Electronic State of Bismuth in $BaBiO_3$ up to 9 GPa Investigated by Optical Spectroscopy *

LIU Xiao-Jun(刘晓峻)[1,2], MORITOMO Yutaka(守友浩)[2]

[1]*Laboratory of Modern Acoustics and Institute of Acoustics, Nanjing University, Nanjing 210093*
[2]*Department of Applied Physics, Nagoya University, Nagoya 464-8601, Japan*

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Effects of hydrostatic pressure on the mixed-valence (MV) bismuth complex $BaBiO_3$ have been investigated up to ∼9 GPa by means of high-pressure Raman scattering and absorption spectra at 300 K. The pressure-induced hardening behaviour of the Bi-O stretching mode suggests that the predicted pressure-induced MV to the single-valence (SV) phase change cannot occur. Investigation of absorption spectra with pressure shows the enhanced optical gap E_{gap}, which further indicates the remained MV state of Bi ions.

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The perovskite-type bismuth oxide $BaBiO_3$ is a patent compound of the copper-free superconducting oxides $Ba_{1-x}K_xBiO_3$ ($x = 0.4$) and $BaPb_{1-x}Bi_xO_3$ ($x = 0.25$).[1,2] Calculation of the electronic band for $BaBiO_3$ indicates that the Fermi level is located in the Bi $6s$–O $2p$ overlapping band, and the metallic conductivity is expected from the half-filled valence band.[3] However, $BaBiO_3$ shows a semiconductor characteristics. Several studies, such as neutron diffraction,[4] Raman scattering and optical absorption,[5,6] x-ray absorption, and photoemission,[7] have been carried out to investigate the origin of the semiconductor characteristics. A frozen breathing-type displacement of oxygen ions around Bi atoms is combined with a tilting of the BiO_6 octahedra due to the fact that the strong electron-lattice coupling is considered for the semiconductor behaviour. According to the distorted structure, Bi captions take two valence states, i.e., Bi^{3+} and Bi^{5+}, forming a three-dimensional (3D) mixed-valence (MV) state, or a charge density wave (CDW) state. Substitution of Pb for Bi or K for Ba has been reported to suppress the MV state, and induces a metallic state.[8,9]

In addition to chemical substitution, hydrostatic pressure is a powerful tool to modify the lattice and hence the electron-lattice interaction.[10−12] In an extreme case, the application of pressure may induce a phase transition of the electronic state. Actually, Liu *et al.*[10,11] have found that the application of pressure can suppress the structural distortion in the MV gold complexes $Cs_2Au_2X_6$ (X = Cl and Br), which have a similar 3D MV state, that is, alternation of the gold monovalence (Au^+) and trivalence (Au^{3+}) states in a pervoskite-like structure. Such a structural change significantly influences the electronic state of the system: a single-valence (SV) state with only Au^{2+} ions is achieved under pressure. In accord with the MV-SV phase transition, the electrical resistivity of $Cs_2Au_2Cl_6$ decreases from $\sim 10^6\,\Omega$cm at ambient pressure to $\sim 10^{-3}\,\Omega$cm at ∼11 GPa,[13] indicating a high-pressure metallic SV phase. Recently, Hashimoto *et al.*[14] have found a pressure-induced monoclinic to orthorhombic structural phase transition at 7.2 GPa and an orthorhombic to cubic structural phase transition at 42.8 GPa in $BaBiO_3$, which is estimated to be an MV-to-SV phase transition.

In this Letter, we have investigated the pressure effects on $BaBiO_3$ by means of the high-pressure Raman scattering and absorption spectra up to ∼9 GPa, which is the maximum pressure of our high-pressure apparatus, to clarify the nature of the high-pressure structural phase transition, especially on the valence states of Bi ions. The Raman spectroscopy is one of the most sensitive probes to detect the variation of the local symmetry. Our results indicate that the valence disproportion of Bi ions remains even up to ∼9 GPa. Such unexpected behaviour has been interpreted by a pressure-induced enhancement of the Madelung potential.

$BaBiO_3$ single crystals were synthesized by heating mixed powder of $BaCO_3$ and Bi_2O_3 in the stoichiometrical ratio at 770 K for 6 h and then at 1000 K for 10 h in air. The mixed powder was then cooled to room temperature and pressed into pellets. The pellets were sintered at 1100 K for 12 h in flowing oxygen gas and cooled to room temperature at a rate of 0.4 K/h. High-pressure Raman measurements were performed at 300 K using a diamond anvil cell and liquid paraffin as a pressure medium. A tiny crystal sample was placed in the gasket hole (0.3-mm in diameter). The applied pressure was monitored with the luminescence peak of a small piece of ruby placed in the gasket hole. At 300 K, pressure inhomogeneity

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is estimated to be 0.3 GPa at ∼8 GPa. The sample was excited at 514.5 nm with an argon laser in a backward configuration. To avoid the sample damage, the laser power density was kept below 50 W/cm^2. Scattered light was detected with a double monochromator equipped with a photon counting system. In the visible absorbance measurements, ground microcrystals were mixed with KCl powder, and then filled in the gasket hole. The absorption spectra were measured using a grating monochromater. The pressure inhomogeneity is estimated to be 0.8 GPa at ∼9 GPa. All of the pressure-induced spectral changes exhibited good reproducibility for repeated pressure cycles.

Before describing the details of pressure effects on the Raman spectra in $BaBiO_3$, the variation of the Bi-O stretching modes is investigated at the postulated MV-to-SV phase transition. In the MV phase, a strong Raman band was observed at 569 cm^{-1}, which has been assigned to the Bi^{5+}-O^{2-} stretching mode A_g due to the large displacement of O^{2-} ions from the central position between the two nearest neighbouring Bi sites.[5] On the other hand, in the postulated SV state, when the O^{2-} ions move to the central position between the two neighbouring Bi sites, this A_g mode should be Raman-inactive. Therefore, the Raman-active band at 569 cm^{-1} would disappear in the high-pressure SV phase.

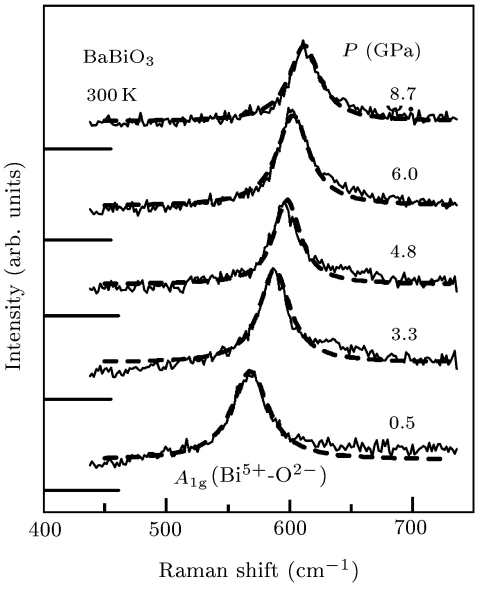

Fig. 1. Pressure dependence of Raman spectra (unpolarized) of $BaBiO_3$ at 300 K. The dotted curves represent the best-fitted results with the Lorentz oscillator model.

The pressure dependence of the Raman spectra for $BaBiO_3$ at 300 K is shown in Fig. 1 in the frequency region of 450–750 cm^{-1}. With increasing pressure, the A_g band shifts to the high-energy side from 570 cm^{-1} at ambient pressure to 611 cm^{-1} at 8.7 GPa. To estimate precisely the optical parameters, the Raman spectra were analysed by the least-square fitting with the Lorentz oscillator model. The dotted lines are the best-fitted results. Thus obtained parameters, i.e., the frequency and intensity of the A_g mode, are plotted against pressure in Fig. 2. The closed circles in Fig. 2(a) represent the variation of the intensity for the A_g mode with increasing pressure up to ∼9 GPa, indicating that the intensity has a negligible pressure dependence. The pressure dependence of the frequency is shown in Fig. 2(b). With increasing pressure, the frequency increases at a rate of 5 cm^{-1}/GPa. Such hardening behaviour of the Bi-O stretching mode indicates the pressure-induced shrinkage of the Bi^{5+}-O^{2-} bond and hence resultant enhancement of the bond. This makes a sharp contrast with the significant pressure-induced softening (−5.8 cm^{-1}/GPa) of the Au^{3+}–Cl^- stretching mode in the MV gold complex $Cs_2Au_2Cl_6$,[11] implying that the pressure-induced SV state cannot be achieved.

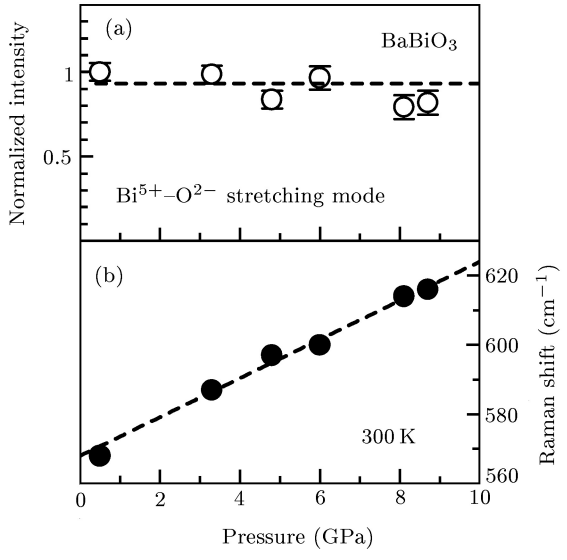

Fig. 2. Pressure variation of (a) intensity and (b) Raman shift of the Bi^{5+}-O^{2-} stretching mode for $BaBiO_3$. The dashed lines are the guide to the eyes.

We further investigate the pressure-induced effect on the absorption spectra at 300 K. The inset of Fig. 3 shows the pressure variation of the electronic absorption spectra for $BaBiO_3$. It should be noted that the background absorption due to the scattering loss was subtracted from the raw data. At ambient pressure, the absorption peak (at ∼ 2 eV) corresponds to the charge-transfer (CT) gap (2.15 eV) excitation from the Bi^{3+} to Bi^{5+} sites derived by the Kramas–Kronig analysis of the reflectivity spectra.[6] The variation of the peak energy was plotted against pressure in Fig. 3. With increasing pressure, the peak energy increases at a rate of 0.033 eV/GPa. This result is contrary to decreasing the optical gap energy (−0.32 eV/GPa) observed in the MV gold complex $Cs_2Au_2Cl_6$.[15]

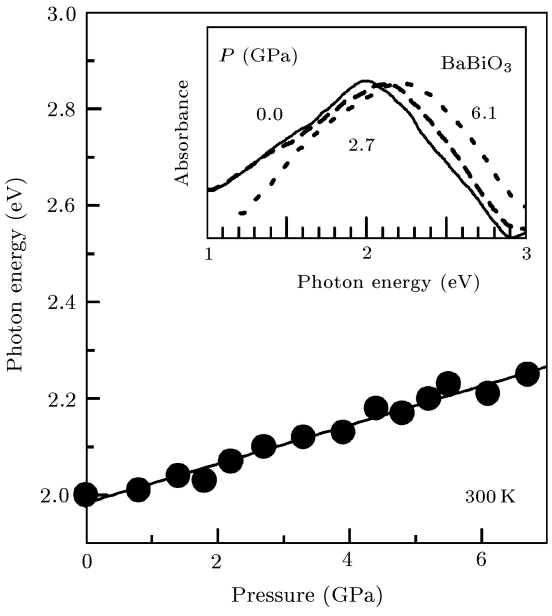

Fig. 3. Pressure variation of the CT gap energy for $BaBiO_3$. The solid curve is merely a guide of the eye. Inset: pressure variation of the electronic absorption spectra for the $BaBiO_3$ dispersed in a KCl pellet. The solid, dashed and dotted curves are the spectra observed at 0.0 GPa, 2.7 GPa and 6.1 GPa, respectively.

The pressure effects of $BaBiO_3$ and $Cs_2Au_2Cl_6$ are compared with each other. In $Cs_2Au_2Cl_6$, the Au $5d$ orbital strongly hybridizes with the Cl $3p$ orbital, and $Cs_2Au_2Cl_6$ show covalent characteristic. With increase of pressure, the energy difference of Au^+ and Au^{3+} sites is reduced due to the enhancement of the one-electron bandwidth W of the Au $5d$ band and hence the resultant suppressed gap energy. With further increase of the pressure above the critical pressure $P_c \sim 11$ GPa, the energy difference of Au^+ and Au^{3+} sites disappears, and a pressure-induced phase transition from the MV state to the SV state occurs. On the other hand, $BaBiO_3$ behaves as an ionic crystal. Therefore, the CT gap energy for $BaBiO_3$ is expressed as a sum of two terms[16]

$$E_g = E_0 + (2\alpha - 1)\left\langle \frac{e^2}{d} \right\rangle, \qquad (1)$$

where the first term E_0 is the energy difference of Bi^{5+} and Bi^{3+} sites, and the second term is the Madelung potential. In the second term, $\alpha\ (>1)$ is the Madelung constant in a cubic lattice symmetry, d and e are the distance of the nearest neighbouring Bi sites and the charge of an electron, respectively. With increasing pressure, the d-value decreases and hence a resultant larger Modelung potential. If the enhanced Modelung potential dominates the change of the CT gap energy, the E_g-value should increase with pressure even though the E_0-value shows a decrease due to the enhanced bandwidth of the Bi $6s$ band. As a result, the electronic state of Bi ions remains the MV state even under high-pressure of ~ 9 GPa.

In summary, we have investigated the pressure effects on Raman scattering and absorption spectra in the mixed valence Bi compound $BaBiO_3$. In contrast with the mixed valence Au compound $Cs_2Au_2Cl_6$, we cannot find the MV-to-SV phase transition in $BaBiO_3$ even under ~ 9 GPa. We further observed the enhanced optical gap energy under pressure, and ascribed it to the larger Modelung potential.

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