Lattice Vibrations in the Strong Electron-Phonon-Interaction System $BaPb_{1-x}Bi_xO_3$ Studied by Raman Scattering

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Lattice vibrations of the high-T_c superconductor $BaPb_{1-x}Bi_xO_3$ are investigated by Raman scattering. The breathing mode of BiO_6 octahedra is assigned to the 569-cm^{-1} peak which has large scattering intensity in $BaBiO_3$. The temperature-dependent soft modes at 121 cm^{-1} in $BaPb_{0.7}Bi_{0.3}O_3$ and 48 cm^{-1} in $BaBiO_3$ are assigned to the rotational modes of $Pb(Bi)O_6$. A remarkable correlation is found between T_c and the scattering intensity of the 43- and 100-cm^{-1} peaks. The origin of these modes is discussed.

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The distorted perovskite-type $BaPb_{1-x}Bi_xO_3$ system arouses much interest because of the high superconducting transition temperature (T_c), in spite of the low carrier concentration and the low density of states at the Fermi energy (E_F).[1-4] The electric and crystallographic properties of this system depend on Bi concentration x. This material changes from a metal to a semiconductor near $x = 0.35$ with increasing x. The highest T_c is 12 K at $x = 0.25$–0.3 which is near the metal-semiconductor transition point in the metallic region. The phase diagram of the crystal structure as a function of x and temperature has not been confirmed yet. The structure reported by Cox and Sleight[5,6] has been generally accepted: orthorhombic ($x < 0.05$)–tetragonal ($0.05 < x < 0.35$)–orthorhombic ($0.35 < x < 0.9$)–monoclinic ($0.9 < x$) at room temperature. In their crystallographic analysis the structural change is derived by the rotation of $Pb(Bi)O_6$ octahedra about the pseudocubic $\langle 001 \rangle$ axis in the tetragonal phase and about the $\langle 110 \rangle$ axis in the orthorhombic phase. The monoclinic structure of $BaBiO_3$ is caused by the combination of the orthorhombic distortion and the freezing of the breathing mode of BiO_6 octahedra. The latter causes an alternate arrangement of expanded $Bi^{3+}O_6$ and contracted $Bi^{5+}O_6$.[5] Khan *et al.*[7] reported the crystal structure as an orthorhombic phase (C_{2v}^{11}) in the whole range of x, different from the results of Cox and Sleight.[5,6] Bogatko and Venevtsev[8] presented a more complicated phase diagram: monoclinic ($0 < x < 0.07$)–orthorhombic ($0.07 < x < 0.56$)–monoclinic ($0.56 < x$) at room temperature.

For the superconductivity of this system Rice and Sneddon[9] proposed a model of real-space electron pairing stabilized by the extremely strong electron-phonon interaction of the breathing mode of $Pb(Bi)O_6$ octahedra. Other new mechanisms of superconductivity were also assumed, involving excitons, plasmons, and bipolarons. However, the band calculation by Mattheiss and Hamann[10] revealed that the transferred charge between Bi atoms is only 0.01 electron, consistent with the experimental results of infrared[11] and x-ray-photoemission spectroscopy.[12] Recent experiments of specific heat[3,4,13] and tunneling spectroscopy[13,14] are favorable to the conventional BCS-type superconductivity. In order to realize the high T_c in spite of the low carrier concentration and the low density of states at E_F in this system, strong electron-phonon interactions are required. The calculation by Mattheiss and Hamann[10] showed that the breathing mode of the $Pb(Bi)O_6$ octahedra has a large deformation potential on the LW surface on which the Fermi surface is located in the case of $BaBiO_3$.

The purpose of this experiment is to investigate the origin of the high-T_c superconductivity in the strong electron-phonon–interaction system $BaPb_{1-x}Bi_xO_3$ from the viewpoint of lattice vibrations. Until now experiments on the lattice vibrations of this system have rarely been done except for infrared absorption in $BaBiO_3$ at room temperature[7,11] and tunneling spectroscopy in $BaPb_{0.75}Bi_{0.25}O_3$ at 4 K.[14] The present investigation was performed by Raman scattering on five single crystals: four in the tetragonal region ($0.17 < x < 0.41$) and one in monoclinic $BaBiO_3$ in the temperature range from 20 to 273 K. In this paper the Raman spectra are analyzed in terms of the crystal structure presented by Cox and Sleight,[5,6] and then the deviation from it will be discussed.

The normal phonon modes in the perovskite structure are four F_{1u} and F_{2u} at the Γ point. One of the F_{1u} modes is an acoustic mode. The other F_{1u} modes are infrared active. In $BaPb_{1-x}Bi_xO_3$ the primitive cell becomes twice the size of the perovskite structure by the rotation of the Pb(Bi)O_6 octahedron.[5,6] The R point (0.5,0.5,0.5) in the cubic phase is folded back to the Γ point in these distorted phases.[15]

The optical phonon modes in the tetragonal (D_{4h}^{18}) phase are

$$A_{1g}+2A_{2g}+2B_{1g}+B_{2g}+3E_g+A_{1u}+3A_{2u}+B_{2u}+5E_u.$$

All the *gerade* modes except for the A_{2g} modes are Raman active and the A_{2u} and E_u modes are infrared active. The soft modes coming from the rotation of Pb(Bi)O_6 at the R point in the cubic phase are A_{1g} and E_g. The breathing mode of the Pb(Bi)O_6 octahedron belongs to A_{2g} symmetry which is silent optically.

The optical modes in the orthorhombic (D_{2h}^{28}) phase are

$$3A_g+3B_{1g}+4B_{2g}+2B_{3g}+2A_u+4B_{1u}+4B_{2u}+5B_{3u}.$$

All the *gerade* modes are Raman active and the B_{1u}, B_{2u}, and B_{3u} modes are infrared active. The Pb(Bi)O_6 breathing mode is B_{2g}. This mode is Raman active in the perpendicular polarization of the incident and scattered light, when the polarizations are along the crystallographic axes.

In the monoclinic (C_{2h}^3) phase the optical modes are

$$7A_g+5B_g+6A_u+9B_u.$$

The *gerade* modes are Raman active and the *ungerade* modes are infrared active. The BiO_6 breathing mode is of A_g symmetry.

Figure 1 shows the Raman spectra of $BaPb_{1-x}Bi_xO_3$ in the tetragonal phase ($x=0.17$, 0.3, 0.38, and 0.41) and in the monoclinic phase ($x=1$) at 273 K. A 5145-Å Ar-ion laser was used for the excitation. The temperature dependence of the spectra of $BaPb_{0.7}Bi_{0.3}O_3$ is shown in Fig. 2. Batlogg[13] reported Raman peaks at 121, 347, and 565 cm^{-1} in $BaPb_{0.75}Bi_{0.25}O_3$. These energies are consistent with the energies of the main peaks in Fig. 1. The Raman spectra of this system are composed of the combination of a one-phonon process and a two-phonon process. Although the cubic perovskite structure has no Raman-active mode, the two-phonon process makes the spectra rich, when the compound is structurally unstable. In $BaPb_{1-x}Bi_xO_3$ ($x < 0.41$) the main part of the broad spectra above 200 cm^{-1} is assumed to come from the two-phonon process, though the dis-

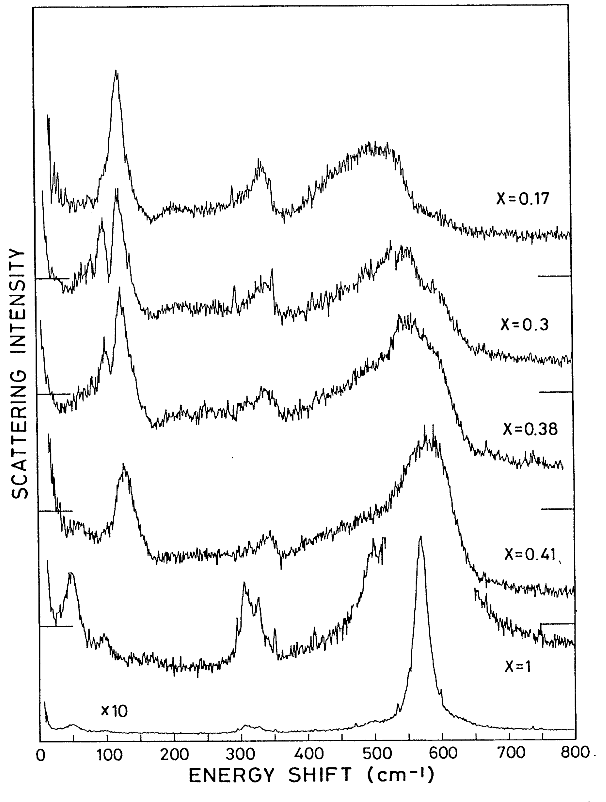

FIG. 1. Raman spectra of $BaPb_{1-x}Bi_xO_3$ for $x=0.17$, 0.3, 0.38, 0.41, and 1 at 273 K. The lowest trace for $x=1$ is plotted by the contracted scale to $\frac{1}{10}$.

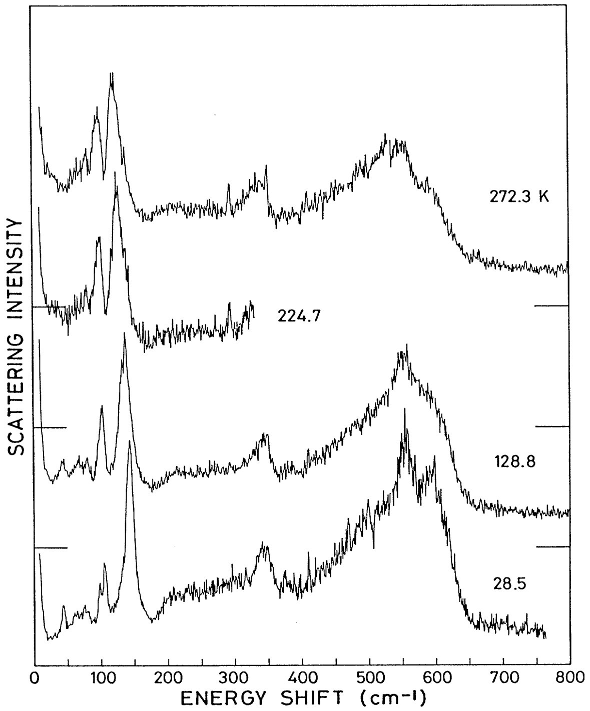

FIG. 2. Raman spectra of $BaPb_{0.7}Bi_{0.3}O_3$ at 272.3, 224.7, 128.8, and 28.5 K.

torted structure makes the one-phonon process available.

The mode at 121 cm^{-1} in $\mathrm{BaPb_{0.7}Bi_{0.3}O_3}$ at 273 K has a large temperature dependence. With an increase of temperature the energy decreases toward the tetragonal-cubic transition temperature which is speculated to be at about 600 K.[8] This mode is assigned to the soft A_{1g} mode derived from the $\mathrm{Pb(Bi)O_6}$ rigid rotation. The corresponding modes in the crystals of $x=0.17$, 0.38, and 0.41 show almost the same temperature dependence as that of $x=0.3$. The companion E_g mode[15] has not been observed yet. In $\mathrm{BaBiO_3}$ the soft mode at 48 cm^{-1} at 272 K depends on temperature strongly. At 28.5 K peaks are observed at 43, 62, 75, 98, and 106 cm^{-1} in $\mathrm{BaPb_{0.7}Bi_{0.3}O_3}$. The polarization selection rule of the Raman scattering revealed that they have strong A_{1g} character. The energy of 43 cm^{-1} at $x=0.3$ is in good agreement with the energy 6 meV (48 cm^{-1}) at $x=0.25$ observed by tunneling spectroscopy[14] and the energy 61 K (42 cm^{-1}) at $x=0.25$ estimated from ultrasonic attenuation.[16] The existence of more than one soft A_{1g} mode is not expected from the commonly accepted tetragonal crystal structure produced by the rotation of the $\mathrm{Pb(Bi)O_6}$ octahedron about the $\langle 001\rangle$ axis.[6] The number of observed soft modes is too many, even if we take into account the possibility of the existence of local modes around Bi atoms. This suggests that the real crystal structure is in lower symmetry than tetragonal, and the primitive cell contains more than two molecular units.

As shown in Fig. 1 the intensity of the 569-cm^{-1} peak in $\mathrm{BaBiO_3}$ is very strong. The A character is larger than the E character. In $\mathrm{BaPb_{0.7}Bi_{0.3}O_3}$ the 551-cm^{-1} peak has a relatively large A character, while at the 598-cm^{-1} peak the E character is larger than the A character. In this paper the terms "A character" and "E character" are used for the relative scattering intensities in the parallel and perpendicular polarization configurations of the incident and scattered light, when the polarizations are along the pseudocubic axes. The symmetry of the modes cannot be specified exactly, because the crystal is assumed to consist of a multidomain structure with three possible orientations of the principal axes. The energy of the 551-cm^{-1} peak at $x=0.3$ increases with increasing Bi concentration x. On the other hand, the energy of the 598-cm^{-1} peak decreases slowly with increasing x, and the intensity increases rapidly. We assign the mode at 598 cm^{-1} in $x=0.3$ and 569 cm^{-1} in $x=1$ to the $\mathrm{BiO_6}$ breathing mode. The breathing mode of $\mathrm{Pb(Bi)O_6}$ is Raman inactive in the tetragonal phase, while it is active with E character in the orthorhombic phase and active with relative A character in the monoclinic phase. The very large scattering intensity of this mode in the monoclinic phase at $x=1$ is due to the large deformation potential of this mode, consistent with the calculation by Mattheiss and Hamann.[10] It is supposed that in the so-called tetragonal phase this mode gets the activity from the lower symmetry of the crystal structure or from the symmetry breaking by the mixing of Pb and Bi. The decrease of the phonon energy with the increase of x is supposed to be due to the increase of the Bi—O bond length[6] and/or the energy renormalization by the strong electron-phonon interaction.

The scattering intensity of the near-100-cm^{-1} peak strongly depends on Bi concentration x, though the peak energy is almost independent of x and temperature. The scattering intensity of this mode is maximized at $x=0.3$, corresponding to the x dependence of the superconducting transition temperature. Figure 3 shows the integrated scattering intensity relative to that of the 120-cm^{-1} peak and T_c. The intensities of the 120-cm^{-1} peaks are almost the same in the so-called tetragonal region. The Raman scattering intensity is proportional to the square of the deformation potential. Therefore it is reasonable to conclude that the deformation potential of this mode attains a maximum near $x=0.3$ and it may be related to the origin of the high T_c. It is to be mentioned that the 43-cm^{-1} peak shows behavior similar to that of the 100-cm^{-1} peak.

At present no report exists on inelastic neutron scattering, nor of a calculation of phonon modes. Therefore it is hard to assign the origin of the 100-cm^{-1} peak exactly, but it is very interesting to speculate on it. This peak is probably not a local mode due to the mixed crystal, but a bulk mode, because this mode exists even in $\mathrm{BaBiO_3}$. It is noteworthy that in-

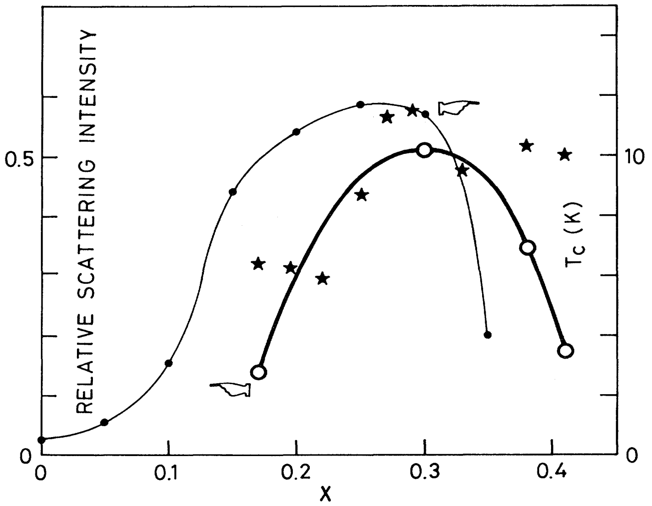

FIG. 3. Integrated scattering intensity of the 100-cm^{-1} peak relative to that of the 120-cm^{-1} peak as a function of Bi concentration x at 273 K (open circles). The T_c's are plotted for two different types of samples: ceramics by filled circles (Ref. 2) and single crystals by stars (Ref. 17).

frared reflection spectroscopy[18] revealed that the energy of this mode coincides with that of the external mode where Ba atoms are displaced relative to other $Pb_{1-x}Bi_xO_3$ atoms. The external mode at the Γ point is Raman inactive, but its zone-boundary mode is Raman active in the distorted perovskite structure. Therefore we tentatively assign the 100-cm^{-1} mode in the Raman spectra to the zone-boundary external mode where adjacent Ba atoms move in opposite directions, because the branch of the external mode is expected to be nearly flat in k space. It is known that in some perovskite compounds the external mode is unstable. For example, a strong softening of this mode toward below 0 K is remarkable in $SrTiO_3$.[19,20]

The $BaPb_{1-x}Bi_xO_3$ crystal becomes heterogeneous in large Bi concentration more than $x = 0.35$. There remains a possibility that the 100-cm^{-1} mode is related to the local mode in a local domain or to the mode coupled to the electronic states originating from the distinctive character of Pb and Bi atoms.

In conclusion, the phonon spectra are obtained by Raman scattering spectroscopy. A noteworthy correlation was found between the superconducting transition temperature and the scattering intensity from the 43- and 100-cm^{-1} modes. The scattering intensity from the mode which is assigned to the breathing mode is very large in $BaBiO_3$, consistent with the strong electron-phonon interaction calculated by Mattheiss and Hamann.[10] The soft mode with large temperature dependence is assigned to the mode related to the rotation of the $Pb(Bi)O_6$ octahedra. This experiment suggests that the crystal structure of $BaPb_{1-x}Bi_xO_3$ in the metallic region is more complex that the commonly accepted tetragonal structure.[6]

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