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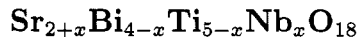
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Doping-Induced Structure Phase Transition of Layered Ferroelectrics

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Raman spectra of layered ferroelectrics $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$ ($0 \leq x \leq 2$) and $\text{Sr}_2\text{Bi}_{4-x}\text{La}_x\text{Ti}_5\text{O}_{18}$ at room temperature in the range of $20\text{--}1000\text{ cm}^{-1}$ were investigated. Vibration modes were assigned with the internal mode approach. Two doping-induced structure phase transitions were observed at about $x = 0.5$ and 1.25 for $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$, separately.

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$\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ (S18) is a member of the ferroelectric family of layered bismuth oxides with a general formula $(\text{Bi}_2\text{O}_2)(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})$, $m = 5$. Their structures are regulated by intergrowth Bi_2O_2 sheets and the perovskite-like layers $\text{A}_{m-1}\text{B}_m\text{O}_{3m+1}$, where A can be a mono-, di-, or trivalent metal ion or a mixture of them, and $\text{B} = \text{Ti}^{4+}$, Nb^{5+} or their combination. Subbarao¹ determined that the structure of S18 is orthorhombic. Above the Curie point (about 285°C), it has a tetragonal crystal structure with a space group $I4/mmm$. Subbarao^{2,3} found that, for $m = 2$ or 3 , combined substitution of $(\text{Bi}^{3+}, \text{Ti}^{4+})$ by $(\text{Me}^{2+}, \text{Nb}^{5+})$ always led to a steep decrease of the Curie temperature (e.g., from 650 to about 200°C). Because the Curie temperature of S18 is around 285°C , we can expect that a Curie point below room temperature can be achieved for S18 with the use of this combined substitution, i.e., $(\text{Bi}^{3+}, \text{Ti}^{4+})$ by $(\text{Sr}^{2+}, \text{Nb}^{5+})$. It is reasonable to expect a structure phase transition in the meantime, which definitely will induce some variations of the Raman spectra of solid solution $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$ (SN18).

Polycrystalline samples were synthesized by solid state reaction. Weighted amounts of the appropriate proportions of high purity SrCO_3 , Bi_2O_3 , La_2O_3 , TiO_2 , and Nb_2O_5 were thoroughly mixed and calcined at a temperature between 800 and 1100°C for 48 h. The calcination time depended on the attaining of stable Raman spectra. The x-ray diffraction result was in agreement with that of Subbarao.¹ Raman spectra were recorded with back scattering geometry by a J-Y T64000 Ramanlog system with a CCD using 488.0 nm emission of an Ar^+ laser source.

Figure 1 exhibits the composition dependence of Raman spectra of SN18 in the range of $20\text{--}1000\text{ cm}^{-1}$. The composition dependence of the peak shift of the Raman bands of SN18 with various x is shown in Fig. 2. Figure 3 is the composition dependence of Raman spectra of $\text{Sr}_2\text{Bi}_{4-x}\text{La}_x\text{Ti}_5\text{O}_{18}$ (SL18). From Fig. 1, it can be found that for all x values, Raman

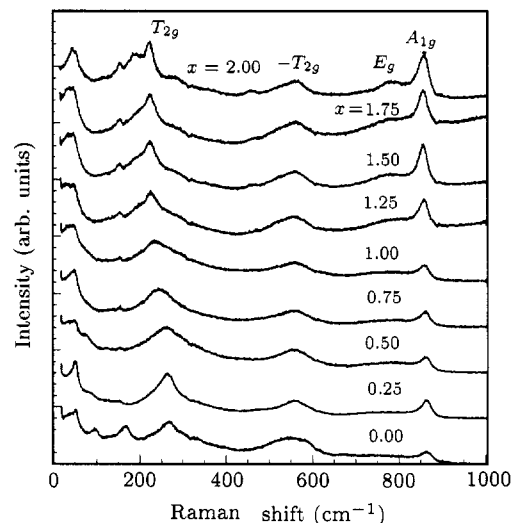


Fig. 1. Composition dependence of Raman spectra of $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$.

spectra exhibit similar profiles which suggests that the mixed-crystal SN18 is the so-called one mode mixed-crystal in which doped sample spectra show a similar Raman profile to that of pure polycrystal S18. This makes the assignment of Raman modes of S18 and SN18 a little convenient. For $x = 0.25$, modes at about 52.43 and 267.69 cm^{-1} soften a little, modes at 94.26 and 168.52 cm^{-1} soften to lower wavenumber, modes 541.23 and 861.77 cm^{-1} stiffen a little, and an indistinct new peak arises at about 758.37 cm^{-1} . For $x = 0.50$, the undoped external mode at 52.43 cm^{-1} splits into two peaks at 35.89 and 50.55 cm^{-1} . The other modes have a similar tendency like in the case with $x = 0.25$. For $x = 0.75$ and 1.00 , the splitting peak returns to its original case, the other modes soften or stiffen a little. For $x = 1.25$, the external mode at 52.43 cm^{-1} again splits into two peaks at 32.22 and 49.14 cm^{-1} , respectively. A new mode begins to arise at about 470.5 cm^{-1} . For $x = 1.50$ and 1.75 , these modes remain similar to the case of

$x = 1.25$. For $x = 2.00$, the splitting peak seems to return to the original case and two new external modes arise at about 120.11 and 195.31 cm^{-1} .

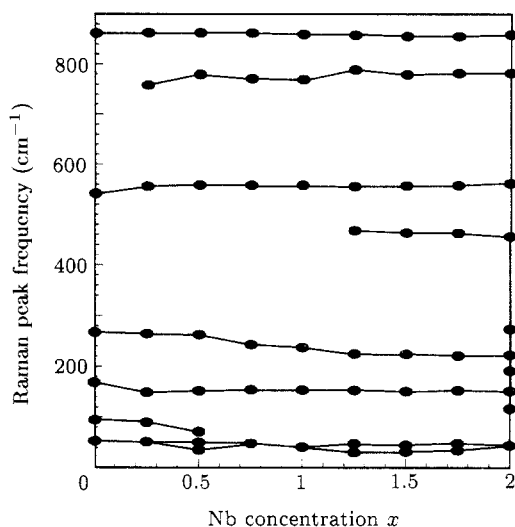


Fig. 2. Composition dependence of Raman peak of $\text{Sr}_{2+x}\text{Bi}_{4-x}\text{Ti}_{5-x}\text{Nb}_x\text{O}_{18}$, $x = 0.50$ and 1.25 corresponding to phase transition points.

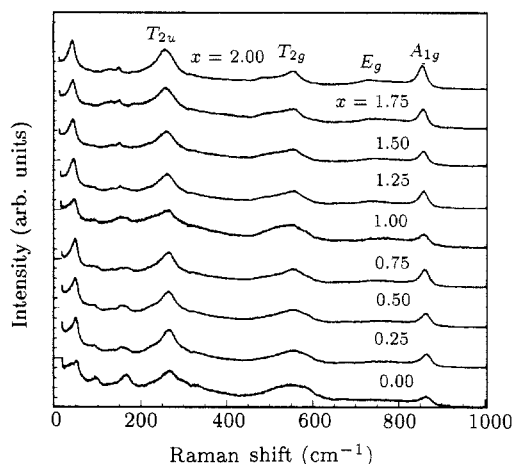


Fig. 3. Composition dependence of Raman spectra of $\text{Sr}_2\text{Bi}_{4-x}\text{La}_x\text{Ti}_5\text{O}_{18}$.

The structure of S18 ($m = 5$) consists of five perovskite-like layers between two $(\text{Bi}_2\text{O}_2)^{2+}$ oxide layers. A half of the unit cell of S18 was depicted in the literature.⁴ Its structure at room temperature is orthorhombic. Liu *et al.*⁵ tried to analyze the vibration modes of $\text{Ba}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$ (B18) in terms of the tetragonal structure with space group $I4/mmm$ as the first approximation. They found that the strict factor group analysis method can supply very little help in assignment of Raman modes of B18 and $\text{Ba}_2\text{Bi}_{4-x}\text{La}_x\text{Ti}_5\text{O}_{18}$ (BL18).

From the similar Raman profiles of S18, SN18, and SL18, we conclude that there exists some structure similarity among them. In fact, in metal oxide systems containing titanium or niobium, the binding

forces within the metal-oxygen octahedra are large compared to the crystal binding forces among the octahedra. The internal vibration of the BO_6 ($B = \text{Ti}, \text{Nb}$) octahedra in the solid should be quite close to the free ion modes. The external modes occur at considerably lower frequencies than internal modes. Therefore, the high frequency bands in the Raman spectra of these oxides can be satisfactorily assigned to the internal modes of these octahedra. This is especially valuable in complex systems like S18, SN18, and SL18 containing corner-shared TiO_6 and/or NbO_6 octahedra.

Our studies show that, despite the complexity of these oxides, vibration spectra provide valuable information when interpreted in conjunction with the known structure features. The internal mode approach, although somewhat simplified, can obtain conclusions as good as strict factor group analysis in the mode assignment of such a complex oxide system.

Of the various modes of isolated octahedron TiO_6 or NbO_6 , the $\nu_1(A_{1g})$ Raman mode usually corresponds to the highest frequency Raman band in the spectra of many perovskite-like structure, which is due to symmetric metal-oxygen stretching vibration. Thus, we interpret the mode at 861.77 cm^{-1} of SN18 as the $\nu_1(A_{1g})$ Raman mode. The mode around 750 cm^{-1} with weak intensity corresponds to $\nu_2(E_g)$, another symmetric stretching vibration mode. The weak intensity comes from the TiO_6 or NbO_6 octahedron which consists of Ti^{4+} or Nb^{5+} . Both of them have a d^0 electron configuration that participates significantly in π -bonding, which leads to a weak intensity according to Wolkenstein's bond polarizability intensity theory.⁶ But we should recall that extensive distortions of TiO_6 octahedra can definitely give rise to a higher intensity ν_2 band as in the case with a highly doped system. The 541.23 cm^{-1} mode arises from the $\nu_5(T_{2g})$ mode, symmetric bending vibration of TiO_6 octahedron. Occurrence of the 267.69 cm^{-1} mode means that the TiO_6 octahedron has a serious distortion which causes the inactive $\nu_6(T_{2u})$ mode to be active.

The free BO_6 octahedron has the symmetry O_h , but in the crystal, its symmetry will have a slight departure from the ideal O_h group, which is responsible for the occurrence of an inactive $\nu_6(T_{2u})$ mode. For $x = 0.50$ and 1.25 , the variations of Raman spectra reflecting the structure phase transitions are due possibly to the symmetry variations of $O_h \rightarrow D_{3d}$ according to the selection rules for the vibrational modes of BO_6 octahedra in the different symmetry. Because D_{3d} is a nonpolar point group, we consider that these structure phase transitions may be from ferroelectric to nonferroelectric.

Armstrong *et al.*⁷ found that, in the system of layered bismuth oxides, $(\text{Bi}_2\text{O}_2)^{2+}$ layers cannot accommodate any substitution. Then, naturally, all the

possible substitutions will happen for the A or B sites of the perovskite-like layers $A_{m-1}B_mO_{3m+1}$, (or in detail, the unit of the hypothetical perovskite structure ABO_3) A site substitution will only have indirect effect on BO_6 octahedra; therefore, A site substitution will bring about very little variations of internal modes of layered bismuth oxides because internal modes come from the vibrations of BO_6 octahedra; SL18 is an example of this case. On the other hand, B site substitution will have obvious effect on BO_6 octahedra, which will cause the vibrations of the internal modes of layered bismuth oxides. An example is SN18, and another example may be $Ba_{2+x}Bi_{4-x}Ti_{5-x}Nb_xO_{18}$ according to Raman spectra observation.

An external mode around 168 cm^{-1} is common to all the oxides which can be assigned metal-metal ion vibration modes.⁸ The external mode around 52 cm^{-1} is the rigid-layer mode marking the symmetry of the layered structure, and corresponds to the relative vibration between the (Bi_2O_2) sheet and the perovskite-like layer. Its shift will induce structure phase transitions. In fact, for $x = 0.50$ and 1.25 , this mode splits into two modes which means that two structure phase transitions happen around $x = 0.50$ and 1.25 . From the similar variations of Raman spectra around $x = 0.50$ and 1.25 , it seems that they are the same structure phase transitions which happen for two x values. In fact, we know that the radius of Sr^{2+} is slightly larger than that of Bi^{3+} , while the electronegativity of Sr^{2+} is far less than that of Bi^{3+} . The same relations of radius and electronegativity exist between

Ti^{4+} and Nb^{5+} , but with much less difference values. These will make the vibrations of Raman spectra of SN18 caused by the combined substitution of (Bi^{3+}, Ti^{4+}) with (Ba^{2+}, Nb^{5+}) a kind of spectra modulation rather than monotonic variations, i.e., the radius and electronegativity effect become the control or major factor alternately with the increasing of x .

Finally, it can be considered that the modulation of Raman spectra caused by the combined substitution is a reasonable response of the structure modulation caused by this combined substitution. It seems that around $x = 0.50$ and 1.25 , SN18 experiences two structure phase transitions. That the soft mode does not soften to zero at the phase transition points may arise from the fact that these phase transitions are not simply a displacive type mechanism, instead they are the combination of displacive and order-disorder types such as those observed in $BaTiO_3$, etc.⁹

REFERENCES

- ¹ E. C. Subbarao, *J. Am. Ceram. Soc.* 45 (1962) 166.
- ² E. C. Subbarao, *Phys. Rev.* 122 (1961) 804.
- ³ E. C. Subbarao, *J. Phys. Chem. Solid*, 23 (1962) 665.
- ⁴ Guangtian Zou, Jianjun Liu, Qiliang Cui and Haibin Yang, *Phys. Lett. A* 189 (1994) 257.
- ⁵ Jianjun Liu, Chunxiao Gao, Guangtian Zou and Yanrong Jin, *Phys Lett. A* 218 (1996) 91.
- ⁶ M. Eliaščevich and M. Wolkenstein, *J. Phys. USSR.* 9 (1945) 101; 326.
- ⁷ R. A. Armstrong and R. E. Newnham, *Mat. Res. Bull.* 7 (1972) 1025.
- ⁸ I. R. Reatle and T. R. Gilson, *J. Chem. Soc. A* (1969) 2322.
- ⁹ A. K. Sood *et al.*, *Phys. Rev. B.* 51 (1995) 8892.