

Dielectric and Ferroelectric Properties of La-Doped SrBi₂Nb₂O₉ Ceramics

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Sr_{1-x}La_{2x/3}Bi₂Nb₂O₉ ($0 \leq x \leq 0.2$) ceramic samples are prepared by the solid-state reaction method. Their structure, dielectric and ferroelectric properties are investigated. The incorporation of La³⁺ improves the densification and decreases the grain size of the ceramics without changing the crystal structure. The remanent polarization $2P_r$ increases with increasing La content and reaches a maximum value of $22.8 \mu\text{C}/\text{cm}^2$ at $x = 0.125$, which is approximately 60% larger than that of pure SrBi₂Nb₂O₉. The Curie temperature keeps almost unchanged at a value of about 440°C. The relationship between doping and the ferroelectric and dielectric properties are discussed.

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Ferroelectric materials have attracted much attention due to their potential applications in ferroelectric random access memories (FeRAMs).^[1] In ABO₃-type ferroelectrics, PbZr_{1-x}Ti_xO₃ (PZT) has been widely investigated because of its large remanent polarization.^[2] However, the fatigue problem associated with the PZT capacitors and the Pb contamination problem restrict its application in FeRAMs.^[3] Recently, lead-free bismuth layer structure ferroelectrics (BLSFs) have received more and more interest due to their good fatigue resistance. The structure of the BLSFs can be considered as an intergrowth of (Bi₂O₂)²⁺ layers and (A_{m-1}B_mO_{3m+1})²⁻ pseudoperovskite layers.^[4] Among BLSFs, SrBi₂Nb₂O₉ (SBN) is one of the most promising candidates due to its high fatigue resistance.^[5] However, it suffers from a relatively low remanent polarization, a relative high dielectric loss and a relative high processing temperature.^[6] Many studies have been made on doping to improve the dielectric and ferroelectric properties of SBN.^[7-9]

Although the effects of doping on the dielectric properties of SBN have been widely investigated, different groups have not reached an agreement on the effect of La doping on the Curie temperature of SBN,^[8,10,11] which implies that La doping may cause complicated effects on the dielectric and ferroelectric properties of SBN. Moreover, there is a lack of sufficient information about the influence of La doping on the ferroelectric properties of SBN. In this Letter, we investigate the effects of La doping on the ferroelectric and dielectric properties of SBN.

The Sr_{1-x}La_{2x/3}Bi₂Nb₂O₉ (LSBN- x , $x = 0-0.2$) ceramic samples were prepared by the traditional

solid-state reaction method, using analytical reagent grade (AR) of SrCO₃, Bi₂O₃, Nb₂O₅ and La₂O₃ as raw materials. The composite powders with 4 wt.% excess Bi₂O₃ are sufficiently mixed by ball milling for 2 h and calcined in air at 775°C for 2 h. The calcined powders were ballmilled again and pressed into pellets, then sintered in closed alumina crucibles at 1050°C for 2 h.

X-ray diffraction [(XRD), D/Max-2400] with Cu K_α radiation was used to determine the crystal structure of the sintered pellets. The microstructure of the sintered samples was observed by scanning electron microscopy [(SEM), JSM-5610LV]. The ferroelectric properties were investigated using an RT6000 ferroelectric tester (Radiant Technology) at room temperature. Dielectric measurements were taken on an LCR meter (YY2810) at a frequency of 100 kHz.

Figure 1 shows the XRD patterns of SBN, LSBN-0.1 and LSBN-0.2. The patterns can be fully indexed using the standard XRD data, indicating a single phase layered perovskite structure without any traces of impurity phase. The XRD result indicates that La³⁺ was fully incorporated into the crystal structure of SBN.

Figure 2 shows the SEM images of the fracture surfaces of $x = 0$ and 0.1 samples. The undoped SBN ceramics consist of lamellar grains with small pores at grain junctions (Fig. 2(a)). With La doping, the samples have a dense fracture surface with plate-like grains (Fig. 2(b)). In addition, the average grain size (about 2 μm) of LSBN-0.1 is smaller than that of undoped SBN (3-4 μm). The improvement of densification and decrease of grain sizes can be attributed to the A-site deficiency caused by the substitution of

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La³⁺ for Sr²⁺,^[8] which favours the diffusion of the constituent ions during the sintering process.^[12]

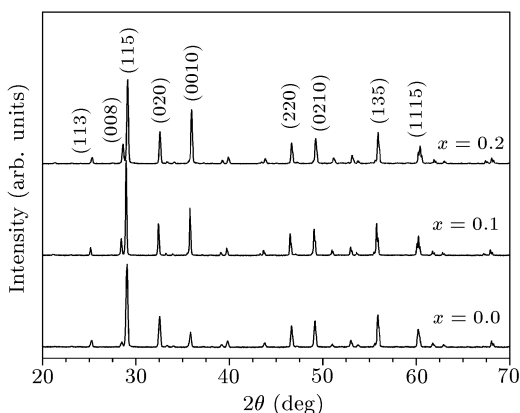


Fig. 1. XRD patterns of LSBN- x ceramics.

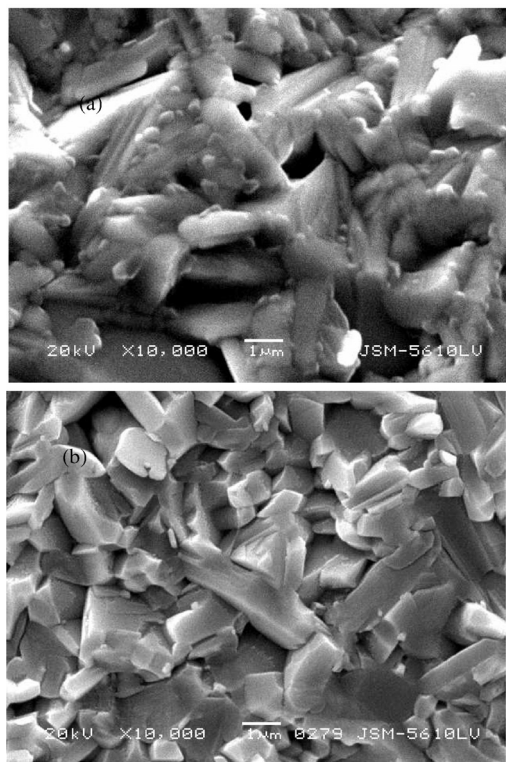


Fig. 2. SEM fracture photographs of LSBN- x ceramics: (a) $x = 0$ and (b) $x = 0.1$.

The hysteresis loops of LSBN- x ($x = 0, 0.125, 0.2$) at an applied electric field of 100 kV/cm are shown in Fig. 3. La doping affects greatly the remanent polarization P_r of SBN. Here $2P_r$ was measured to be close to $22.8 \mu\text{C}/\text{cm}^2$ for LSBN-0.125, which is approximately 60% larger than that of pure SBN. The dependences of $2P_r$ and coercive field E_c , on La doping content x under an applied electric field of 100 kV/cm are shown in Fig. 4. With increasing x , $2P_r$ increases gradually and reached a maximum value at $x = 0.125$,

then decreases slightly with further increasing x , while E_c decreases slightly from 73.5 kV/cm to less than 70 kV/cm as the La doping level x increases from 0 to 0.20.

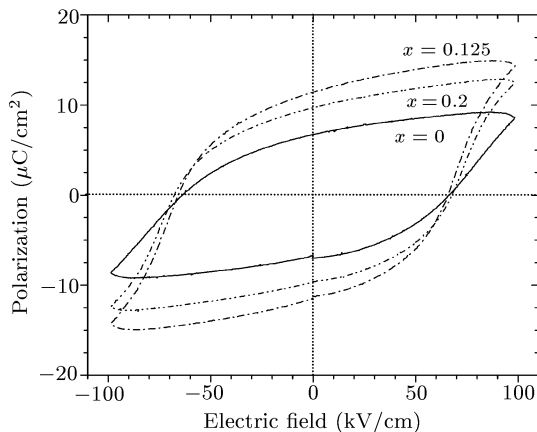


Fig. 3. Polarization-field hysteresis loops of LSBN- x ceramics.

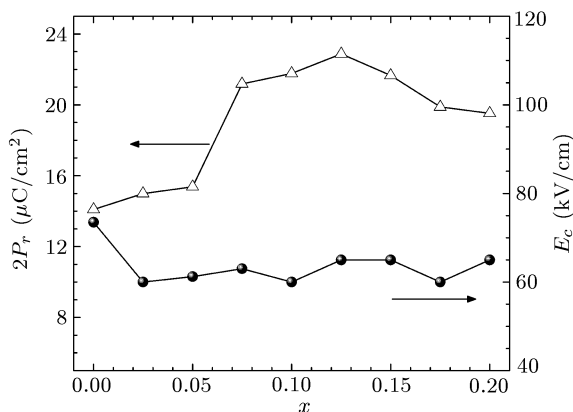


Fig. 4. Dependence of $2P_r$ and E_c on the La content x in $\text{Sr}_{1-x}\text{La}_{2x/3}\text{Bi}_2\text{Nb}_2\text{O}_9$ ($0 \leq x \leq 0.2$).

Recently, it has been reported that in rare-earth doped BLSFs, only A -site ions could be replaced at light doping levels and both A -site ions and Bi^{3+} in $(\text{Bi}_2\text{O}_2)^{2+}$ layer could be replaced at high doping levels.^[13–15] To satisfy the charge neutrality in LSBN- x , the replacement of Sr^{2+} by La^{3+} results in Sr vacancies at A sites.^[8] The A -site vacancies greatly enhance the rotation of the octahedra in the $a-b$ plane accompanied with the whole shift of the octahedra along the a axis. This causes the enhancement of polarization in $\text{SrBi}_2\text{Ta}_2\text{O}_9$ (SBT).^[12] Thus, we argue that the A -site vacancies favour the improvement of polarization of SBN due to the very similar crystal structure and physical properties of SBN and SBT.^[16,17] However, La occupying the Bi^{3+} sites may weaken the role of $(\text{Bi}_2\text{O}_2)^{2+}$ layer which acts as free electron reservoirs and insulating layers. This leads to the decrease of polarization.^[13] Therefore, the change of polarization

of LSBN- x with doping level x is the competitive result of La^{3+} incorporation into Sr^{2+} sites and Bi^{3+} sites. When $x \leq 0.125$, La^{3+} insertion into Sr^{2+} sites is dominant, which brings about the enhancement of polarization in LSBN- x . As $x > 0.125$, La^{3+} incorporation into Bi^{3+} is significant, which results in the decrease of polarization. In addition, the slight decrease of the coercive field with La doping level can be related to the dipolar defects formed by $V_{\text{Sr}}^{//}$ (Sr vacancies with two negative charges) and $\text{La}_{\text{Sr}}^{\bullet}$ (a La^{3+} ion in the Sr^{2+} site with one positive charge), since the random field around the dipolar defects lowers the activation barrier required for the domain nucleation leading to a decrease in E_c .^[18]

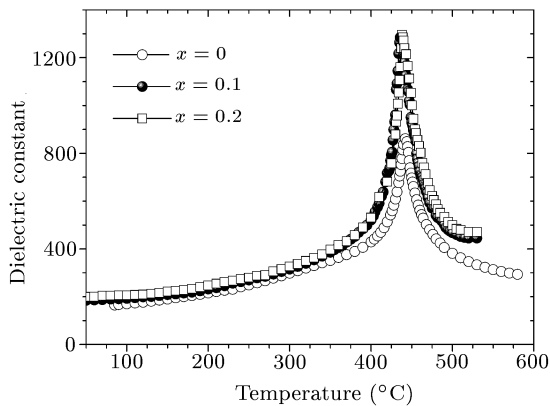


Fig. 5. Dependence of dielectric constant on the temperature of LSBN- x .

Figure 5 shows the dielectric constants of SBN ceramics as a function of temperature at different doping levels, obtained at a frequency of 100 kHz. The Curie temperature T_c almost depends on the La content. This is different from the previous reports, in which A site substitution with small radius ions generally increases the Curie temperature of SBN.^[8,19] The deviation might be attributed to the resulting A -site vacancies. It has been found that A -site vacancies may weaken the coupling between the neighbouring octahedra in La doped SBT,^[20] leading to the decrease of the Curie temperature. Thus, on the one hand, small-radius La^{3+} ions occupy A sites, and on the other hand, Sr^{2+} vacancies appear on A sites. Therefore, the competitive effects between the two sides make

the Curie temperature remaining unchanged over the doping range ($0 \leq x \leq 0.2$).

In summary, the effects of La doping on the structure, dielectric and ferroelectric properties of SBN are investigated. The remanent polarization increases first and then decreases with increasing La content, which is the competitive result of La incorporation into Sr^{2+} sites and Bi^{3+} sites. The coercive field decreases lightly after La doping due to the resulting A site vacancies. The Curie temperature keeps unchanged after La doping. Therefore, appropriate La doping can lead to great improvement in the ferroelectric properties of SBN without lowering the Curie temperature.

References

- [1] Scott J F and Paz de Araujo C A 1989 *Science* **246** 1400
- [2] Ishida J, Yamada T, Sawabe A, Okuwada K and Saito K 2002 *Appl. Phys. Lett.* **80** 467
- [3] Mihara T, Watanabe H and Paz de Araujo C A 1994 *Jpn. J. Appl. Phys.* **33** 3996
- [4] Kojima S, Imaizumi R, Hamazaki S and Takashige M 1994 *Jpn. J. Appl. Phys.* **33** 5559
- [5] Paz de Araujo C A, Cuchiari J D, McMillan L D, Scott M C and Scott J F 1995 *Nature* **374** 627
- [6] Scott J F 1997 *Thin Film Ferroelectric Materials and Devices* ed Ramesh R (Norwell, MA: Kluwer)
- [7] Wu Y and Cao G Z 1999 *Appl. Phys. Lett.* **75** 2650
- [8] Forbess M J, Seraji S, Wu Y, Nguyen C P and Cao G Z 2000 *Appl. Phys. Lett.* **76** 2934
- [9] Gu H S, Xue J M and Wang J 2001 *Appl. Phys. Lett.* **79** 2061
- [10] Shrivastava V, Jha A K and Mendiratta R G 2006 *Mater. Lett.* **60** 1459
- [11] Song T K, Park S E, Cho J A and Kim M H 2003 *J. Korean Phys. Soc.* **42** 1343
- [12] Noguchi Y, Miyayama M and Kudo T 2001 *Phys. Rev. B* **63** 214102
- [13] Zhu J, Chen X B, Zhang Z P and Shen J C 2005 *Acta Mater.* **53** 3155
- [14] Osada M, Tada M, Kakihana M, Watanabe T and Funakubo H 2001 *Jpn. J. Appl. Phys.* **40** 5572
- [15] Hervoche C H and Lightfoot P 2000 *J. Solid State Chem.* **153** 66
- [16] Chen T C, Thio C L and Desu S B 1997 *J. Mat. Res.* **12** 2628
- [17] Miura K 2002 *Appl. Phys. Lett.* **80** 2967
- [18] Viehland D and Chen Y H 2000 *J. Appl. Phys.* **88** 6696
- [19] Wu Y, Forbess M J, Seraji S, Limmer S J, Chou T P, Nguyen C and Cao G Z 2001 *J. Appl. Phys.* **90** 5296
- [20] Noguchi Y, Miyayama M, Oikawa K and Kamiyama T 2004 *J. Appl. Phys.* **95** 4261