



Ionic Doping Effects in SrBi₂Nb₂O₉ Ferroelectric Ceramics

S.E. PARK,¹ J.A. CHO,¹ T.K. SONG,^{1,*} M.H. KIM,¹ S.S. KIM² & H.-S. LEE²

¹Department of Ceramic Science and Engineering, Changwon National University, Changwon, Kyongnam 641-773, Korea

²Department of Physics, Changwon National University, Changwon, Kyongnam 641-773, Korea

Submitted March 3, 2003; Revised March 12, 2004; Accepted March 16, 2004

Abstract. Ionic doping effects of various ions in Bi-layered ferroelectric SrBi₂Nb₂O₉ (SBN) ceramics were studied. Un-doped and doped SBN ceramics with Ba²⁺, Pb²⁺, Ca²⁺, Bi³⁺, La³⁺, Ti⁴⁺, Mo⁶⁺, and W⁶⁺ ions were made with solid state reactions. Temperature dependent dielectric constants were measured. Ferroelectric transition temperature (T_C) decreased with Ba²⁺ and Pb²⁺ ions but increased with Ca²⁺ ion which substitutes the 12-coordinated Sr²⁺ site. T_C increased with Ti⁴⁺, Mo⁶⁺, and W⁶⁺ ions which substitute the 6-coordinated Nb⁵⁺ sites. With trivalent Bi³⁺ and La³⁺ ions, T_C increased with Bi³⁺ ion but much decreased with La³⁺ ion. These results showed that the ion size plays an important role in ferroelectricity of SBN ceramics.

Keywords: SrBi₂Nb₂O₉, ionic doping, ion size, ferroelectric phase transition

1. Introduction

Bi-layered ferroelectric materials including SrBi₂Nb₂O₉(SBN) have attracted much attention because they show good long-term reliability properties such as fatigue, imprint, and retention for ferroelectric memory (FRAM) applications [1]. But they have relatively low remanent polarizations and need relatively high processing temperature. Ionic doping or substitution effects in Bi-layered ferroelectric materials have been studied to overcome these problems. La³⁺ substituted Bi₄Ti₃O₁₂ (BIT) was reported to show high polarizations and lower processing temperature [2]. Recently, La³⁺ and Ca²⁺ ion doping in SBN ceramics were reported to show increased transition temperature and decreased dc conductivity [3], and vanadium doped BIT was reported to show higher polarizations than un-doped one [4].

Ionic doping effects on ferroelectric Pb(Zr,Ti)O₃ (PZT) have been well studied to improve long-term reliability properties by reducing oxygen deficiency or other defects in PZT systems [5, 6]. It has been reported

that La³⁺ or Nb⁵⁺ ions act as donor ions, which reduce the leakage currents and improve long-term reliability properties. But ionic doping effects in Bi-layered ferroelectrics such as SBN, SrBi₂Ta₂O₉, and BIT have not been studied well enough for comparison to PZT [7]. Increase in polarization values and decrease in processing temperature are expected in ion doped Bi-layered ferroelectric materials [2–4].

In this work, un-doped SBN ceramics and SBN ceramics doped with various ions were made by a conventional solid reaction method. Structural properties were studied by the X-ray diffraction method and dielectric constants were measured from room temperature to 650°C. Ionic doping effects on ferroelectric transition temperatures were studied.

2. Experimental

Powders of SrO(99.9%, Aldrich), Bi₂O₃(99.9%, Aldrich), Nb₂O₅(99.99%, Aldrich) were used for the SBN ceramics. For the ionic doping of various ions, metal oxide powders of CaO(99.9% Aldrich), BaO(99.9% Aldrich), PbO(99.9% Aldrich), Bi₂O₃(99.9%, Aldrich), La₂O₃(99.9% Aldrich), TiO₂(99.9% Aldrich), MoO₃(99.9% Aldrich), and WO₃(99.9% Aldrich) were used for 10 mol% doping

*To whom all correspondence should be addressed. E-mail: tksong@changwon.ac.kr

(90SBN + 10MO, where M is metal ion of Ca, Ba, or Pb; 90SBN + 5M₂O₃, where M is metal ion of Bi or La; 90SBN + 10TiO₂; 90SBN + 10MO₃, where M is metal ion of Mo or W). Starting materials were weighed and mixed for 24 hours. The mixed powders were dried at 80°C and calcined at 800°C for two hours. The calcined powders were mixed for 24 hours and dried again. 1 mm thick pellets with 8 mm in diameter were made and sintered for 1 hour at 1150°C [3]. The densities of sintered ceramics are about 6.95 g/cm³, higher than Subbarao's report [8] and about 95% of theoretical density of SBN (7.3 g/cm³).

Structural properties of sintered ceramic pellets were studied with X-ray diffraction (XRD) patterns. To measure dielectric properties of SBN ceramics, electrodes were applied on both sides of the pellets with silver paste and annealed at 650°C for 1 hour. Dielectric constants and losses were measured at 100 kHz at temperatures ranging from 25 to 650°C with an impedance analyzer (HP4192A). The applied voltage amplitude was 1.0 V_{rms}. The heating and cooling rates were maintained at ±1°C/min during the measurements.

3. Results

Figure 1 shows XRD patterns of un-doped SBN ceramic and SBN ceramics doped with Ca²⁺, Ba²⁺, Pb²⁺ ions. For all the patterns, *polycrystalline* orthorhombic (pseudo-tetragonal) SBN crystal structure were well defined. Neither secondary phase nor structure change was observed. With La³⁺, Bi³⁺, Ti⁴⁺, Mo⁶⁺, W⁶⁺ ions doping, polycrystalline

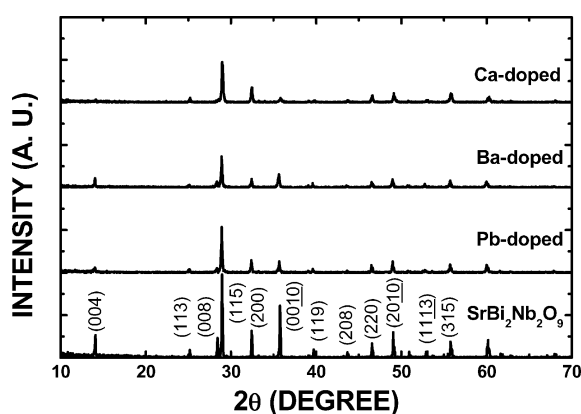


Fig. 1. X-ray diffraction patterns of un-doped SBN ceramic and SBN ceramics doped with Ca²⁺, Ba²⁺, and Pb²⁺ ions.

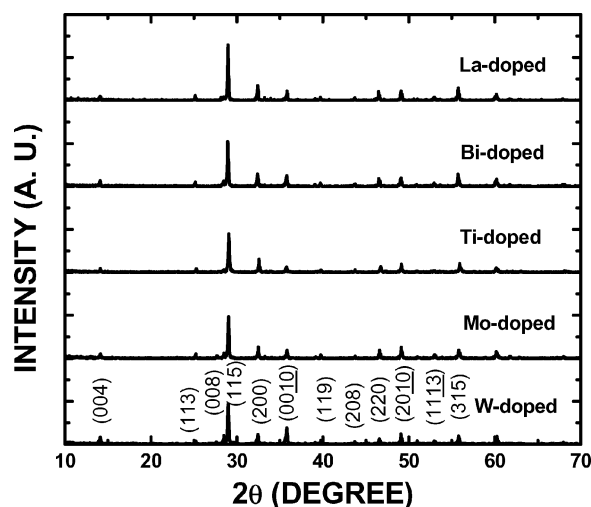


Fig. 2. X-ray diffraction patterns of SBN ceramics doped with La³⁺, Bi³⁺, Ti⁴⁺, Mo⁶⁺, and W⁶⁺ ions.

Bi-layered structures were also observed as shown in Fig. 2.

Temperature dependent dielectric constants of un-doped SBN ceramic and doped SBN ceramics with divalent Ca²⁺, Ba²⁺, and Pb²⁺ ions are shown in Fig. 3. Ferroelectric transition temperature ($T_C = 414^\circ\text{C}$) of SBN is a little lower than the previously reported value because of the non-stoichiometric composition of our SBN ceramic [3, 7]. The SBN ceramic was Bi-deficient phase due to the volatility of Bi during the sintering process at 1150°C. With Ba²⁺ or Pb²⁺ ionic doping, T_C decreased (with Ba²⁺ $T_C = 375^\circ\text{C}$, with Pb²⁺ $T_C = 396^\circ\text{C}$). A little

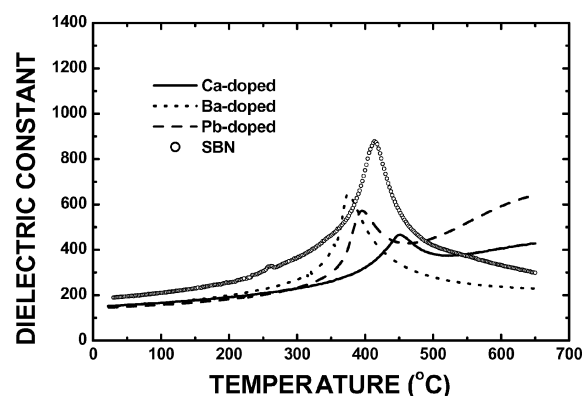


Fig. 3. Dielectric constants of un-doped SBN ceramic and SBN ceramics doped with Ca²⁺, Ba²⁺, and Pb²⁺ ions as functions of temperature measured at a frequency of 100 kHz.

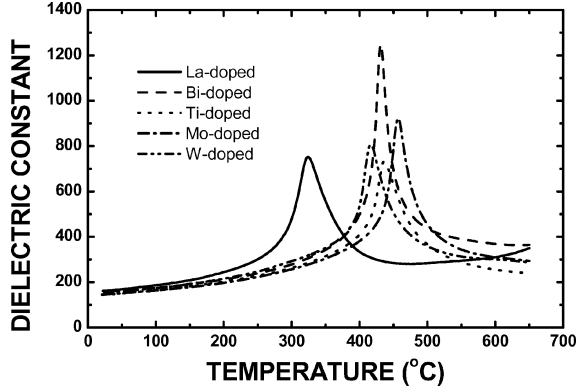


Fig. 4. Dielectric constants of SBN ceramics doped with La³⁺, Bi³⁺, Ti⁴⁺, Mo⁶⁺, and W⁶⁺ ions as functions of temperature measured at a frequency of 100 kHz.

increase of T_C (452°C) is observed with Ca²⁺ ionic doping.

Temperature dependent dielectric constants of doped SBN ceramics with La³⁺ ($T_C = 324^\circ\text{C}$), Bi³⁺ ($T_C = 431^\circ\text{C}$), Ti⁴⁺ ($T_C = 437^\circ\text{C}$), Mo⁶⁺ ($T_C = 457^\circ\text{C}$), and W⁶⁺ ($T_C = 417^\circ\text{C}$) ions are shown in Fig. 4. Except for the La³⁺ ion, T_C increased with ionic doping. Bi³⁺ ionic doping, very sharp peak of transition was observed. This increase of T_C with Bi³⁺ ion was consistent with the results of dielectric properties of non-stoichiometric SBN ceramics. Sr-deficient/Bi-excess SBN showed higher T_C [9]. In comparison with La³⁺ ion, Bi³⁺ ion has the same valence, but its effect on T_C is opposite to that of La³⁺ ion [9]. This result implies that the valence of doped ion is not an important factor for ferroelectricity in SBN ceramics.

4. Discussion

From the results, it was summarized that ionic valence does not play an important role in T_C of SBN ceramics. However, ion size is an important factor as summarized in Table 1 [10]. With same valence ion doping, Ca²⁺, Pb²⁺ and Ba²⁺ for Sr²⁺, or V⁵⁺ and Ta⁵⁺ for Nb⁵⁺, it has been reported that the smaller ions induce the higher T_C [11]. This result was attributed to the lattice mismatch between TaO₂ and SrO planes in the perovskite-type unit of SrTa₂O₇, causing structural distortion and hence leading to higher T_C and higher polarizations in SrBi₂Ta₂O₉ [12, 13]. Doping different valence ions doping in SBN ceramics showed simi-

Table 1. Doped ionic radii (Å) [10] and transition temperatures.

Ion	Sr ²⁺	Ba ²⁺	Ca ²⁺	Pb ²⁺
12-fold	1.44	1.61	1.34	1.49
T_C (°C)	414	375	452	396
Ion	Bi ³⁺		La ³⁺	
8-fold	1.17		1.16	
T_C (°C)	431		324	
Ion	Nb ⁵⁺	Ti ⁴⁺	Mo ⁶⁺	W ⁶⁺
6-fold	0.64	0.605	0.59	0.6
T_C (°C)	414	437	457	417

lar results. The smaller ions, even though they were of different valences, induced higher transition temperature. For the divalent ionic doping which would substitute Sr²⁺ ion in 12-fold coordinated A-site, our result is consistent with this trend. PbBi₂Nb₂O₉ was, however, reported to show higher T_C by about 110°C than SrBi₂Nb₂O₉, although Pb²⁺ ion is larger than Sr²⁺ ion [11]. However, T_C decreased with Pb²⁺ doping in SBN ceramic in our result. Even though Pb²⁺ has valence of 2, Pb is not an alkaline earth metal ion and has different electronic structure from that of Ca²⁺, Sr²⁺ or Ba²⁺ ions, and thus the effect of Pb²⁺ ion doping differs from those of alkaline earth metals.

The trivalent La³⁺ ion would substitute Bi³⁺ ion. Then Bi³⁺ ions would not be located in the perovskite-like layer but in (Bi₂O₂)²⁺ layer. Its effects on ferroelectricity in SBN were different from the effects of the other ions which substituted Sr²⁺ or Nb⁵⁺ ions in perovskite-like layer. Decrease of T_C with La³⁺ doping in Bi³⁺ sites has already reported in BIT [14]. For the hexa-valent ions of Mo⁶⁺ and W⁶⁺, these two ions have almost same ion sizes but their effects on T_C were very different. Before we conclude the effects of ionic doping on ferroelectric properties of SBN ceramics, more detailed studies on the chemistry/physics of doping—interstitial or substitutional—should be performed. Studies of the effects of ionic doping in Bi-layered ferroelectric materials on ferroelectric transition and polarization could give good information for the ferroelectric memory and high temperature piezoelectric device applications [15].

5. Conclusion

In conclusion, various ions doped SBN ceramics were made and their dielectric properties were studied. T_C

decreased with Ba²⁺ and Pb²⁺ ions but increased with Ca²⁺ ion which substitutes the 12-coordinated Sr²⁺ site. T_C increased with Ti⁴⁺, Mo⁶⁺, and W⁶⁺ ions which substitute the 6-coordinated Nb⁵⁺ sites. With trivalent Bi³⁺ and La³⁺ ions, T_C increased with Bi³⁺ ion but decreased with La³⁺ ion. With smaller ion doping than the constituent ions, T_C increased, and *vice versa*.

Acknowledgment

This work was supported by Grant No. (R01-2000-000-00029-0) from the Basic Research Program of the Korea Science and Engineering Foundation.

References

1. K. Watanabe, M. Tanaka, E. Sumitomo, K. Katori, H. Yagi, and J.F. Scott, *Appl. Phys. Lett.*, **73**, 126 (1998).
2. B.H. Park, B.S. Kang, S.D. Bu, T.W. Noh, J. Lee, and W. Jo, *Nature*, **401**, 682 (1999).
3. M.J. Forbess, S. Seraji, Y. Wu, C.P. Nguyen, and G.Z. Cao, *Appl. Phys. Lett.*, **76**, 2934 (2000).
4. Y. Noguchi and M. Miyayama, *Appl. Phys. Lett.*, **78**, 1903 (2001).
5. B. Yang, T.K. Song, S. Aggarwal, and R. Ramesh, *Appl. Phys. Lett.*, **71**, 3578 (1997).
6. G.H. Haertling and C.E. Land, *J. Am. Ceram. Soc.*, **54**, 1 (1971).
7. T.K. Song, S.E. Park, J.A. Cho, M.H. Kim, J.S. Kim, H.-S. Lee, and S.S. Kim, *J. Korean Phys. Soc.*, **42**, S1343 (2003).
8. E.C. Subbarao, *J. Phys. Chem. Solids.*, **23**, 665 (1962).
9. J.S. Kim, C.-I. Cheon, H.-S. Shim, and C.H. Lee, *J. Eur. Ceram. Soc.*, **21**, 1295 (2001).
10. R.D. Shannon, *Acta Crystallogr.*, **A32**, 751 (1976).
11. M.E. Lines and A.M. Glass, *Principles and Applications of Ferroelectrics and Related Materials* (Oxford University Press, Oxford, 1982).
12. Y. Shimakawa, Y. Kubo, Y. Nakagawa, S. Goto, T. Kamiyama, H. Asano, and F. Izumi, *Phys. Rev. B*, **61**, 6559 (2000).
13. Y. Wu, Mike J. Forbess, S. Seraji, S.J. Limmer, T.P. Chou. C. Nguyen, and G. Cao, *J. Appl. Phys.*, **90**, 5296 (2001).
14. M. Shimazu, J. Tanaka, K. Muramatsu, and M. Tsukioka, *J. Solid State Chem.*, **35**, 402 (1980).
15. A. Ando, M. Kimura, and Y. Sakabe, *Jpn. J. Appl. Phys.*, **42**, 150 (2003).