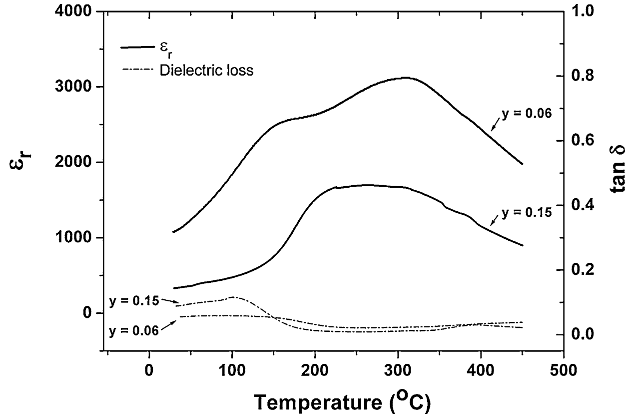

Fig. 4 Temperature dependences on dielectric constant and dielectric loss of $(1-y)$BNLT$-y$BT ceramics ($y = 0.06$ and 0.15) at frequency of 10 kHz

ever, more detailed study is needed to be carried out in order to establish the complete phase diagram near MPB of this system.

The temperature dependences on dielectric constant and dielectric loss of the selected ceramic samples of $y = 0.06$ and 0.15 are presented in Fig. 4. The ceramic sample having $y = 0.06$ has two phase transition of $T_2 = 156$ ˚C and $T_C = 314$ ˚C. The phase transitions of other samples in our work and some researchers are also tabulated in Table 1. Li et al [12] studied the $(Bi_{1/2}Na_{1/2})TiO_3$(BNT) – $BaTiO_3$(BT) system, they added 1 at.%La in the BNBT-6 sample which was at MPB of BNT-BT system and found similar result of ε_r versus temperature curve as observed in our work ($y = 0.06$ sample). However, their two phase transitions of T_2 and T_C are at the lower temperature as compared in Table 1. This may be due to the slightly different in La^{3+} content as in our work the 1.7 at.%La was chosen. Consequently, the addition of rare earth ion $La^{3+}$and alkaline earth ion Ba^{2+} may shift these two phase transitions: T_2 and T_C, to a lower side of that found in a normal BNT ceramic where T_2 and T_C are 200 and 320 ˚C respectively. [16] In addition, it can be recognized that the increase of BT(y) content lowers the T_2 and T_C of the ceramics in the $(1-y)$BNLT$-y$(BT) system. However, the second phase transition (T_2) is very broad for the ceramic sample of $y = 0.15$, remaining only one broad dielectric peak of T_C related to tetragonal-cubic phase transition at approximately 269 ˚C. Interestingly, the corresponding dielectric loss of this sample shows the sharply drop at about 100 ˚C indicating the evidence of phase transition from ferroelectric to antiferroelectric phase similar to that found in the ceramic sample of $y = 0.06$ showing the drop of dielectric loss at its T_2 of around 156 ˚C. This result is consistent with the work done by Takenaka and his coworkers who revealed the drop of dielectric loss at around T_2 of the $(Bi_{0.5}Na_{0.5})_{1\text{-}x}Ba_xTiO_2$ ceramic where $x = 0.05$. [9] Even though, the diffuseness of the dielectric curve could be enhancing in this sample but overall dielectric constant is low. Moreover, it is interesting that the maximum piezoelectric coefficient (d_{33}) was obtained at this 0.85BNLT-0.15BT sample which is about 112 pC/N. This may be useful in ultrasonic applications where low dielectric constant and high frequency content is needed [13].

Figure 5(a) and (b) show the SEM micrographs of BNT and $(1-y)$BNLT$-y$BT ceramics respectively. No significant change in grain size and shape was observed where La^{3+} was doped in BNT ceramics (BNLT) as can be seen in Fig. 5(a) and (b). This may be due to the similar ionic radius between La^{3+} (130 pm) and Bi^{3+} (131pm) or the doping amount is very low. However, the small addition of BT into the BNLT ceramic inhibited the grain growth considerably as can be clearly seen in Fig. 5(c). It can be noticed that the ionic radius of Ba^{2+}(156 pm) is larger than that of Bi^{3+}. In this case, the grain growth mechanism seems to depend on the ionic radii of A-site ions. However, the further addition of BT up to 0.15

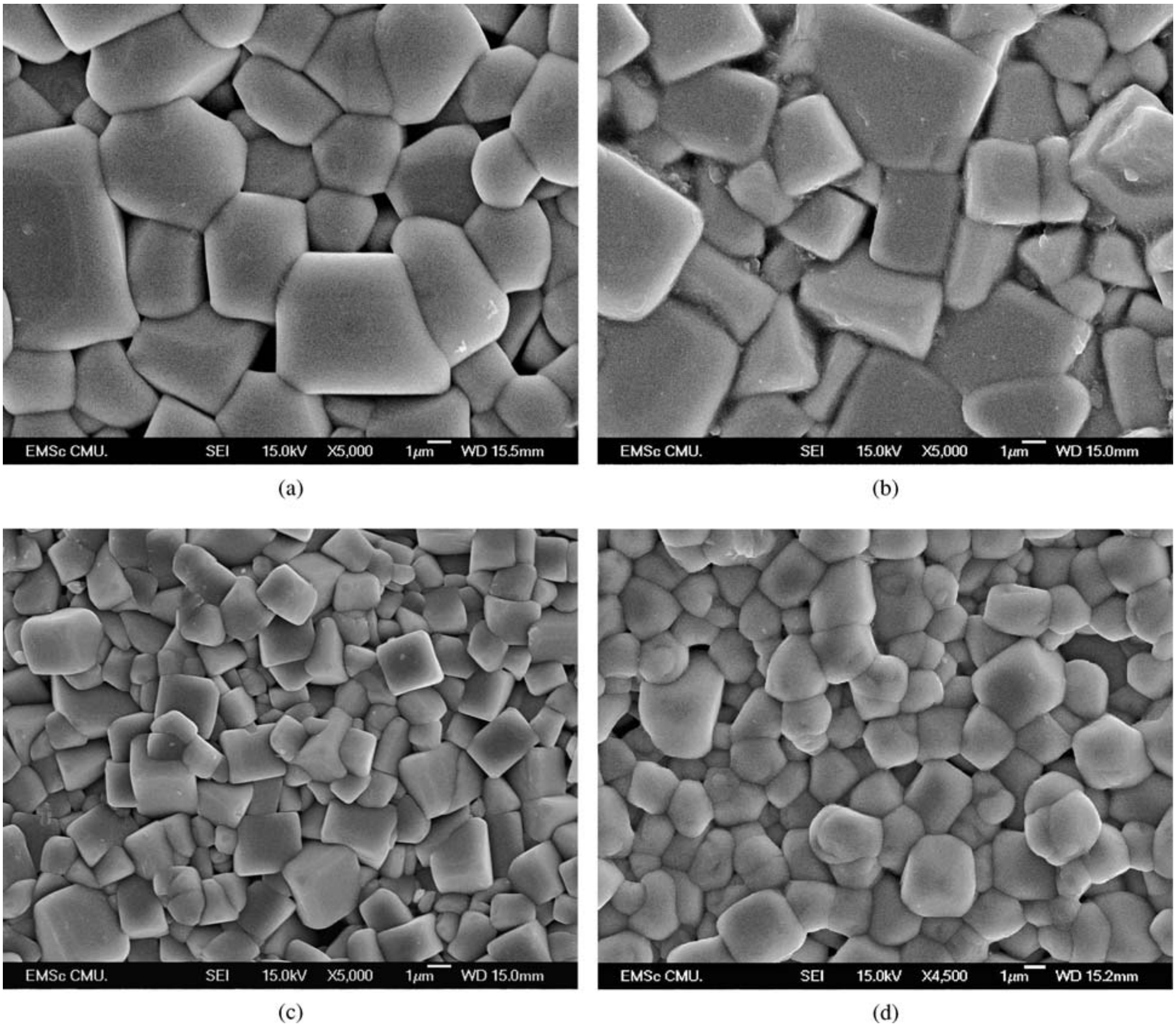

Fig. 5 SEM micrographs of (a) BNT and (b)–(d) $(1-y)$BNLT$-y$BT ceramics where (b) $y = 0$, (c) $y = 0.06$ and (d) $y = 0.15$

mole (Fig. 5(d)) caused insignificant effect on grain growth of this ceramic but the grain shape became rounder with high porosity.

4 Conclusions

The system of $(1-y)(\mathrm{Bi}_{0.5}\mathrm{Na}_{0.5})_{(1-1.5x)}\mathrm{La}_x\mathrm{TiO}_3$(BNLT) $-y\mathrm{BaTiO}_3$(BT) where $x = 0.0172$ and $y = 0 - 0.2$ was investigated. The optimum sintering temperatures for producing a relatively dense ceramics were at 1150 °C for all value of y. The MPB was found to be around $y = 0.1$ where at this point the maximum ε_r at room temperature was also obtained. The maximum d_{33} was found together with relatively low ε_r from the $(1-y)$BNLT$-y$BT ceramic sample of $y = 1.5$. In this sample, the very broad peak of the ε_r curve over the wide range of temperature with low dielectric constant was obtained which may be useful in ultrasonic applications.

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References

1. G.A. Smolenskii, V.A. Isupov, A.I.Agranovskaya, and N.N. Kraink:Sov. *Phys.Solid State*, **2**, 2651 (1961).
2. I.P. Pronin, P.P. Syrnikov, V.A. Isupov, V.M. Egorov, N.V. Zaitseva, and A.F. Ioffe, “Peculiarities of phase transition in bismuth sodium titanate”, *Ferroelectrics*, **25**, 395 (1980).
3. J.V. Zvirgzds, P.P. Kapostis, and T.V. Kruzina, “X-ray study of phase transition in ferroelectric $\mathrm{Bi}_{0.5}\mathrm{Na}_{0.5}\mathrm{TiO}_3$,” *Ferroelectrics*, **40**, 75 (1980).

4. K. Sakata, T. Takenaka, and Y. Naitou, *Ferroelectrics*, **131**, 219 (1992) .
5. K. Sakata and Y. Masuda, *Ferroelectrics*, **5**, 347 (1994).
6. J. Suchanicz, J. Kusz, H. Bohm, H. Duda, J.P. Mercurio, and K. Konieczny, *J. Eur. Ceram. Soc.*, **23**, 1559 (2003).
7. T. Takenaka, K. Sakata, and K. Toda, *Jpn. J. Appl. Phys.*, **28**, 59 (1989).
8. Chun Peng, Jing-Feng, and Wen Gong, *Mater. Lett.*, In press.
9. T. Takenaka, K.-I. Maruyama, and K. Skata, *Jpn. J. Appl. Phys.*, **30**(9B), 2246 (1991).
10. K. Sakata and Y. Masuda, *Ferroelectrics,* **7**, 347 (1974).
11. S. Said and J.P. Mercario, *J. Eur. Ceram. Soc.*, **21**, 1333 (2001).
12. H.D. Li, C. Feng, and W.L. Yao, *Mater. Lett.*, **58**, 1194 (2004).
13. B.J. Chu, D.R. Chen, G.R. Li, and Q.R. Yin, *J. Euro. Ceram. Soc.*, **22**, 2115 (2002).
14. X.X. Wang, K.W. Kwok, X.K. Tang, H.L.W. Chan, and C.L. Choy, *Solid State Comm.*, **129**, 319 (2004).
15. A. Herabut and A. Safari, *J. Am. Ceram. Soc*, **80**(11), 2954 (1997).
16. H. Nagata and T. Takennaka, *J. Euro. Ceram. Soc*, **21**, 1299 (2001).