Raman scattering study of La-doped SrBi$_2$Nb$_2$O$_9$ ceramics

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Abstract
La doped SrBi$_2$Nb$_2$O$_9$ (LSBN) ferroelectric ceramics prepared by the solid-state reaction technique exhibit composition-dependent remanent polarization. X-ray diffraction (XRD) and Raman scattering have been carried out to investigate the effects of La doping on the crystal structure of SrBi$_2$Nb$_2$O$_9$ (SBN). The XRD study shows that the ceramics exhibit increasing preferred c orientation with increasing La content. The results of Raman scattering reveal that the doping La^{3+} ions prefer to replace Sr^{2+} in the A sites of the perovskite blocks (SrNb$_2$O$_7$) at a low doping content and they may also occupy the Bi^{3+} sites in the Bi$_2$O$_2$ layers with further increasing La content. Accordingly, the observed variation of the ferroelectric properties with the La content in LSBN ceramics can be attributed to the competitive results of La substitution in A sites and Bi^{3+} sites. Our results demonstrate that the ferroelectric properties of La doped SBN are strongly related to the occupied sites of La^{3+} ions.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Bismuth layer structured ferroelectrics (BLSFs) have attracted much attention because of their potential application in ferroelectric random access memories (FeRAMs). The chemical formula of BLSFs is generally given as (Bi$_2$O$_2$)$^{2+}$(A$_{m-1}$B$_m$O$_{3m+1}$)$^{2-}$, where A = Na^{1+}, K^{1+}, Ba^{2+}, Bi^{3+}, rare earths and B = Fe^{3+}, Ti^{4+}, Nb^{5+}, Ta^{5+}, W^{6+}, [1]. Among the BLSFs, SrBi$_2$Nb$_2$O$_9$ (SBN) shows excellent fatigue resistance and reasonable spontaneous polarization [2, 3]. However, there are also some problems associated with SBN, such as relatively low spontaneous polarization, relatively high processing temperature and relatively high dielectric loss [4]. Therefore, significant efforts have been made to improve the dielectric properties and decrease the processing temperature of SBN. It has been reported that doping can greatly affect the crystal structure, dielectric properties and electrical conductivities of SBN ferroelectrics [5–9]. In addition, it is also found that the incorporation of vanadium or BiFeO$_3$ into SBN resulted in a dramatic decrease in the processing temperature [8, 10].

In our previous work, we reported that appropriate La doping in SBN ceramics can lead to great enhancement of polarization (up to 60%) [11]. However, there is still the absence of a clear understanding of the mechanism for polarization enhancement in SBN. Raman scattering is a sensitive technique for investigating the lattice vibrational modes, which can give the information for the changes of lattice vibrations and the occupying positions of doping ions, and it is thus a useful tool for studying the doping-related ferroelectric behaviour. In this paper, Raman scattering study of La doped SBN ceramics is presented to analyse the effects of La doping on the microstructure and ferroelectric properties of SBN.

2. Experimental

La$_{2x/3}$Sr$_{1-x}$Bi$_2$Nb$_2$O$_9$ (LSBN-x, x = 0–0.2) ceramic samples were prepared by the traditional solid-state reaction. The starting materials that were used were Bi$_2$O$_3$, SrCO$_3$, Nb$_2$O$_5$ and La$_2$O$_3$, all with a purity of 99%. The powders were mixed together at a stoichiometric rate by ball milling for 2 h.
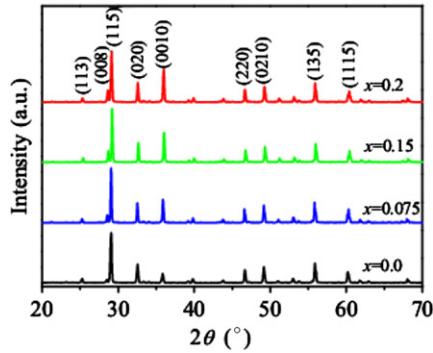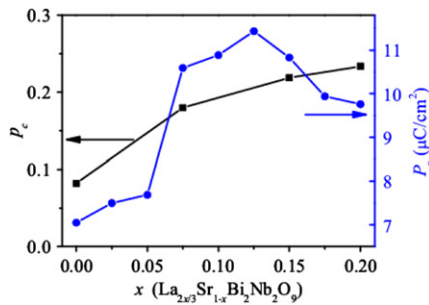
Figure 1. XRD patterns of LSBN-*x* ceramics.

Figure 2. Degree of *c*-axis orientation p_c and remanent polarization P_r of LSBN-*x* as a function of the La content.

Excess Bi_2O_3 of approximate 4 wt% was added to compensate for the loss of volatile Bi_2O_3 during the sintering process. The mixtures were first calcined in air at $775\,^\circ C$ for 2 h. The calcined powders were ground and pressed into pellets, then sintered in closed crucibles at $1050\,^\circ C$ for 2 h.

X-ray diffraction (XRD) measurements for polished ceramics were carried out with Cu K_α radiation. Ferroelectric measurements were performed using a RT6000 ferroelectric tester (Radiant Technology). Raman scattering was performed in the back scattering geometry using a JY-HR800 Raman spectrometer with a 532 nm wavelength Ar$^+$ laser and a resolution of $0.5\,cm^{-1}$.

3. Results and discussion

3.1. XRD and polarization results

Figure 1 shows the XRD patterns of LSBN-*x* samples at various *x*. All the samples show a layered perovskite structure without the secondary phase detectable, indicating that La^{3+} is completely incorporated into the crystal lattice of SBN at $x \leqslant 0.2$. Moreover, it is observed that the peak intensity of (0 0 8) increases with increasing La content compared with that of (1 1 5). Defining the degree of preferred *c*-axis orientation as $p_c = \sum I(0\,0\,l)/\sum I(hkl)$, the calculated p_c, together with the obtained remanent polarization for LSBN-*x* ceramics, are shown in figure 2. It can be seen that the remanent polarization P_r of LSBN-*x* increases first with increasing La content and maximizes at $x = 0.125$, then decreases with a further increase in the La content; however, p_c increases continuously with the increase in the La content. Since polarization P is along the *a*-axis ($P||a$) in SBN [12], the increase in P_r cannot
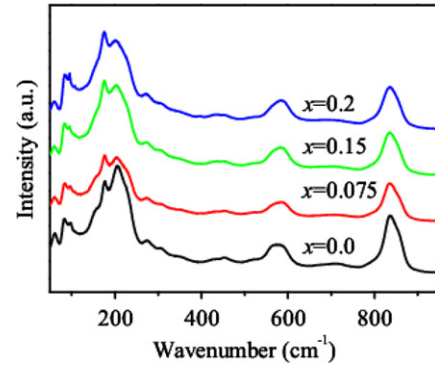
Figure 3. Raman spectra of LSBN-*x* ceramics in the spectral range 50–$1100\,cm^{-1}$.

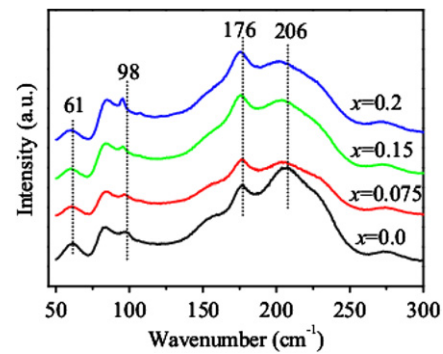**Figure 4.** Raman spectra of LSBN-*x* ceramics in the spectral range 50–$300\,cm^{-1}$.

be simply ascribed to the orientation effect (increasing non-*c*-axis orientation usually increases polarization). To obtain an insight into composition-dependent polarization, Raman scattering has been carried out to investigate the effects of La doping on the crystal structure of SBN.

3.2. Raman scattering results

The Raman spectra of the LSBN-*x* ceramics in the spectral range 50–$1100\,cm^{-1}$ at room temperature are shown in figure 3. There are some intense Raman bands at around 61, 98, 176, 206, 575 and $835\,cm^{-1}$ and some weak peaks. Four obvious peaks in the spectral range 50–$300\,cm^{-1}$ exhibit different composition-dependent changes, as shown in figure 4. The dependence of the frequency shift on the doping content for each peak is shown in figures 5(*a*)–(*d*), respectively. The lowest frequency mode at $61\,cm^{-1}$, assigned as a 'rigid layer' mode reflecting the Bi^{3+} ions vibration in Bi_2O_2 layers, shifts slightly to a lower frequency at $x \geqslant 0.075$. A similar behaviour of shifting to low frequency is also observed at the $176\,cm^{-1}$ mode, corresponding to Nb *z*-axis vibrations [13]. The modes at 98 and $206\,cm^{-1}$, related to the vibration of the A-site ions of the pseudoperovskite blocks [14], redshift obviously at $x \leqslant 0.075$ and shift slightly at $x > 0.075$. In addition, the intensity of the $206\,cm^{-1}$ mode decreases with increasing *x*.

For the modes above $300\,cm^{-1}$, the mode at $575\,cm^{-1}$ corresponds to a rigid sublattice mode in which all negative- and positive-ion displacements are equal and opposite, and the mode at $835\,cm^{-1}$ reflects the stretching mode of NbO$_6$ octahedra [13]. The $575\,cm^{-1}$ mode exhibits an obvious
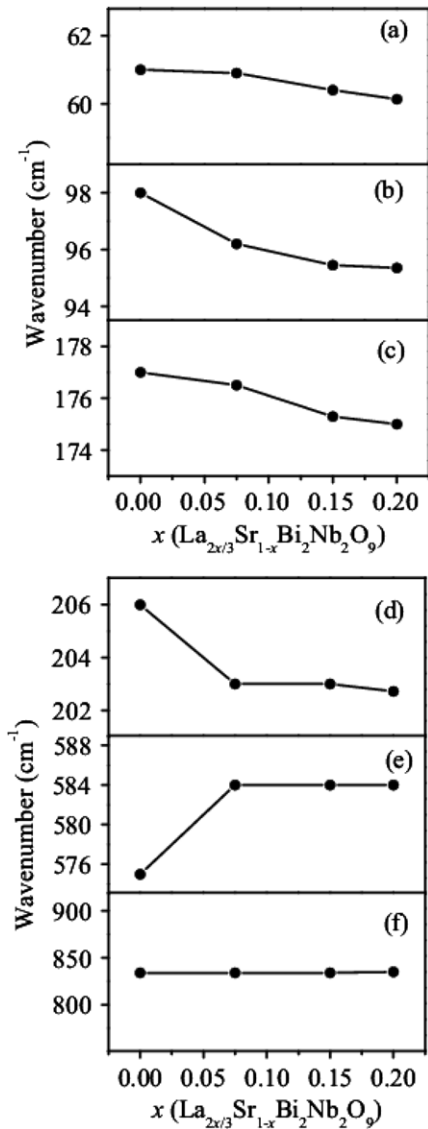
Figure 5. Compositional dependence of some frequency modes for LSBN-x.

blueshift at $x \leqslant 0.075$ and negligible change at $x > 0.075$, while the mode at 835 cm^{-1} remains unchanged after La doping.

3.3. Origin of Raman shift

For the lowest mode at 61 cm^{-1}, the peak position moves to a low frequency when $x > 0.075$. It has been found that in Bi-layered perovskite materials, when Bi^{3+} is replaced by other ions, the chemical bonds in Bi$_2$O$_2$ layers would be undermined, resulting in the redshift of the mode corresponding to Bi^{3+} vibration [15, 16]. Thus, we can ascribe the variation of the 61 cm^{-1} mode to the weakening of chemical bonds as a result of La^{3+} substituting for Bi^{3+} in Bi$_2$O$_2$ layers. For those modes at 98 and 206 cm^{-1} responsible for the vibrations of A site ions, there is obvious redshift after La doping. Such changes in the peak position may be ascribed to the heavier mass of La and also to the lowering of the binding strength [15]. Besides the weakening of the chemical bonds after doping, the redshift of

the 176 cm^{-1} mode might also be attributed to the doping of the larger La^{3+} ions because the Nb z-axis vibrations at 176 cm^{-1} mode could be influenced by the variation of the environment around NbO$_6$ octahedra due to the substitution of La into the Sr or Bi site [17]. The Raman mode at 575 cm^{-1} shifts to a high frequency with La doping, which is similar to the behaviour in Ba-doped SrBi$_2$Ta$_2$O$_9$ [17]. The mode blueshift implies the reinforcement of the binding strength related to the connection of NbO$_6$ octahedra and Bi$_2$O$_2$ layers. Since La^{3+} incorporation into Bi$_2$O$_2$ layers induces the bond relaxation in the Bi$_2$O$_2$ layers, the neighbouring NbO$_6$ octahedra might shrink, resulting in the increase in the bond energy and the consequent blueshift in the frequency [15].

3.4. Analysis of La substitution sites

Raman frequency is mainly determined by the mass over all corresponding ions and the strength of the chemical bond between them and hence is a very useful tool to analyse the occupied position of the doping ions. Generally, it is thought that the substitution is in the A site when SBN is doped with Ca, Ba, La [5, 6] due to the asymmetric coordination environment of Bi cations in the Bi$_2$O$_2$ layers [12]. However, recently, it has been reported that some doping ions could appear in the Bi$_2$O$_2$ layers in BLSFs [15, 18]. This suggests that Bi^{3+} in Bi$_2$O$_2$ layers may also be replaced by other ions.

For La-doped SBN, the stretching mode of NbO$_6$ at 835 cm^{-1} remains unchanged after La doping, suggesting that La^{3+} does not substitute into the B site (Nb site) of the perovskite-like (SrNb$_2$O$_7$)$^{2-}$ slabs. For the A-site ion vibrations at 98 and 206 cm^{-1}, there are obvious changes after doping, so it is indicated that part of the A sites must be occupied by the doping La ions. Although the changes in the Raman mode confirm that La occupy A sites, it is still necessary to check if some La ions also substitute into the Bi^{3+} sites in Bi$_2$O$_2$ layers. Compared with Sr^{2+} at A sites, La^{3+} shows a marked preference for Bi^{3+} in Bi$_2$O$_2$ layers due to similar chemical valence and close ion radii (La^{3+} : 1.16 Å, Bi^{3+} : 1.17 Å). For the 61 cm^{-1} mode corresponding to the vibration of Bi^{3+} ions in Bi$_2$O$_2$ layers, there is an increasing redshift with the increase in the La content, especially for $x > 0.075$, suggesting that more and more Bi^{3+} ions are substituted by La^{3+} ions when the La content increases above a certain value.

Accordingly, when $x \leqslant 0.075$, the modes associated with the vibration of A site ions show an obvious change while that corresponding to Bi^{3+} in Bi$_2$O$_2$ layers changes less, indicating that occupation of A sites by La ions is significant. As $x > 0.075$, the variations in the modes related to A-site ions slow down whereas the shift for the 61 cm^{-1} mode becomes obvious, implying that the La ion starts occupying the Bi^{3+} site. Thus, it can be concluded that La ions mainly substitute for A site ions at a low doping content ($x \leqslant 0.075$), and the doping ions occupy both the A site in perovskite-like slabs and Bi^{3+} sites in Bi$_2$O$_2$ layers at a higher doping content ($x > 0.075$).

3.5. Mechanism of the doping effects on ferroelectric polarization

Based on the analysis of the Raman modes, the composition-dependent polarization in LSBN-x can be well understood. For

La-doped SBN, trivalent ion La^{3+} occupying the divalent Sr^{2+} site results in cation vacancies at A sites to satisfy the charge neutrality condition. Due to A-site vacancies, the rotation of NbO_6 in the a–b plane may double whereas the tilting from the c-axis changes little. Thus, the A-site vacancies greatly enhance the rotation of NbO_6 octahedra in the a–b plane accompanied by an entire shift of NbO_6 octahedra to the a-axis, resulting in the increase in polarization [19]. Therefore, La substitution at the A site enhances the ferroelectricity of LSBN-x. With the increase in La content, a part of the La ions substitutes into Bi_2O_2 layers; this weakens the chemical stability of Bi_2O_2 layers and hence partly destroys the original functions of the Bi_2O_2 layers as electron reservoirs and insulating layers, leading to the decrease in remanent polarization [16]. So the structural change in NbO_6 octahedra, competing with the bond weakening in Bi_2O_2 layers, induces the variation in the remanent polarization of LSBN-x. When x is less than 0.125, the change in NbO_6 octahedra is dominant, resulting in the improvement in remanent polarization. As x is higher than 0.125, the change in Bi_2O_2 layers is significant, which brings about the decrease in remanent polarization.

4. Conclusions

In conclusion, the Raman scattering study has been performed on La doped SBN ceramics to investigate the influences of La doping on the microstructure and ferroelectric polarization. The Raman investigation indicates that the La^{3+} ions replace Sr^{2+} ions at a low La content and are incorporated into both Sr^{2+} sites and Bi_2O_2 layers at a higher La content. The La^{3+} ions occupying A sites improves the remanent polarization while incorporating into Bi_2O_2 layers impairs the ferroelectricity. Thus, the observed composition-dependent polarization of LSBN-x results from the competitive effect of these two cases. The understanding of the mechanism of doping effects on the ferroelectric properties of SBN is helpful for obtaining large remanent polarization in BLSFs for FeRAMs.

Acknowledgments

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