

Raman-scattering study of the metal-insulator transition in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$

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We have investigated the Raman-scattering spectra of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, using epitaxially grown sputtering films with various x as well as single crystals of BaBiO_3 . It was confirmed that in BaBiO_3 the Raman excitation due to the breathing-mode phonon at 570 cm^{-1} is just in resonance with the electronic excitation across the charge-density-wave gap. With increasing x , this phonon-scattering intensity decreases and finally disappears at the metallic composition ($x > 0.38$). We could not identify the Raman continuum at high energies as intrinsic at metallic compositions. All these experimental results strongly suggest a rather conventional metallic state realized in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$.

Among the high- T_c superconducting oxides, $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ occupies a unique position for the following reasons. (i) The gap in the parent insulator BaBiO_3 originates from the charge-density wave (CDW) as a consequence of the strong electron-phonon coupling.¹ (ii) The perovskite crystal structure results in an isotropic conduction as well as an isotropic superconductivity. (iii) The insulator to metal transition at $x = 0.4$ is accompanied by the structural phase transition to the cubic symmetry,² suggesting a relevance of electron-phonon coupling in this material.

Most of the studies for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ done so far were on the superconducting state, for example, the tunneling spectroscopic measurements^{3,4} and the isotope-effect measurements.⁵ They indicated a more conventional BCS-type superconductivity than that in the high- T_c superconducting cuprates. However, the studies on the normal state of this material are rare and the results are still controversial. In our previous work, it was shown by the optical-absorption measurements that K doping reduces the CDW gap energy and, in the metallic phase ($x > 0.4$), the gap, if any, would become extremely small.⁶ However, there have been experimental results which suggested the persistence of the breathing-mode lattice distortion⁷ as well as the mid-infrared absorption in the optical spectrum of the metallic compounds.⁸ The background Raman intensity extending to higher energies was also considered to be an evidence for an unconventional metallic state. The conspicuous Raman background⁹ and the mid-infrared absorption¹⁰ are commonly observed in the metallic state of the high- T_c superconducting cuprates. According to the marginal Fermi-liquid model by Varma *et al.*,¹¹ these anomalies in the optical properties are closely related to each other and also to the superconductivity mechanism. Thus, the above-referenced optical measurements in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ might be an indication of a similarity between the cuprates and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ in the normal-state electronic structure of the metallic phase as well as the superconductivity mechanism. Re-

cently, based on the tunneling spectrum, Sharifi, Pargellis, and Dynes have suggested a similarity in the normal state between the cuprates and $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$.¹²

In the present work, we have measured the Raman-scattering spectra of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, using a single crystal of BaBiO_3 and the epitaxially grown sputtering films of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ with high quality over a wide compositional range. We have confirmed that in BaBiO_3 the scattering intensity of the breathing mode phonon at 570 cm^{-1} is remarkably enhanced when the incident photon energy comes near the CDW gap energy. It suggests that this phonon Raman excitation is just in resonance with the electronic excitation across the CDW gap. As the K content increases, this resonant Raman peak becomes weak and finally disappears for metallic compositions. The electronic Raman continuum cannot be clearly identified in the high-quality metallic samples. All these results suggest that the metallic state in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is distinct from that in the cuprates but rather conventional.

The single crystal of BaBiO_3 used for examination of the resonant Raman scattering was directly grown from the melt of BaCO_3 and Bi_2O_3 . Because of the difficulty in getting homogeneous crystals with various K content, we have tried to prepare the thin-film samples. $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ thin films with thickness of 3000 \AA were epitaxially grown on SrTiO_3 (110) substrates at temperature of 320°C , using a rf-magnetron sputtering method. The details of the film preparation are described in Ref. 4. The K composition (x) was estimated from the lattice constant determined by the x-ray-diffraction patterns,¹³ assuming that the lattice parameters of films are the same as those of bulk samples. The chemical composition was roughly determined by electron-probe microanalysis and an x-ray fluorescence analysis.

After oxygen annealing, only the film with $x > 0.38$ exhibited a metallic temperature dependence of the resistivity with a sharp superconducting transition at $T_c = 21\text{ K}$ ($\Delta T_c \sim 0.2\text{ K}$), as shown in Fig. 1. The films with

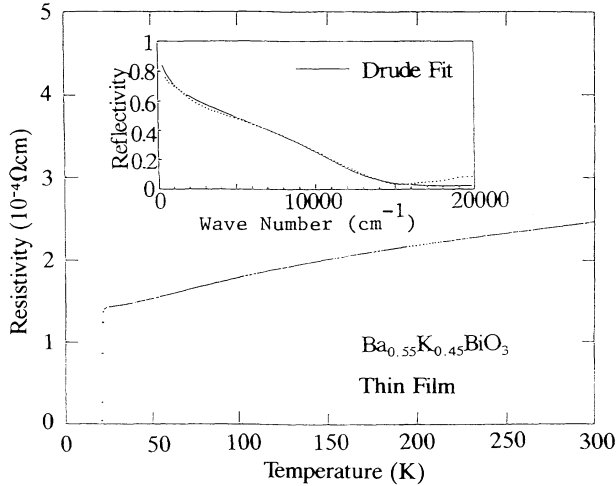


FIG. 1. Temperature dependence of resistivity for the $\text{Ba}_{0.55}\text{K}_{0.45}\text{BiO}_3$ film. The inset shows its reflectivity spectrum at room temperature. The dashed line is a fitting curve based on the Drude model.

$x < 0.38$ were semiconductive.¹⁴ The resistivity of the metallic film was $240 \mu\Omega \text{ cm}$ at room temperature and $140 \mu\Omega \text{ cm}$ just above T_c , which is the lowest among the values reported up to now. Moreover, the I - V characteristics in the superconducting state shows no grain-boundary Josephson effect which is specific to the polycrystalline films. These facts guarantee good quality of the present films. The room-temperature reflectivity spectrum in the inset of Fig. 1 also shows good metallic behavior of this film.

Raman-scattering spectra were measured at room temperature in the backscattering configuration using 4880-\AA and 5145-\AA beams from an Ar laser and 6328-\AA beam from a He-Ne laser as excitation lights. The incident beam with the power of 35 mW was focused on the sample surface with a diameter of about 0.1 mm. The scattered light was monochromized by a Jobin Yvon U-1000 double monochromator and detected by a photon-counting detector system with a Hamamatsu R-943 photomultiplier. To calibrate the Raman intensities for different excitation lights, we have measured the phonon-scattering peak at 1430 cm^{-1} of a diamond crystal as a reference.

The Raman-scattering spectrum of BaBiO_3 is dominated by the extremely strong peak at 570 cm^{-1} with several overtones (see Fig. 3). While there is originally no Raman-active mode in an ideal cubic perovskite structure, several modes become Raman active by the monoclinic lattice distortion in BaBiO_3 .¹⁵ However, most of the Raman-allowed phonons are very weak in the spectrum except for the 570-cm^{-1} phonon which was assigned to the breathing-mode phonon, the alternating expansion and contraction of the oxygen octahedra.¹⁶ Since the breathing-mode vibration modulates the mixing of O $2p$ and Bi $6s$ orbitals, this mode is expected to couple strongly with the electronic system and overtones up to 8–9 higher harmonics were observed. We have observed a strong dependence of the 570-cm^{-1} peak intensity on the incident photon energy as well as the K content, as

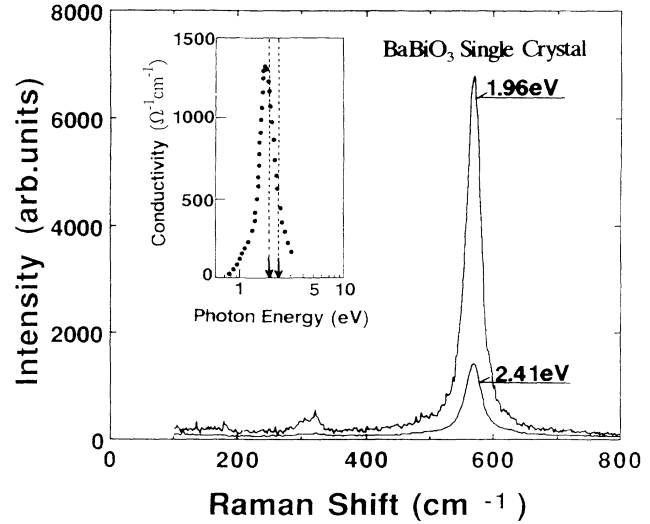


FIG. 2. Raman-scattering spectra of the BaBiO_3 single crystal for two different excitation energies shown by the arrows in the inset of its optical conductivity spectrum. As the excitation energy comes near the CDW-gap energy, the Raman-scattering intensity of the 570-cm^{-1} peak is remarkably enhanced. The spectrum for 2.54 eV is almost the same as that for 2.41 eV.

shown in Figs. 2 and 3. The excitation energy of 1.96 eV is very close to the CDW gap energy ($\sim 1.9 \text{ eV}$) for BaBiO_3 determined by the optical absorption spectrum in the inset of Fig. 2. A remarkable enhancement of the scattering intensity suggests that this phonon Raman excitation is just in resonance with the CDW gap excitation, indicating a strong electron-phonon coupling.

Next, we see the composition dependence of the Raman spectrum for $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$. Figure 3 shows the Raman spectra of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ films with various x . As in the monoclinic phase for $0 < x < 0.1$, only the 570-cm^{-1} peak is very strong, compared with the other Raman-allowed phonons in the orthorhombic phase for $0.1 < x < 0.4$.¹⁵ As x increases, the scattering intensity of the 570-cm^{-1} peak as well as its higher harmonics decreases and finally disappears at the metallic composition ($x = 0.45$). The decrease in intensity is partly related to the decrease of the gap energy shown in the inset of Fig. 3. It means that the Raman-scattering process goes out of the resonant condition with increasing x .

The most noticeable point is that the 570-cm^{-1} phonon peak completely disappears at the metallic composition $x = 0.45$, although some weak features are observed at the different energies which are perhaps due to a slight inhomogeneity in the film. The absorption coefficient and thus the penetration depth for the 5415-\AA (2.4 eV)-light does not appreciably change even when the sample becomes metallic because the plasma edge in the reflectivity spectrum is located at lower energy than 2.4 eV, as shown in the inset of Fig. 1. Considering the fact that the scattering process is far from the resonant condition at both of the compositions $x = 0.38$ and 0.45, this significant change in the Raman spectrum must also be triggered by any other fact, for example, the structural phase transition at $x = 0.4$ to the cubic structure as well as the disappearance of CDW. It should be noted that,

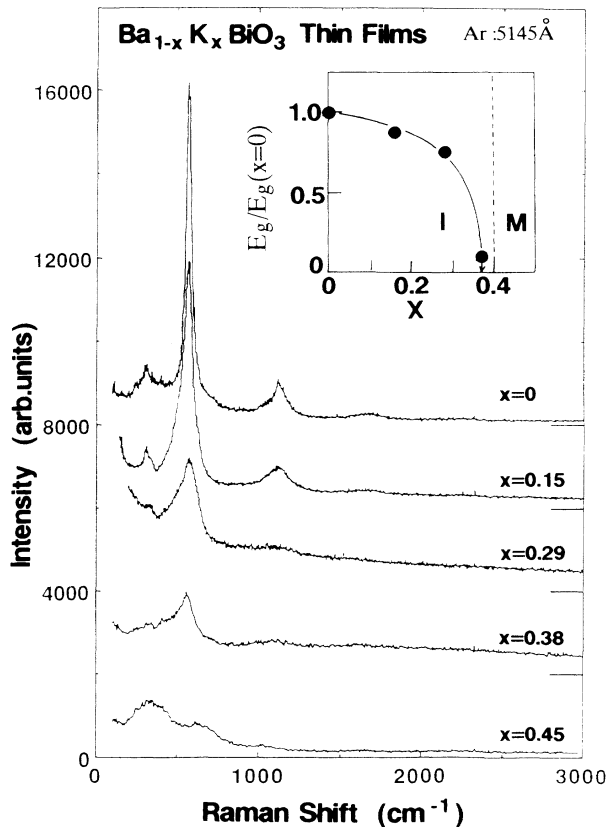


FIG. 3. Raman-scattering spectra of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ films with various x . The inset shows the compositional dependence of the optical gap which is estimated from the absorption spectra.

even in the cubic symmetry, if the breathing-mode-type static distortion remains, the breathing-mode phonon is Raman active. [In the cubic symmetry with breathing-mode distortion (O_h^5),

$$\Gamma_{\text{opt}} = A_{1g} + E_g + 2F_{2g} + F_{1g} + F_{2u} + 4F_{1u}$$

and the breathing mode (A_{1g}) is Raman allowed.] However, our result in Fig. 3 shows the complete disappearance of the 570-cm^{-1} peak at $x=0.45$. It should result not only from the structural change into the cubic symmetry but also from the disappearance of the breathing-mode distortion. It is consistent with the neutron-diffraction result, which shows the cubic symmetry without breathing-mode distortion (O_h^1) in the metallic phase.¹⁷ The disappearance or otherwise of this mode in the Raman spectrum is so sensitive to the K composition that it might be seen even if only a small part of the sample had composition less than $x=0.4$.

The destruction of the CDW gap or breathing-mode distortion restores the original O $2p$ and Bi $6s$ hybridized conduction bands with less than half-filling. This is just what one expects from the band theory but is completely different from the picture where the holes are doped into the parent insulator BaBiO_3 by the K substitution. The CDW-gap destruction is also supported by other experimental evidence such as the negative sign of the Hall coefficient R_H in the metallic phase⁵ and the optical reflectivity spectrum shown in the inset of Fig. 1. The

spectrum seems to fit to the Drude curve shown by the dots from the far-infrared to the visible region. Actually the conductivity at $\omega=0$, which is extrapolated from the optical conductivity $\sigma(\omega)$ on the assumption of the Drude model, is in fair agreement with the dc conductivity of this film. Although our data do not rule out a small deviation from the Drude curve in the lowest-energy region as pointed out by Schlesinger *et al.*,⁷ the deviation is appreciably smaller than in the predecessor $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ (Ref. 10) and/or the superconducting cuprates.⁹ We suppose that this may not be intrinsic and further improvement in the sample homogeneity would diminish the deviation from the Drude curve.

In $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ with $T_c=11$ K, the optical spectrum show a pronounced deviation from the Drude curve, from which a large pseudogap (0.2 eV) is estimated.¹⁸ From this result emerges a picture that the CDW with small coherence length of 3 Å persists, localized around the Bi site. Although a strong electron-phonon coupling is presumably favorable for the relatively high- T_c superconductivity, too strong coupling gives rise to the persistence of a local CDW which causes the reduction of the density of states at E_F and hence decreases the value of T_c . Thus, the fact that the CDW as well as the breathing-mode lattice distortion almost disappears apparently favors the occurrence of superconductivity with a higher T_c of 30 K in the $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ system than that in $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$.

In the high- T_c cuprates, the most characteristic features in the optical spectra are the mid-infrared absorption in the optical spectrum and the electronic continuum in the Raman-scattering spectrum. In the Raman spectrum of $\text{Ba}_{0.55}\text{K}_{0.45}\text{BiO}_3$, the intensity of such a continuum is too small to be regarded as an intrinsic structure. For semiconducting compositions including $x=0$, an appreciable Raman intensity can be observed up to 3000 cm^{-1} but not for the bulk single-crystal BaBiO_3 . Therefore, the previously reported Raman continuum in the metallic phase¹⁹ may be caused by the compositional inhomogeneity as well as by an artifact of the thin films on SrTiO_3 substrates.

In conclusion, we have investigated the Raman-scattering spectra of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$, using high-quality sputtering films with various K contents. By the measurements for various incident photon energy from 2.54 to 1.96 eV, it has been confirmed that the phonon at 570 cm^{-1} in BaBiO_3 is strongly coupled with the excitation across the CDW gap. As the K content increases, this phonon-scattering intensity decreases, in accordance with the reduction of the CDW-gap energy. When x exceeds 0.4, this phonon peak completely disappears, which implies that the static CDW distortion disappears and simultaneously the gap energy becomes zero. Based on this result, we conclude that the metallic state of $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$ is realized in an almost ideal structure of the cubic perovskite where the band picture is appropriate. The intensity of the Raman electronic continuum at high energies is too small to be identified as an intrinsic effect, which is quite contrast to the case of cuprates. It suggests a rather conventional metallic state in $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$.

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- ¹⁴Our films with $x=0.38$ are semiconductive, which is in contradiction with the phase diagram reported by S. Pei *et al.* (Ref. 13). There might be a slight difference in the phase diagram between the film and bulk samples.
- ¹⁵The optical modes in each crystal symmetry are as follows: in the cubic symmetry (O_h^1), $\Gamma_{\text{opt}}=F_{2u}+3F_{1u}$; in the monoclinic symmetry (C_{2h}^3), $\Gamma_{\text{opt}}=7A_g+5B_g+6A_u+9B_u$; in the orthorhombic symmetry (D_{2h}^{28}), $\Gamma_{\text{opt}}=3A_g+3B_{1g}+4B_{2g}+2B_{3g}+2A_u+4B_{1u}+4B_{2u}+5B_{3u}$. All the gerade modes in D_{2h}^{28} and C_{2h}^3 , including the breathing mode (A_g), are Raman active.
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