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## LETTER TO THE EDITOR

**Optical mode softening of ferroelectric SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> and related bismuth layer-structured oxides**

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**Abstract.** The lattice instability related to ferroelectric phase transitions of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> and its family has been studied by Raman scattering in the temperature range between 293 K and 958 K. The lowest optical mode of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> of 29 cm<sup>-1</sup> at room temperature shows remarkable temperature variation towards  $T_C = 608$  K. Its mode frequency decreases markedly and the damping factor increases rapidly below  $T_C$ . The composition dependence of the low-frequency modes has been investigated in the family ABi<sub>2</sub>M<sub>2</sub>O<sub>9</sub> (A = Ba, Ca, Sr, M = Nb, Ta) and Bi<sub>3</sub>TiMO<sub>9</sub> (M = Nb, Ta). All the lowest modes soften upon heating, except BaBi<sub>2</sub>M<sub>2</sub>O<sub>9</sub> (M = Nb, Ta). The nature of the damping of the soft modes is discussed in relation to the ionic radius of the A site of a pseudo-perovskite unit.

Currently, among bismuth layer-structured ferroelectrics, SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> (SBT) has become the most important material in the field of ferroelectric memory because of its low fatigue endurance and low switching voltage [1, 2]. However, the fundamental properties related to a ferroelectric phase transition have not yet been well studied.

Since the 1960s, the series of bismuth layer-structured compounds has been extensively studied, and it was found that above room temperature they mostly undergo ferroelectric or ferroelectric-like phase transitions. The chemical formula is generally given by Bi<sub>2</sub>A<sub>m-1</sub>BmO<sub>3m+3</sub> = [Bi<sub>2</sub>O<sub>2</sub>]<sub>2</sub>+[A<sub>m-1</sub>B<sub>m</sub>O<sub>3m+1</sub>]<sup>2-</sup>, where A = Na<sup>+</sup>, K<sup>+</sup>, Ba<sup>2+</sup>, Ca<sup>2+</sup>, Pb<sup>2+</sup>, Sr<sup>2+</sup>, Bi<sup>3+</sup>, ... and B = Fe<sup>3+</sup>, Ti<sup>4+</sup>, Nb<sup>5+</sup>, Ta<sup>5+</sup>, W<sup>6+</sup>, ... A pseudo-perovskite layer [A<sub>m-1</sub>B<sub>m</sub>O<sub>3m+1</sub>]<sup>2-</sup> is sandwiched between the fluorite type sheets [Bi<sub>2</sub>O<sub>2</sub>]<sup>2+</sup>;  $m$  and  $m-1$  are the numbers of oxygen octahedra and pseudo-perovskite units in a pseudo-perovskite layer, respectively [3–6].

Since the x-ray diffraction studies suggested the displacive nature for ferroelectricity, the clear evidence of soft modes by Raman or far-infrared studies has been requested. Although there does not seem to be any earlier far-infrared study of these compounds, systematic Raman study of the compounds  $m = 3$  and 4 have been already reported [7, 8]. As for the Raman study of compounds  $m = 2$ , the softening of the lowest optical mode was reported in a ferroelectric phase by using a powder sample of SrBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> (SBN) [9]. Recently, the optical phonon modes of single crystals of PbBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> (PBN) were also studied, and the partial softening of the lowest optical mode was observed below the Curie temperature  $T_C = 833$  K [10].

In the present work, the temperature dependence from ferroelectric to paraelectric phases was systematically studied by Raman spectroscopy for bismuth layer-structured oxides ( $m = 2$ ), ABi<sub>2</sub>M<sub>2</sub>O<sub>9</sub> (A = Ba, Ca, Sr, M = Nb, Ta) and Bi<sub>3</sub>TiMO<sub>9</sub> (M = Nb, Ta).

The Raman scattering spectra were measured in the following processes. A 5145 Å light, with 100 mW of power from an Ar ion laser, was focused on a surface of the ceramic

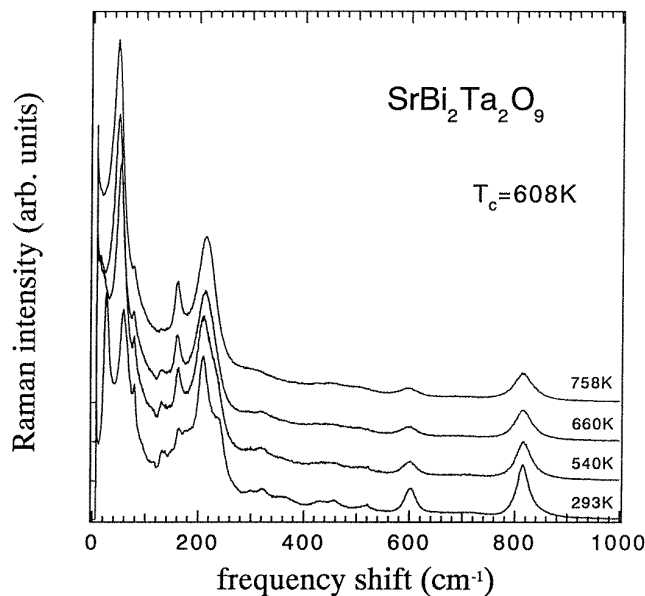
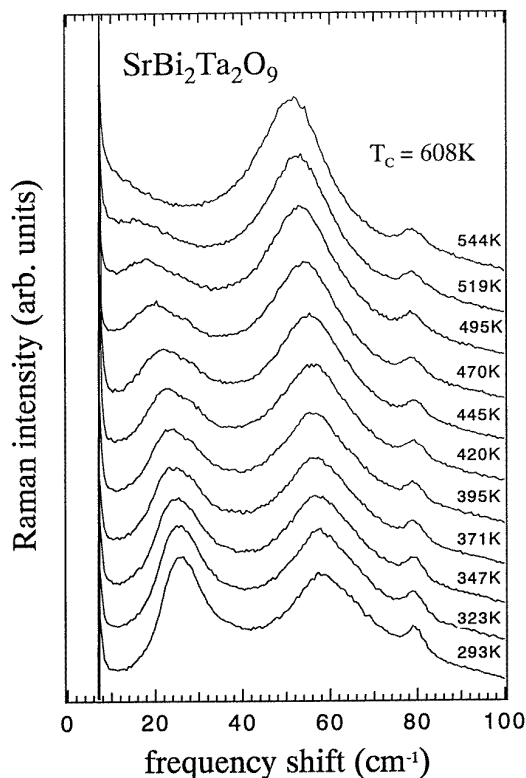


Figure 1. Temperature dependence of Raman scattering spectra of  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ .

samples kept in a temperature controlled oven with quartz windows. The temperature of the sample was controlled to within  $\pm 0.25$  K. The scattered light from the samples was collected by an F4 collecting lens in a backward scattering geometry, and focused on the entrance slit of a triplegrating spectrometer for additive dispersion (Jobin Yvon, T64000), with a spectral resolution of  $2 \text{ cm}^{-1}$ . The depolarized output signals from the spectrometer were detected by a photon counting technique. The ceramic samples of bismuth layer-structured oxides,  $\text{ABi}_2\text{M}_2\text{O}_9$  ( $A = \text{Ba, Ca, Sr}$ ,  $M = \text{Nb, Ta}$ ) and  $\text{Bi}_3\text{TiMO}_9$  ( $M = \text{Nb, Ta}$ ) were supplied from the Material System Laboratory, Department of Toshima MFG Co., Ltd.

SBT undergoes a ferroelectric phase transition at about  $T_C = 608$  K. The structural change was previously reported from tetragonal to orthorhombic with a space group  $Fmmm$ . Subsequently Newnham *et al* proposed that the structure of  $(\text{Sr,Ba})\text{Bi}_2\text{Ta}_2\text{O}_9$  is best described as orthorhombic  $A2_1am$  at room temperature [11]. Recently, the crystal structure of SBT, SBN has been refined at room temperature [12, 13]. The structure can be described in terms of small displacive perturbations from a tetragonal  $I4/mmm$  ( $Z = 2$ ,  $a_p = b_p = 3.85 \text{ \AA}$ ,  $p = \text{perovskite}$ ) prototype structure. It is common to assume a doubled orthorhombic cell as a parent  $Fmmm$  structure, a derivative of a prototypic  $I4/mmm$ . It has been customary to define the  $a$ -axis as a polar axis direction for ferroelectricity. Then the spontaneous polarization is derived by several displacive mechanisms involving rigid displacements of the Sr ion at the A site of a pseudo-perovskite unit along the ferroelectric  $a$ -axis, as well as rotations of an octahedron around the polar  $a$ -axis and the  $c$ -axis. The space group of a ferroelectric phase was assigned to be  $A2_1am$  with a doubled unit cell ( $Z = 4$ ,  $a = 5.5306 \text{ \AA}$ ,  $b = 5.5344 \text{ \AA}$ ,  $c = 24.98 \text{ \AA}$  at room temperature).

Figure 1 shows the temperature dependence of Raman scattering spectra of SBT from  $8 \text{ cm}^{-1}$  to  $1000 \text{ cm}^{-1}$ . It reveals the internal modes of a perovskite unit,  $\text{TaO}_6$  octahedra and a  $\text{Bi}_2\text{O}_2$  unit above  $200 \text{ cm}^{-1}$ . The temperature behaviour can relate to the deformations of these structural units below  $T_C$ . However, since most bands become broad near  $T_C$  because

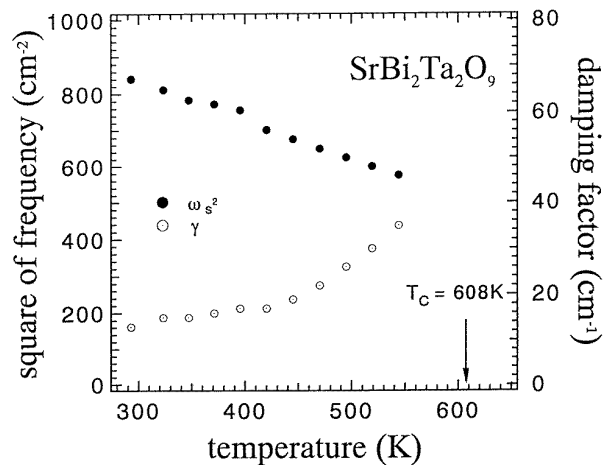


**Figure 2.** Temperature dependence of the low-frequency Raman spectra of  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ .

temperature is relatively high, we cannot discuss the slight structural changes by estimating exact frequency shifts or line-splittings of these modes. On the other hand, a very intense mode appearing at  $59\text{ cm}^{-1}$ , common to the other bismuth layer-structured oxides [7], can be assigned to a rigid layer mode.

The temperature dependence of the low-frequency spectra is shown in figure 2. The lowest peak appears at  $26\text{ cm}^{-1}$  and at room temperature. In bismuth layer-structured compounds of  $m = 3$  and 4, the lowest modes mostly soften towards a ferroelectric or a ferroelectric-like phase transition temperature [7]. This lowest peak changes markedly upon heating [14]. These spectra were fitted by multi-independent damped harmonic oscillators after the correction of the Bose factor. The obtained frequency of this lowest mode  $\omega_s$  is  $29\text{ cm}^{-1}$  at room temperature. Figure 3 shows the temperature dependence of the square of the frequency  $\omega_s^2$  and the damping factor  $\gamma$  of the lowest mode determined by fitting. It is also found that this soft mode disappears below  $T_C$ . This means that this mode becomes Raman inactive in the paraelectric phase. Therefore, it is concluded that this lowest mode at  $29\text{ cm}^{-1}$  is the soft mode of  $A_1(z)$  symmetry responsible for a ferroelectric phase transition at 608 K.

The marked increase of damping near  $T_C$  may suggest that the nature of the phase transition shows a crossing over from displacive to order-disorder types in the neighbourhood of  $T_C$ . It is found that the extrapolated value of  $\omega_s^2$  is still finite at  $T_C = 608\text{ K}$ . This relatively large finite value at  $T_C$  may be originated from not only to the first order phase transition, but also to the coupling between the soft mode and the

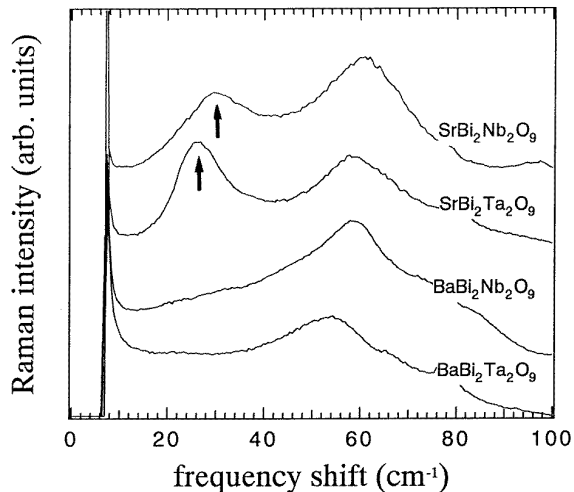


**Figure 3.** Temperature dependence of the square of the mode frequency and the damping factor of the soft mode of  $\text{SrBi}_2\text{Ta}_2\text{O}_9$ .

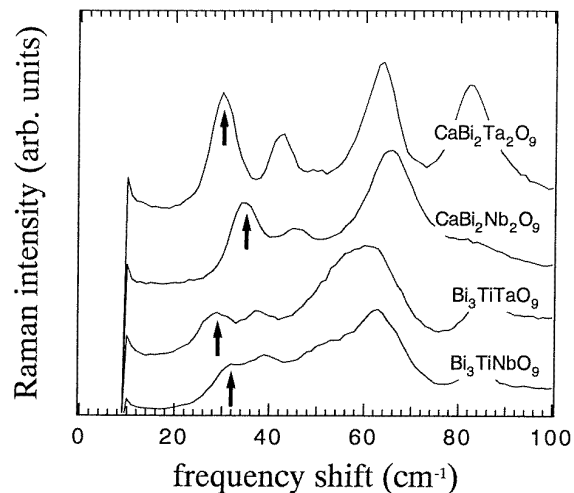
other physical parameters like strain.

Another possibility is that the soft modes are degenerate above  $T_C$ . Such a condition frequently holds when a phase transition occurs at a Brillouin zone boundary. In this case, the number of soft modes is plural. The space group of a paraelectric phase has not yet been determined in SBT. But if the cell doubling actually occurs below  $T_C$ , it belongs to improper ferroelectrics like  $\beta\text{-Gd}_2(\text{MoO}_4)_3$  (GMO). GMO undergoes an improper ferroelectric phase transition at  $T_C = 432$  K. Its order parameters are doubly degenerate optical phonon modes  $q_1$ ,  $q_2$  at the M point: a spontaneous strain  $x_6$  appears at first below  $T_C$  by the coupling term of  $x_6 q_1 q_2$ , and simultaneously the spontaneous polarization  $P_3$  appears by the piezoelectric term of  $d_{36} x_6 P_3$ , where  $d_{36}$  is a piezoelectric constant. In GMO the fitting of the lowest soft mode, by assuming a single peak, shows similar behaviour as figure 2 [15]. Subsequently Shigenari *et al* performed a fitted, by assuming two modes, because this mode shows a splitting into two peaks below 193 K. They found that the lower mode shows remarkable softening towards  $T_C$  [16]. However, in SBT, the line-splitting of the soft mode was not observed above 100 K. Even if the degeneracy of soft modes is confirmed in SBT, the possibility still remains that the intensity of the higher mode is very weak. In order to solve this problem a measurement on a single crystal at very low temperatures is being planned.

The related bismuth layer-structured ferroelectric oxides,  $\text{ABi}_2\text{M}_2\text{O}_9$  ( $A = \text{Ba, Ca, Sr}$ ,  $M = \text{Nb, Ta}$ ) and  $\text{Bi}_3\text{TiMO}_9$  ( $M = \text{Nb, Ta}$ ) were also studied. The composition dependences of the low-frequency spectra are shown in figures 4 and 5. Upon heating all the lowest modes denoted by arrows show marked softening similar to SBT. When the A site of a pseudo-perovskite unit is occupied by Ca, Sr and Bi ions, all the lowest soft modes are underdamped at room temperature. While the A site is occupied by a Ba ion with an ionic radius of 1.4 Å, larger than that of a Ca ion (1.0 Å) and a Sr ion (1.1 Å), the lowest mode becomes overdamped. Regarding the structural disorder of a Ba ion, Smolenskii suggested that a broad dielectric peak of  $\text{BaBi}_2\text{Nb}_2\text{O}_9$  (BBN) around  $T_C$  results from the presence of a Ba ion in the Bi site [6]. However, the recent study of BBN by the powder neutron diffraction technique did not support this explanation, since there was no evidence that a Bi cation occupies the Ba site [13]. Therefore it is concluded that the overdamping of the soft modes in BBN and BBT can be caused not by the structural disorder of the Bi and Ba



**Figure 4.** The low-frequency Raman spectra of  $ABi_2M_2O_9$  ( $A = Ba, Sr, M = Nb, Ta$ ) at room temperature. Arrows denote the soft modes responsible for ferroelectric phase transitions.



**Figure 5.** The low-frequency Raman spectra of  $CaBi_2M_2O_9$  ( $M = Nb, Ta$ ) and  $Bi_3TiMO_9$  ( $M = Nb, Ta$ ) at room temperature. Arrows denote the soft modes responsible for ferroelectric phase transitions.

sites, but by the relatively large ionic radius of Ba at the A site.

Regarding  $Bi_3TiMO_9$  ( $M = Nb, Ta$ ), where the A site is occupied by a Bi ion (1.2 Å), the lowest soft modes are still underdamped at room temperature as shown in figure 5, but their damping factors are relatively larger than that of the case  $A = Ca, Sr$ . The tendency of the damping factor to increase with the ionic radius still holds, and is almost independent of the ions at the B site (Nb, Ta or Ti) of a pseudo-perovskite unit.

Next we discuss the compounds of  $m > 2$ . According to the Raman study of the series of compounds  $ABi_4Ti_4O_{15}$  ( $A = Ba, Ca, Pb, Sr; m = 4$ ) [17], such a tendency of soft

mode damping also holds for  $\text{ABi}_4\text{Ti}_4\text{O}_{15}$  ( $A = \text{Ba}, \text{Ca}, \text{Sr}$ ). Remarkable softening has been observed in the lowest underdamped modes of  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ,  $\text{CaBi}_4\text{Ti}_4\text{O}_{15}$ ,  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$ . A soft mode in  $\text{Sr}_2\text{Bi}_4\text{Ti}_5\text{O}_{18}$  ( $m = 5$ ) was also reported [18]. As a common feature of  $m = 2$  and 4, for  $A = \text{Ba}, \text{Ca}$ , and  $\text{Sr}$ , the Curie temperature decreases linearly with the increase of the ionic radius. This linearity does not hold true in the case  $A = \text{Pb}$  for  $m = 2$  and 4. The main reason is possibly the covalency of the bond between the  $\text{Pb}$  and  $\text{O}$  atoms, similar to  $\text{PbTiO}_3$  with a perovskite structure [19]. Therefore, we remove the case  $A = \text{Pb}$  from the present discussion.

Among the compounds of  $A = \text{Ba}, \text{Bi}, \text{Ca}$  and  $\text{Sr}$ , the soft mode becomes overdamped only when the  $A$  site is occupied by a  $\text{Ba}$  ion. The large ionic radius of  $\text{Ba}$  increases the damping of the soft mode. In the perovskite structure ferroelectrics  $\text{ATiO}_3$  ( $A = \text{Ba}, \text{Sr}$  etc) although the sign of the linearity between  $T_C$  and ionic radius is positive, it is confirmed that the occupation of the  $\text{Ba}$  ion at the  $A$  site also causes overdamping of the  $E$  symmetry soft modes below  $T_C$ . The reason was given recently by first principles calculations, where the shallow potential barrier is pointed out [19]. To clarify the mechanism of the soft mode damping in bismuth layer-structured ferroelectrics, such a calculation is also desired.

Finally we discuss briefly the other related layered perovskite ferroelectrics. The crystal structure of  $\text{SBT}$  and  $\text{SBN}$  include  $[\text{SrTa}_2\text{O}_7]^{2-}$  and  $[\text{SrNb}_2\text{O}_7]^{2-}$  perovskite layers, respectively. It is very interesting that the compounds  $\text{Sr}_2\text{Ta}_2\text{O}_7$  and  $\text{Sr}_2\text{Nb}_2\text{O}_7$  with a perovskite slab structure undergo ferroelectric phase transitions. It is already known that the underdamped lowest  $A_1(z)$  mode of  $\text{Sr}_2\text{Nb}_2\text{O}_7$  at  $54 \text{ cm}^{-1}$  shows marked softening towards  $T_C = 1342^\circ\text{C}$  [20]. All the facts mentioned above may suggest that the perovskite layer-structured ferroelectric oxides reveal essentially a displacive nature except when the  $A$  site of a pseudo-perovskite unit is occupied by a relatively large ion like  $\text{Ba}$ .

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