

# Niobium doping effects and ferroelectric relaxor behavior of bismuth lanthanum titanate

Jin Soo Kim · Min Su Jang · Ill Won Kim · Kwang Sei Lee

Received: 26 June 2005 / Revised: 23 September 2005 / Accepted: 6 October 2005  
© Springer Science + Business Media, LLC 2006

**Abstract** Ferroelectrics  $\text{Bi}_{3.25}\text{La}_{0.75}(\text{Ti}_{3-x}\text{Nb}_x)\text{O}_{12}$  (BLTN,  $x = 0 \sim 0.1$ ) solid solution systems were prepared, and Nb doping effects and relaxor behaviors were investigated. The BLTN single phases were confirmed by XRD. The phase transition temperature decreased as the Nb content increased, and the corresponding dielectric constant maximum broadened. The temperature  $T_m$  of the dielectric maximum depended on frequency and increased, which indicate that the relaxor behavior was caused by Nb substitution. The substitution of Nb for Ti ions affected the degree of disorder and modified the dielectric properties from those of normal ferroelectrics to relaxor ferroelectrics.

**Keywords** BLT · BIT · Relaxor · Ferroelectrics · Dielectric relaxation · FRAM · BLSF

## 1 Introduction

For devices such as optic, electro-optic, piezoelectric and nonvolatile ferroelectric random access memory (FRAM) devices, much attention has been paid to bismuth layer structured ferroelectrics (BLSFs) [1–5]. Among them, the

ferroelectric and electrical properties of strontium bismuth tantalite (SBT), bismuth titanate (BIT) and bismuth lanthanum titanate (BLT) have been extensively investigated [2–13]. The BLSFs structure can be written with a general formula of  $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{n-1}\text{B}_n\text{O}_{3n+1})^{2-}$  where A can be mono-, di-, trivalent ions or a mixture of them, B represents  $\text{Ti}^{4+}$ ,  $\text{Nb}^{5+}$ , and  $\text{Ta}^{5+}$ , etc., and  $n$  can have values of 2, 3, 4, ... Bi and Ti ions in the  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  (BIT) structure occupies the A and B sites, respectively. The BIT consists of three perovskite-like units,  $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ , sandwiched between bismuth oxide layers,  $(\text{Bi}_2\text{O}_2)^{2+}$ .

The ferroelectric properties are known to arise in the perovskite block,  $(\text{Bi}_2\text{Ti}_3\text{O}_{10})^{2-}$ . To enhance the ferroelectric properties, the doping effects of lanthanoid elements such as La, Nd and Sm ions have been studied [3, 7–13]. On the other hand, the dielectric and ferroelectric properties were also changed by the high-valent cation substitution such as Nb, V and W elements [2, 7, 8,]. However, the ion doping effects [13–22] on the relaxor behavior of BLT has seldom been studied in detail. Previously, the ferroelectric relaxor behaviors [13–18] have been well established for various solid solution such as  $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$  (PMN) with perovskite structure and  $\text{Sr}_{1-x}\text{Ba}_x\text{Nb}_2\text{O}_6$  (SBN) with tungsten bronze structure. Specifically, the relaxor behavior of the  $\text{A}(\text{B}_1, \text{B}_2)\text{O}_3$  perovskite structure was explained by the partially ordered  $\text{B}_1$  and  $\text{B}_2$  sites. Owing to the outstanding dielectric, piezoelectric and pyroelectric properties, the ferroelectric relaxor has attracted much attention. In this work, the dielectric properties and relaxor behaviors of the Nb doped BLT ceramics were investigated.

## 2 Experimental work

$(\text{Bi}_{3.25}\text{La}_{0.75})(\text{Ti}_{3-x}\text{Nb}_x)\text{O}_{12}$  ceramics (BLTN:  $x = 0, 0.01, 0.03, 0.05, 0.07$  and  $0.10$ ) were prepared by a solid state

J. S. Kim (✉) · M. S. Jang  
Department of Physics, and Research Center for Dielectric and Advanced Matter Physics, Pusan National University,  
Busan 609-735, Korea  
e-mail: kimjjin@pusan.ac.kr

I. W. Kim  
Department of Physics, University of Ulsan, Ulsan 680-749,  
Korea

K. S. Lee  
School of Computer Aided Science, Inje University,  
Kimhae 621-749, Korea

reaction method. The powders for BLTN ceramics were mixed by ball milling with ethanol for 24 h, and were dried at 80°C for 24 h and fired at 850°C for 4 h. The powders were ground and milled again with ethanol, and then pressed into pellets. The BLTN ceramic pellets were sintered at 1000 ~ 1200°C for 5 h in air. The BLTN single-phase was confirmed by X-ray diffraction (XRD). To investigate the dielectric properties, Pt-electrodes with an area of 30 mm<sup>2</sup> were coated by dc sputtering on the ceramic samples. The temperature dependence of capacitance and dissipation factor ( $\tan \delta$ ) were measured at the frequency of 1, 10, 100 kHz and 1 MHz by an impedance analyzer (HP4192A).

### 3 Results and discussion

Figure 1 shows the indexed XRD peaks of BLTN ceramics. Layered perovskite (117) and other perovskite (00 $l$ ) peaks were found, which agrees with previous results. This indicates that BLTN single phase Bi-layered perovskite structures were formed for all BLTN ceramics. It may be assumed that doped Nb-ion incorporated Ti ions in the perovskite structures because the ionic radii and electronegativity of Nb ions are similar to those of Ti ions.

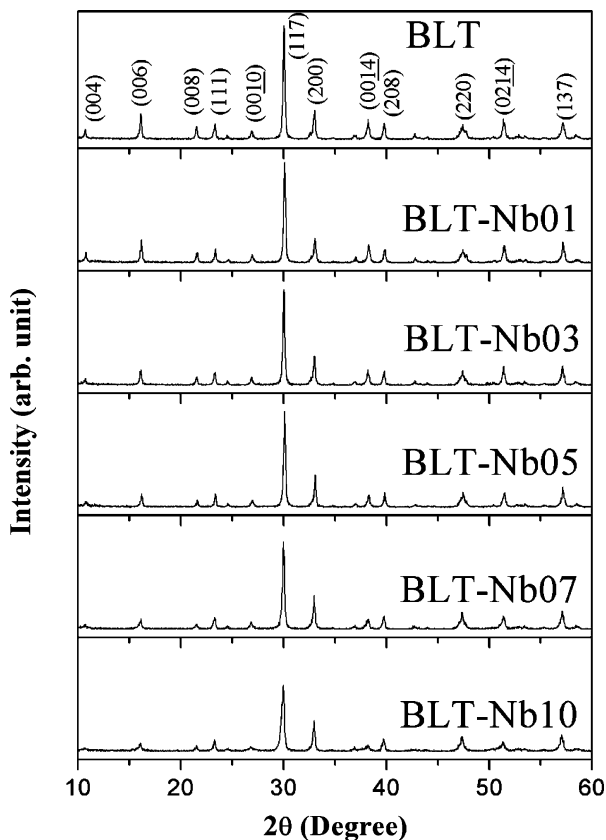


Fig. 1 XRD patterns of BLT and BLTN ceramics

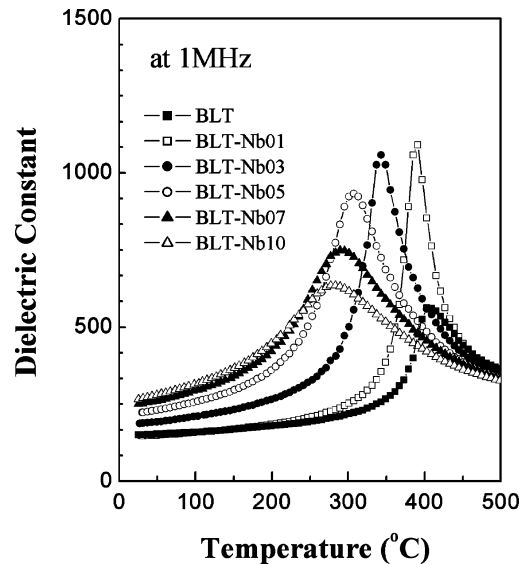


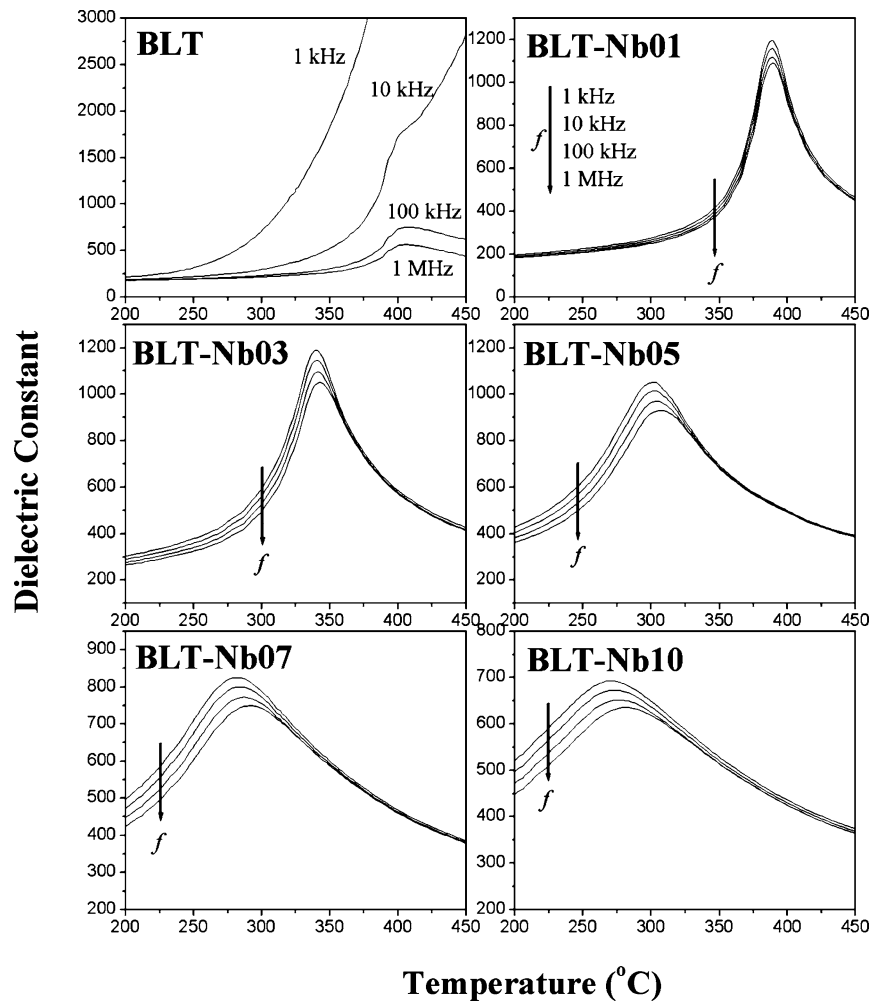
Fig. 2 Temperature dependence of dielectric constant of BLTN ceramics measured at the frequency of 1 MHz

Figure 2 shows the temperature dependences of the dielectric constant measured against a frequency of 1 MHz. For Nb doping, the dielectric constant maximum increased at the Curie temperature, may be explained by enhanced polarizability caused by the distortion of oxygen octahedra. The  $T_c$  of the BLT-Nb01, BLT-Nb03, BLT-Nb05, BLT-Nb07 and BLT-Nb10 ceramics is 389, 343, 307, 291 and 281°C, respectively. As the Nb content increased,  $T_c$  tended to decrease and the corresponding dielectric constant maximum broadened, which is similar the results for SBN [17]. As the larger Nb<sup>5+</sup> ions ( $r = 0.64 \text{ \AA}$ ) substituted for the Ti<sup>4+</sup> ions ( $r = 0.61 \text{ \AA}$ ) at the B-site, it is assumed that the phase transition temperature decreased. In addition, differences were found in the Curie temperature regions and broadness of the dielectric constant maximums [14–18]. The phase transition behaviors were caused by the substitution of Nb for Ti ions.

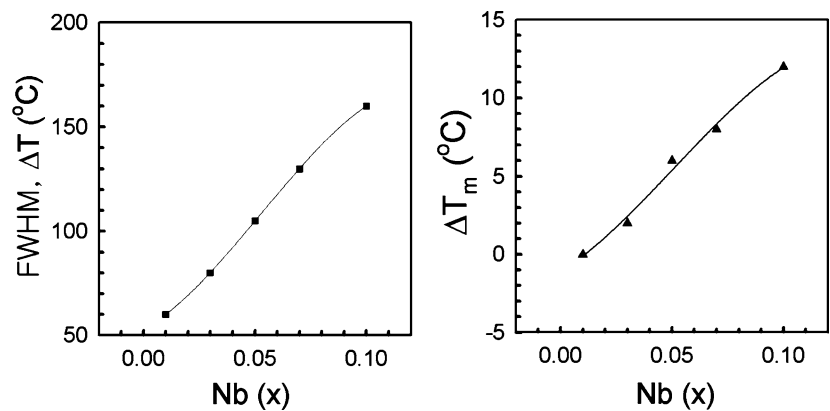
Figure 3 shows the temperature dependence of the dielectric constant measured at the frequencies of 1 k, 10 k, 100 k and 1 MHz. Specifically, BLT ceramics were found to have low-frequency dielectric dispersions at the temperature above 200°C. Remarkably, however, the dielectric dispersion of the BLTN ceramics decreased. Therefore, the donor doping of Nb<sup>5+</sup> for Ti<sup>4+</sup> resulted in a decrease of low frequency dispersions, which were caused by the compensations that were made for defect such as bismuth and oxygen vacancies [19–22].

As the frequency increased, the temperature  $T_m$  of the dielectric constant maximum increased. The phase transition corresponded to the ferroelectric relaxor behaviors, which agrees with the previous results such as PMN and SBN solid solution systems [17, 18]. Particularly, the

**Fig. 3** Temperature dependence of dielectric constant of BLTN ceramics measured at the frequency of 1 k, 10 k, 100 k and 1 MHz



**Fig. 4** The variation of the FWHM and  $\Delta T_m$  of dielectric maximum as a function of Nb content

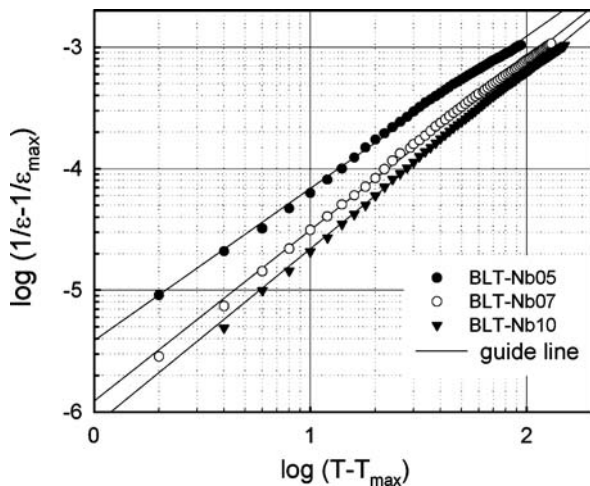


shifting of  $T_m$  to the higher temperature side was obviously observed for the BLTN-Nb05, BLTN-Nb07 and BLTN-Nb10 ceramics each of which had higher Nb contents. This indicates that the relaxor behaviors are related to the disordered state of the Nb and Ti ions in the B-site.

Figure 4 shows the full width at half maximum (FWHM),  $\Delta T$ , and the difference of the dielectric constant maximum

temperature on frequency,  $\Delta T_m$ , which corresponds to the degree of diffuse phase transition. As the Nb content increased, the FWHM and  $\Delta T_m$  increased. As the frequency increased from 1 kHz to 1 MHz, the  $\Delta T_m$  increased.

Figure 5 shows the plot of  $\ln(1/\epsilon' - 1/\epsilon'_m)$  vs.  $\ln(T - T_m)$  for the BLTN ceramics. The curve of  $1/\epsilon'$  vs. temperature in the paraelectric phase of the ferroelectric relaxor do



**Fig. 5** The plot of  $\ln(1/\varepsilon' - 1/\varepsilon'_m)$  vs.  $\ln(T - T_m)$  for the BLTN ceramics

not follow the Curie-Weiss law. In fact,  $\varepsilon'$  vs. temperature followed the general expression:

$$1/\varepsilon' - 1/\varepsilon'_m = C''(T - T_m)^\gamma$$

where  $\gamma = 1 \sim 2$  and  $C''$  is a constant. The calculated  $\gamma$  of the BLT-Nb05, BLT-Nb07 and BLT-Nb10 are 1.25, 1.43 and 1.64, respectively. As Nb content increased, the value of  $\gamma$  increases, which indicates that the degree of diffuse phase transition increased [15, 18]. Nb substitution increases the structural disorder due to the presence of Nb or Ti ions located in the same crystallographic B-site [18]. Thus, the  $T_m$ ,  $\Delta T_m$  and  $\gamma$  gradually varied, which caused the relaxor behaviors. The relaxor behavior were similar to that of SBN and PMN [17, 18].

The relaxor behaviors of BLTN ceramics are explained by the nonisoelectric substitution of the Nb for Ti ion. The radius of  $\text{Nb}^{5+}$  is similar to that of  $\text{Ti}^{4+}$ , thus the doped  $\text{Nb}^{5+}$  occupied the  $\text{Ti}^{4+}$  and partially formed  $\text{NbO}_6$  groups associated with six oxygen atoms. The crystal structure of the BLT consisted of a  $\text{Bi}_2\text{O}_2$  layer and perovskite-type unit with triple octahedral layers. Because of the substitution for the Nb ion, the perovskite-unit is consisted of a Ti or Nb ion located at the center of the oxygen octahedron. Thus Nb and Ti ions randomly occupied the B-sites. There were differences in the charge valences between  $\text{Ti}^{4+}$  and  $\text{Nb}^{5+}$  ions, nonisoelectric substitutions induced local lattice deformation and led to changes in the local field, which polarized the off-center impurities in random directions and thus lowered the  $T_m$ . As the Nb content increased, doped Nb ions may be attributed to the enhancement in the degree of disorder having two site ions to occupy the same lattice site. Therefore, there were different compositional orders at each domain, which caused the frequency-dependent

dielectric response and the relaxor behavior. Nb doping was attributed to the inhomogeneous composition with disorder structure, which led to the changes in the ferroelectric properties from normal ferroelectric to relaxor ferroelectric.

## 4 Conclusions

As  $x$  increased, the dielectric properties of the Nb-doped  $\text{Bi}_{3.25}\text{La}_{0.75}\text{Ti}_{3-x}\text{Nb}_x\text{O}_{12}$  (BLTN) ceramics changed from normal ferroelectrics to relaxor ferroelectrics. As Nb increased from  $x = 0$  to 0.1, the phase transition temperature decreased from 405 to 269°C, and the dielectric maximum broadened. In addition, the temperature,  $T_m$ , of dielectric constant maximum depended on the measuring frequency and shifted toward the higher temperature. Thus, the partial substitution of Nb for Ti ions at B-site resulted in the relaxor behaviors, which may be explained by the structural disorder due to the presence of Nb or Ti ions in the same crystallographic B-sites.

**Acknowledgments** This work was supported by Korean Science & Engineering Foundation (KOSEF) through Grant No. R08-2004-000-10557-0.

## References

1. K. Kato, C. Zheng, J.M. Finder, S.K. Dey, and Y. Torii, *J. Am. Ceram. Soc.*, **81**, 1869 (1998).
2. B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, and W. Jo, *Nature*, **401**, 682 (1999).
3. J.S. Kim, S.S. Kim, and T.K. Song, *Jour. Kor. Phys. Soc.*, **43**, 548 (2003).
4. I.W. Kim, C.W. Ahn, J.S. Kim, J.-S. Bae, B.C.C. J.-H. Jeong, and J.S. Lee, *Appl. Phys. Lett.*, **80**, 4006 (2002).
5. J.S. Kim, S.S. Kim, and J.K. Kim, *Jpn. J. Appl. Phys.*, **42**, 6486 (2003).
6. T. Watanabe, H. Funakubo, M. Osada, Y. Noguchi, and M. Miyayama, *Appl. Phys. Lett.*, **10**, 100 (2002).
7. J.S. Kim, H.J. Lee, S.H. Kang, S.Y. Lee, and I.W. Kim, *Integrated Ferroelectric*, **65**, 39 (2004).
8. Y. Noguchi, I. Miwa, Y. Goshima, and M. Miyayama, *Jpn. J. Appl. Phys.*, **39**, L1259 (2000).
9. D. Wu, A. Li, T. Zhu, Z. Liu, and N. Ming, *J. Appl. Phys.*, **88**, 5941 (2000).
10. J.S. Kim, H.J. Lee, S.Y. Lee, S.H. Kang, C.W. Ahn, I.W. Kim, K.S. Lee, and H.S. Lee, *Jour. Kor. Phys. Soc.*, **46**, 147 (2005).
11. U. Chon, K. Kim, H.M. Jang, and G. Yi, *Appl. Phys. Lett.*, **79**, 3137 (2001).
12. Y. Wu, M.J. Forbess, S. Seraji, S.J. Limmer, T.P. Chou, C. Nguyen, and G. Cao, *J. Appl. Phys.*, **90**, 5296 (2001).
13. Y. Shimakawa, Y. Kubo, Y. Tauchi, T. Kamiyama, H. Asano, and F. Izumi, *Appl. Phys. Lett.*, **77**, 2749 (2000).
14. M. Li, T. Chong, X. Xu, and H. Kumagai, *Appl. Phys. Lett.*, **89**, 5644 (2001).

15. J.S. Kim and J.N. Kim, *J. Phys. Soc. Jpn.*, **69**, 1880 (2000).
16. M.M. Kumar and Z.-G. Ye, *J. Appl. Phys.*, **90**, 934 (2001).
17. A.M. Glass, *J. Appl. Phys.*, **40**, 4699 (1969).
18. L.E. Cross, *Ferroelectrics*, **76**, 241 (1987).
19. J.S. Kim, H.J. Lee, S.Y. Lee, S.H. Kang, C.W. Ahn, I.W. Kim, K.S. Lee, *J. Korean Phys. Soc.*, **46**, 143 (2005).
20. C.H. Song, W. Li, J. Ma, J. Gu, Y.Y. Yao, Y. Feng, X.M. Lu, J.S. Zhu, Y.N. Wang, W.L.H. Chan, and C.L. Choy, *Solid State. Comm.*, **129**, 775 (2004).
21. J.S. Kim, H.J. Lee, S.H. Kang, S.Y. Lee, and I.W. Kim, *Integr. Ferroelectrics*, **65**, 39 (2004).
22. J.S. Kim and S.S. Kim, *Appl. Phys. A*, **81**, 1427 (2005).