Infrared observation of the CDW amplitude decreasing due to hole doping in $Ba_{1-x}K_xBiO_3$

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Abstract

Optical reflectivity measurements in a frequency range 50-1000cm^{-1} have been carried out for semiconducting $Ba_{1-x}K_xBiO_3$ (BKBO) single crystals. The oscillator strength of the transverse optical (TO) phonon related to the charge-density-wave (CDW) decreases with K-doping and becomes nearly zero at a critical composition of the semiconductor-metal transition (SMT), resulting from the diminishing of the amplitude of the CDW with increasing x.

Key words: optical reflectivity; CDW; $Ba_{1-x}K_xBiO_3$

A perovskite oxide, $Ba_{1-x}K_xBiO_3$ (BKBO), derived from a charge-density-wave (CDW) semiconductor $BaBiO_3$ (BBO) is known to be a superconductor with relatively high superconducting temperature T_c in the metallic region and exhibits an extended semiconducting region (x<0.3) prior to undergoing the semiconductor-metal transition (SMT) [1]. Two mechanisms are mainly suggested for the SMT; 1) a Peierls-like scenario [2]and 2) a transition [3] from a bipolaronic state to a metallic state. However, neither has been assigned to the real transition completely.

In this paper we report an infrared spectrum and its compositional dependence for BKBO single crystals. Results suggest that the mechanism of the SMT is identified with that of a Peierls-like transition.

Single crystals used for the present measurements except a BBO sample were grown by an electrochemical technique [4]. Compositions of these single crystals were determined by an electron-probe microanalysis (EPMA). A single crystal of BBO was prepared by a slow cooling method. The reflectivity spectra were measured at room temperature by using a Fourier-transform infrared spectrometer and were analyzed by either the K-K transformation or the oscillator fit.

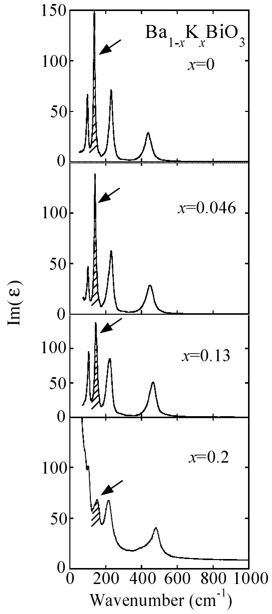

Fig. 1. The imaginary part of the dielectric function.

The imaginary parts of the dielectric functions for x=0, 0.046, 0.13 and 0.20 are shown in Fig. 1. We have

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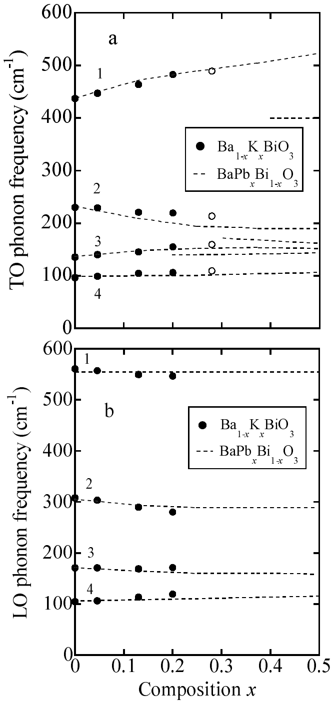

Fig. 2. a.The compositional changes of the TO-phonon frequencies in BKBO (cloesd circles) and those in BPBO (dashed lines). b. The compositional changes of the LO-phonon frequencies. Open circles denote data obtained by Puchkov et al. (Ref. 3).

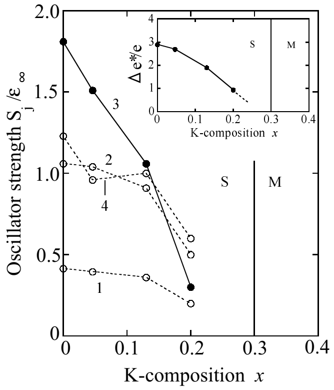

Fig. 3. The compositional dependence of the oscillator strength for each mode. The inset shows the Szigeti-effective charge difference between inequivalent Bi sites.

observed that the intensity of the third highest TO phonon mode in the frequency indicated by the arrows in Fig.1 decreases remarkably with increasing x, as reported for $\mathrm{BaPb}_x\mathrm{Bi}_{1-x}\mathrm{O}_3$ (BPBO) [5].

Figures 2a and 2b show compositional changes of the TO- and LO-phonon frequencies, respectively, and those [5] in BPBO for comparison. The TO-phonon frequencies in BKBO almost coincide with the upper-mode frequencies for the two-mode type BPBO, although there is a small deviation for the second highest TO-phonon frequency (the ferroelectric mode).

Figure 3 shows the compositional changes of the oscillator strength S_j for each mode. We note that the oscillator strength of the third highest mode S_3 decreases remarkably with increasing x in comparison with that of the other modes. The third highest mode corresponds to the vibrational motion that modulates the Bi-Bi bond distance through O [6]. This mode becomes infrared-active in the CDW state [6]; therefore the emergence of this infrared-active mode in the spectrum gives eloquent evidence for the charge disproportionation of the Bi atoms.

The inset in Fig.3 shows the compositional change of the Szigeti-effective charge difference between inequivalent Bi sites estimated by using S_3 and the high frequency dielectric constant [7]. This gives an apparent degree of the ionic-charge difference between inequivalent Bi sites. However it shows much larger value of 3e at x=0 than the formal-charge difference of 2e . We infer that there is a strong dynamic charge transfer along the Bi-O-Bi bond. The decrease of the ionic-charge difference, i.e., the amplitude of the CDW, with increasing x implies the decrease of the Peierls gap. A tendency that the difference goes to zero as x approaches metallic compositions suggests disappearance of the Peierls gap at the critical point of the SMT. These suggest that the mechanism of the SMT is identified with that of a Peierls-like transition rather than a bipolaron-metal transition.

In summary, we estimate the effective charge difference between inequivalent Bi sites from S_3 and find that the disproportionation charge decreases with increasing x and tends to become zero at the critical point of the SMT. This supports strongly a Peierls scenario.

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