[논 문] 한국재료학회지
Korean J. Mater. Res.
Vol. 25, No. 10 (2015)

http://dx.doi.org/10.3740/MRSK.2015.25.10.566

Structural, Dielectric and Field-Induced Strain Properties of La-Modified $Bi_{1/2}Na_{1/2}TiO_3$-$BaTiO_3$-$SrZrO_3$ Ceramics

Ali Hussain[1], Adnan Maqbool[1], Rizwan Ahmed Malik[1], Arif Zaman[1,2], Jae Hong Lee[1], Tae Kwon Song[1], Jae Hyun Lee[1], Won Jeong Kim[3] and Myong Ho Kim[1†]

[1]School of Advanced Material Engineering, Changwon National University, Gyeongnam 641-773, Korea
[2]Department of Physics, Abdul Wali Khan University, Mardan, KPK, Pakistan
[3]Department of Physics, Changwon National University, Gyeongnam 641-773, Korea

(Received July 27, 2015 : Revised August 25, 2015 : Accepted September 8, 2015)

Abstract $Bi_{0.5}Na_{0.5}TiO_3$ (BNT) based ceramics are considered potential lead-free alternatives for $Pb(Zr,Ti)O_3$(PZT) based ceramics in various applications such as sensors, actuators and transducers. However, BNT-based ceramics have lower electromechanical performance as compared with PZT based ceramics. Therefore, in this work, lead-free bulk $0.99[(Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}]_{(1-x)}La_xTiO_3$-$0.01SrZO_3$ (BNBTLax-SZ, with $x = 0$, 0.01, 0.02) ceramics were synthesized by a conventional solid state reaction The crystal structure, dielectric response, degree of diffuseness and electric-field-induced strain properties were investigated as a function of different La concentrations. All samples were crystallized into a single phase perovskite structure. The temperature dependent dielectric response of La-modified BNBT-SZ ceramics showed lower dielectric response and improved field-induced strain response. The field induced strain increased from 0.17 %_for pure BNBT-SZ to 0.38 % for 1 mol.% La-modified BNBT-SZ ceramics at an applied electric field of 6 kV/mm. These results show that La-modified BNBT-SZ ceramic system is expected to be a new candidate material for lead-free electronic devices.

Key words lead-free, piezoelectric, relaxor, BNT-BT.

1. Introduction

New lead-free piezoceramics with enhanced electromechanical properties are required for environmentally benign commercial piezoelectric applications.[1)] Many research efforts have been devoted to the solid solutions of bismuth-based perovskite ceramics.[2-6)] Among these systems, the $Bi_{1/2}Na_{1/2}TiO_3$-$BaTiO_3$ (BNT-BT) is considered a good candidate for technical applications because its properties can be easily engineered through proper chemical modifications.[7-10)]

The binary system of BNT-BT exhibits a morphotropic phase boundary (MPB) around 5-7 mol% BT,[7)] and show good electromechanical properties. The high piezoelectric coefficient and low permittivity make it superior candidate for high-frequency ultrasonic applications and piezoelectric actuator devices. Numerous researchers have focused to modify this system with perovskite solid solutions to achieve improved electromechanical properties.[11-13)] Among them many efforts have been concentrated on A- and/or B-site doping to improve the electromechanical performance.[14-16)] It has been reported that either replacing Bi on the A-site or all A-site cations in BNT-based ceramics are effective strategies for enhancing the electromechanical properties.[17,18)] Compositional modifications with aliovalent cations are scientifically interesting since small dopants can considerably enhance the electromechanical properties because of the cation vacancy formation.

La has been used to modify several archetypal perovskites, such as $Pb(Zr,Ti)O_3$, and $Ba_{1/2}Na_{1/2}TiO_3$.[19-21)] Isovalent doping has shown to be a reliable approach to tailor the dielectric and electromechanical properties of the BNT-based ceramics.[18,19)] However, to examine the effect of aliovalent doping in BNT-based ceramics, this work was carried out on the conventional synthesis of La doping in the BNBT-SZ ceramic system. Furthermore, the effect of La doping on crystal structure, dielectric, relaxor pro-

†Corresponding author
E-Mail : mhkim@changwon.ac.kr (M. H. Kim, Changwon Nat'l Univ.)

perties and field-induced strain properties of BNBT-SZ ceramics were investigated in detail.

2. Experimental

$0.99[(Bi_{0.5}Na_{0.5})_{0.935}Ba_{0.065}TiO_3]$-$0.01SrZO_3$ (BNBT-SZ) system was selected as a base material and La was introduced according to the chemical formula $0.99[(Bi_{0.5}$-$Na_{0.5})_{0.935}Ba_{0.065}]_{(1-x)}La_xTiO_3$-$0.01SrZO_3$ in composition range $x = 0$-0.02. All samples were produced by a conventional solid state method using Bi_2O_3 (99.90 %), Na_2CO_3 (99.95 %), $BaCO_3$ (99.0 %), $SrCO_3$ (99.90 %), TiO_2 (99.99 %) ZrO_2 (99.99 %) and La_2CO_3 (99.99 %) as raw materials (Sigma Aldrich Co. St. Louis, MO). The powders were first dried in an oven at 100 °C for 24 h. The dried powders were then weighed according to the stoichiometric formula and ball-milled with zirconia ball as media for 24 h in ethanol. The dried slurries were calcined at 850 °C for 2 h and ball-milled again to dissociate the agglomerates. After further drying, the powders were pulverized, passed through a sieve with a 150 mesh, and mixed with an aqueous polyvinyl alcohol (PVA) solution as a binder for granulation. The granulated powders were subsequently pressed into green disks of diameter 10 mm at 150 MPa. The green bodies were embedded in a powder of the same composition to minimize the evaporation of the volatile elements (Bi, Na); all the compositions were then sintered at 1160 °C for 2 h in air.

The crystal structure of the sintered samples was characterized using an X-ray diffractometer (XRD: Miniflex II Rigaku). To measure the electrical properties, silver paste was coated on both polished faces of the sintered samples and fired at 650 °C for 0.5 h to form electrodes. The dielectric constant and loss of samples were measured using an automatic acquisition system with an impedance analyzer (Agilent HP4292A, USA) in the temperature range of 25-500 °C. Field-induced strain curves were measured using a contact type displacement sensor (Millitron: Model 1240) at 50 mHz.

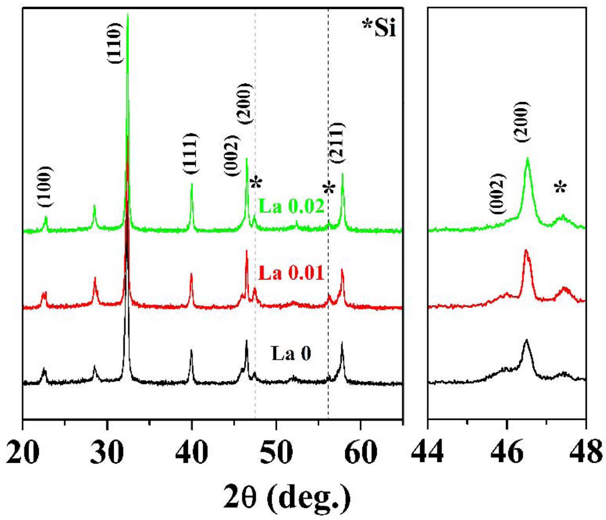

Fig. 1. X-ray diffraction patterns of La-modified BNBT-SZ ceramics.

3. Results and Discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of BNBTLa-SZ ceramics. All sample showed a single phase perovskite structure without any evidence of secondary phases. This indicates that La is successfully diffused into BNBT-SZ lattice to form a complete solid solution. The symbol (*) in the XRD pattern shows Si peak that is used as an internal standard for clarifying the peaks shifting behavior of different samples. The diffraction peaks of pure BNBT-SZ ceramics show tetragonal symmetry evident by splitting (002)/(200) at 2θ angle 46°. This splitted (002)/(200) at 2θ angle 46° merge into a single peak (002) of a pseudo-cubic symmetry with increasing amount of La content. This result is consistent with the previous reports found in the literature for similar lead-free materials.[22-24] When La is substituted into BNBT-SZ lattice, it is possible to form either cation vacancies, reduced concentration of oxygen vacancies or

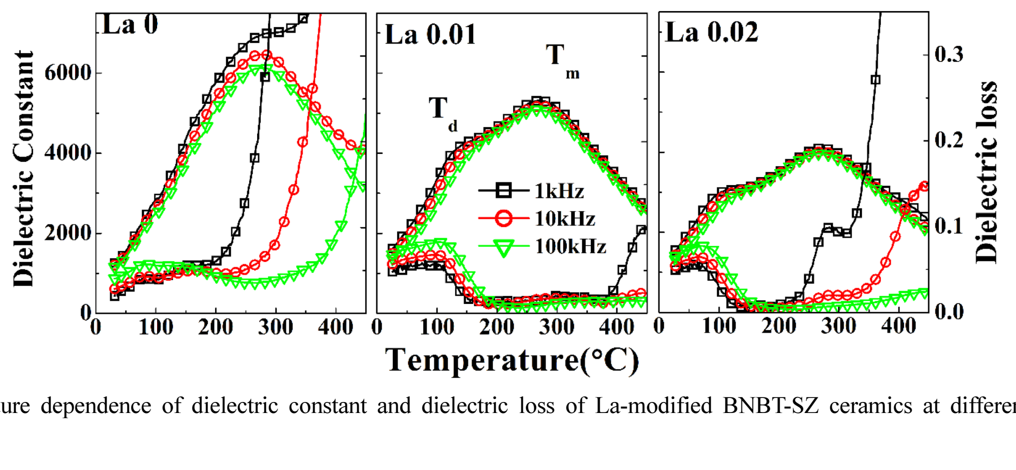

Fig. 2. Temperature dependence of dielectric constant and dielectric loss of La-modified BNBT-SZ ceramics at different frequencies.

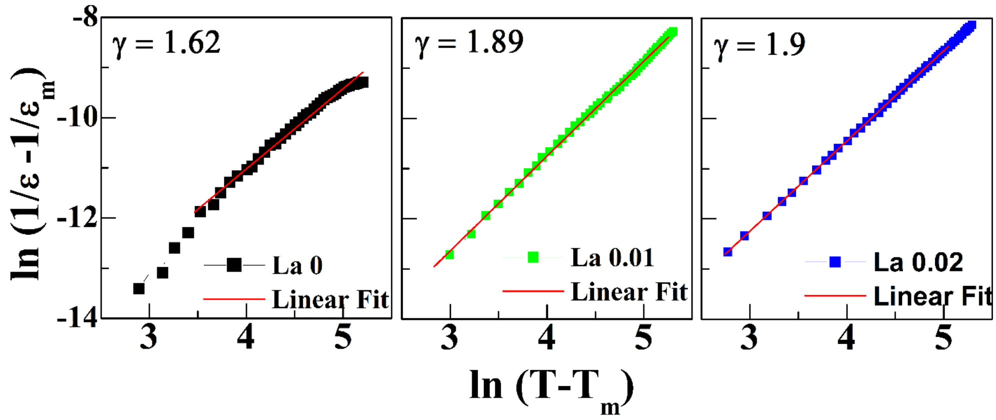

Fig. 3. Plots of $ln\left(\frac{1}{\varepsilon}-\frac{1}{\varepsilon_m}\right)$ versus $ln(T-T_m)$ of the La-modified BNBT-SZ ceramics.

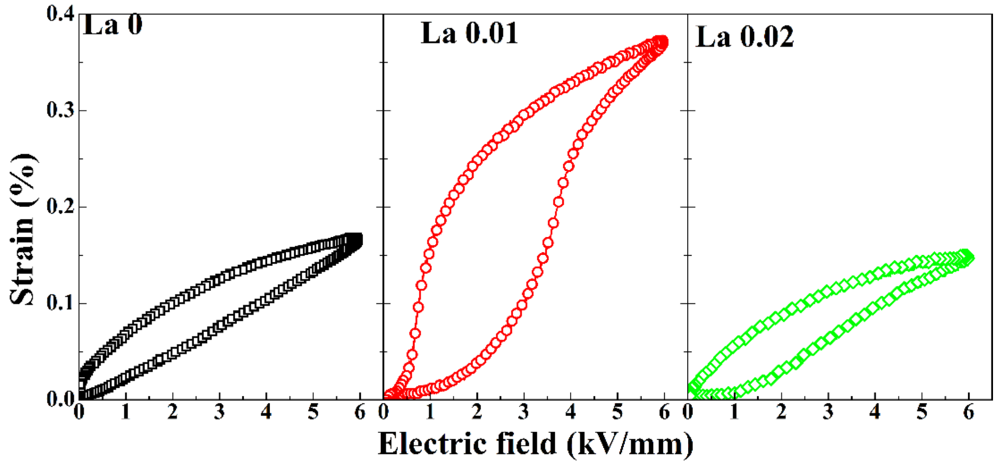

Fig. 4. Bipolar field-induced strain curves of La-modified BNBT-SZ ceramics.

form free electrons during the incorporation process[25,26) to compensate the charge of the aliovalent La dopant. It is assumed that La^{3+} would replace Bi^{3+} cations on the A-site taking into account similar radii (Bi^{3+} ~ 1.36, La^{3+} ~ 1.34 Å)[27) and oxidation states along with a non-negligible volatilization of Bi^{3+} during calcination and sintering.[28)

Fig. 2 shows the temperature-dependent dielectric constant (ε_r) and loss ($\tan\delta$) of La-modified BNBT-SZ ceramics measured at different frequencies (1, 10 and 100 kHz). Two dielectric anomalies, a depolarization temperature (T_d) below 100 °C and a maximum dielectric constant peaks at temperature (T_m) were observed below 300 °C in La-modified BNBT-SZ ceramics. Dielectric peaks at T_m gradually broadened and maximum permittivity (ε_r) decreased with increasing amount of La concentration which is consistent with previous reports.[29,30) The room temperature dielectric loss slightly increased and the broad dispersion at high temperature (200 °C and above) slightly decreased as compared with pure BNBT-SZ ceramics. The diffused character in the La-modified BNBT-SZ ceramics could be due to La substitution on the A-site, which could be the sources of random fields that break the long-range order of BNBT-SZ and stabilize the polar nanoregions at low temperature and zero field in a way similar to that proposed for other BNT-based ceramics.[7,31) The observed diffuse and/or relaxor behavior could be attributed to the disordering of the A-site cations and the compositional fluctuation in the present work.

The dielectric constant curves of BNBT-SZ ceramics became flaten (more diffuse) with increasing amounts of La substitution. The degree of diffuseness was characterized for all samples and are shown in Fig. 3. Modified Curie-Weiss law[32) was used to calculate γ values according to following equation.

$$\frac{1}{\varepsilon}-\frac{1}{\varepsilon_m}=\frac{(T-T_m)^{\gamma}}{c},\ 1\le\gamma\le 2$$

Where T_m is the temperature at which the dielectric constant reaches maximum and ε_m is the maximum dielectric constant, γ the diffusivity for phase transition (which indicates the degree of dielectric relaxation), and c the Curie constant. When $\gamma = 1$, the materials are said to be normal ferroelectrics; when $\gamma = 2$, the materials are termed as relaxor ferroelectrics. The values of γ and c are both materials constants that depend on the composition and structure of materials. The γ values as a function of La concentrations were plotted at 1 kHz. The γ was found to be 1.62, 1.89 and 1.90 for $x = 0$, 0.01, and 0.02, respectively; which shows that the diffuse and relaxor character increased with increasing amount of La addition.

Fig. 4 shows the field-induced unipolar strain loops of the BNBTLa-SZ ceramics at measuring frequency of 50 mHz. Pure BNBT-SZ ceramics show a maximum strain (S_{max}) of 0.17 % at an applied electric field of 6 kV/mm. However, introduction of La in BNBT-SZ, brought a significant enhancement in the field induced strain response. A large unipolar strain of 0.38 % was observed for $x = 0.01$ sample. Beyond this composition, the maximum strain decreased. This enhanced strain response for $x = 0.01$ composition can be attributed to the ferroeletric and relaxor phase transition facilitated by the structural phase transition from the tetragonal phase to a pseudo-cubic phase. This behavior is consistent with previous reports of BNT-based ceramics modified on A-site.[18,26] This finding of field induced strain is promising from the view point of electromechanical actuator applications.

4. Conclusions

The crystal structure, dielectric, relaxor and field-induced strain properties of La-modified BNBT-SZ ceramics were investigated as a function of different La concentration. Replacing A-site of BNBT-SZ by La changed the crystal structure from tetragonal to a pseudo-cubic symmetry. The temperature dependent dielectric response revealed relaxor behavior which increased with increasing amount of La concentration. The unipolar field-induced strain curves show enhancement with La-modification. A maximum field-induced strain 0.17 % was observed for pure BNBT-SZ ceramics which increased to 0.38 % for 1 mol% La-modified BNBTLa-SZ ceramics.

Acknowledgements

This work is supported by the National Research Foundation of Korea (NRF) grant funded by the Korean government, Ministry of Education (MOE) (2013R1A1-A2058345) and Basic Research program through the National Research Foundation of Korea (NRF) funded by Ministry, Science and Technology (MEST) (2011-0030058).

References

1. Directive 2002/95/EC of the European Parliament and of the Council of 27 January 2003, Off. J. Eur. Union **L37**, 19 (2003).
2. J. Rödel, K. G. Webber, R. Dittmer, W. Jo, M. Kimura and D. Damjanovic, J. Eur. Ceram. Soc., **35**, 1659 (2015).
3. K. Yoshii, Y. Hiruma, H. Nagata and T. Takenaka, Jpn. J. Appl. Phys., **45**, 4493 (2006).
4. X. X. Wang, H. L. W. Chan and C. L. Choy, J. Am. Ceram. Soc., **86**, 1809 (2003).
5. Y. Hiruma, H. Nagata and T. Takenaka, J. Appl. Phys., **104**, 124106 (2008).
6. A. B. Kounga, S. T. Zhang, W. Jo and J. Rödel, Appl. Phys. Lett., **92**, 222902 (2008).
7. T. Takenaka, K. Maruyama and K. Sakata, Jpn. J. Appl. Phys., Part 1 **30**, 2236 (1991).
8. C. Xu, D. Lin, and K. W. Kwok, Solid State Sci., **10**, 934 (2008).
9. M. Chen, Q. Xu, B. H. Kim, B. K. Ahn, J. H. Ko, W. J. Kang, and O. J. Nam, J. Eur. Ceram. Soc., **28**, 843 (2008).
10. E. Dul'kin, E. Mojaev, M. Roth, S. Greicius, and T. Granzow, Appl. Phys. Lett., **92**, 012904 (2008).
11. A. B. Kounga, S. T. Zhang, W. Jo and J. Rödel, Appl. Phys. Lett., **92**, 222902 (2008).
12. S. T. Zhang, A. B. Kounga, E. Aulbach, H. Ehrenberg and J. Rödel, Appl. Phys. Lett., **91**, 112906 (2007).
13. F. Wang, M. Xu, Y. Tang, T. Wang, W. Shi and C. M. Leung, J. Am. Ceram. Soc., **95**, 1955 (2012).
14. G. Yao, X. Wang, Y. Wu and L. Li, J. Am. Ceram. Soc., **95**, 614 (2012).
15. R. Zuo, C. Ye, X. Fang and J. Li, J. Eur. Ceram. Soc., **28**, 871 (2008).
16. S. K. Acharya. B. G. Ahn, C. U. Jung, J. H. Koh, I. H. Choi and S. K. Lee, J. Alloy. Compd., **603**, 248 (2014).
17. W. Lu, Y. Wang, G. Fan, X. Wang and F. Liang, J. Alloy. Compd., **509**, 2738 (2011).
18. T. H Dinh, H. Y Lee, C. H Yoon, R. A Malik, Y. M. Kong, J. S Lee and V. D. N. Tran, J. Korean Phys. Soc., **62**, 1004 (2013).
19. Q. Zheng, C. Xu, D. Lin, D. Gao and K. W. Kwok, J. Phys. D Appl. Phys., **41**, 125411 (2008).
20. X. Dai, Z. Xu and D. Viehland, Phil. Mag. B, **70**, 33 (1994).
21. J. K. Lee, J. Y. Yi and K. S. Hong, J. Appl. Phys., **96**, 1174 (2004).
22. A. Hussain, C. W. Ahn, J. S. Lee, A. Ullah and I. W. Kim, Sens. Actuators A, **158**, 84 (2010).
23. R. A. Malik, J. K. Kang, A. Hussain, C. W. Ahn, H. S. Han and J. S. Lee, Appl. Phys. Exp., **7**, 061502 (2014).
24. A. Maqbool, A. Hussain, J. U. Rahman, T. K. Song, W. J. Kim, J. H. Lee and M. H. Kim, Ceram. Int., **40**, 11905 (2014).
25. J. Y. Yi, J. K. Lee and K. S. Hong, J. Am. Ceram. Soc., **85**, 3004 (2002).

26. M. Acosta, N. Liu, M. Deluca, S. Heidt, I. Ringl, C. Dietz, R.W. Stark and W. Jo, J. Appl. Phys., **117**, 134106 (2015).
27. R. Shannon, Acta Cryst. A **32**, 751 (1976).
28. A. Popovič, L. Bencze, J. Koruza, B. Malič and M. Kosec, Int. J. Mass Spectrom., **309**, 70 (2012).
29. A. Zaman, Y. Iqbal, A. Hussain, M. H. Kim and R. A. Malik, J. Mater. Sci., **49**, 3205 (2014).
30. J. U. Rahman, A. Hussain, A. Maqbool, G. H. Ryu, T. K. Song, W. J. Kim and M. H. Kim, J. Alloy. Compd., **593**, 97 (2014).
31. N. B. Do, H. B. Lee, C. H. Yoon, J. K. Kang and J. S. Lee, Trans. Electr. Electron. Mater., **12**, 64 (2011).
32. K. Uchino and S. Nomura, Ferroelectrics Lett., **44**, 55 (1982).