A new IR excitation in semiconducting $Ba_{1-x}K_xBiO_3$ single crystals

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Abstract

We report optical reflectivity measurements on $Ba_{1-x}K_xBiO_3$ ($x = 0$, 0.15) single crystals in the frequency range 70 - 30000 cm^{-1} and at different temperatures in an attempt to understand the transport mechanism in the semiconducting state before it undergoes semiconductor-metal transition. For $x = 0.15$, at 400 K, we find a hump in reflectivity at ≈ 1280 cm^{-1}. N_{eff} of total IR transition shifts towards low frequency as temperature increases above 300 K. We suggest the presence of new and thermally excited states in the peierls band gap and the possible new IR excitations.

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

$Ba_{1-x}K_xBiO_3$ (BKBO) possess exotic semiconducting state below x = 0.3. The experimentally observed frozen breathing-type lattice distortions [1] led to a suggestion that the undoped $BaBiO_3$, which has one electron per Bi atom, is made semiconducting by a charge density wave (CDW) instability that opens a gap on the Fermi level, splitting the half filled conduction band into two subbands: a filled lower Bi^{3+} subband and an empty upper Bi^{5+} one [2].

We report temperature dependent optical reflectivity of BKBO for $x = 0.15$, at potassium doping well below the one where semiconductor to metal transition takes place and compare the results with that of undoped $BaBiO_3$.

Fig. 1 shows the reflectivity spectra of BKBO at different temperatures. The results at 300 K are consistent with previous room temperature results [3]. For $x = 0.15$, reflectivity at 400 K shows a hump that reaches its maximum at frequency ≈ 1280 cm^{-1}. The reflectivity remains high up to frequency ≈ 3800 cm^{-1}. Thereafter, it crosses the one at lower temperature followed by a reflection band (hereafter called IR band) appears at ≈ 12900 cm^{-1} (1.6 eV). For comparison, fig. 1-a shows reflectivity of $x = 0$ sample where we find no 1280 cm^{-1} hump and an IR band appears at ≈ 15400 cm^{-1} (1.9 eV).

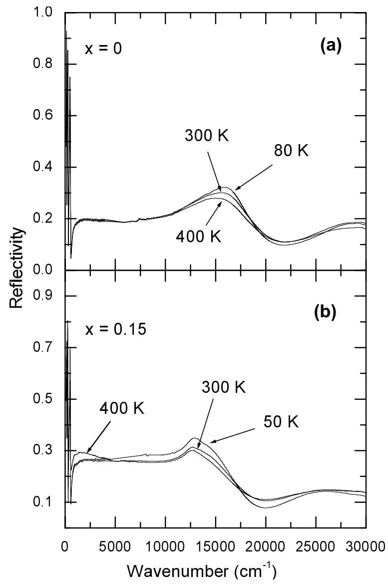

Fig. 1. Reflectivity vs frequency spectra of BKBO for (a) $x = 0$ and (b) $x = 0.15$ at different temperatures. Low frequency region shows phonons.

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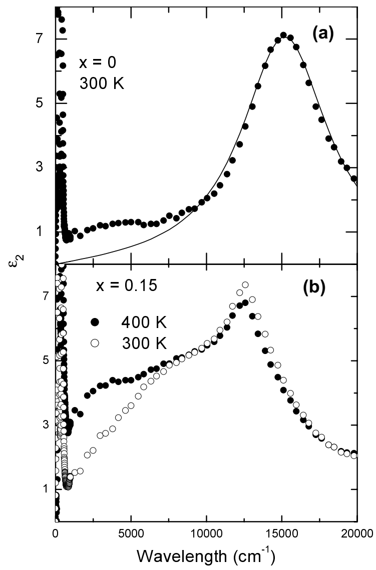

Fig. 2. ϵ_2 of BKBO for (a) $x = 0$ at 300 K(filled dots). Solid line is the best fit obtained, using Lorentz oscillator model by excluding Drude and high energy terms.(b) $x = 0.15$ at 300 K (open dots) and 400 K (filled dots). Note the difference in shape of ϵ_2.

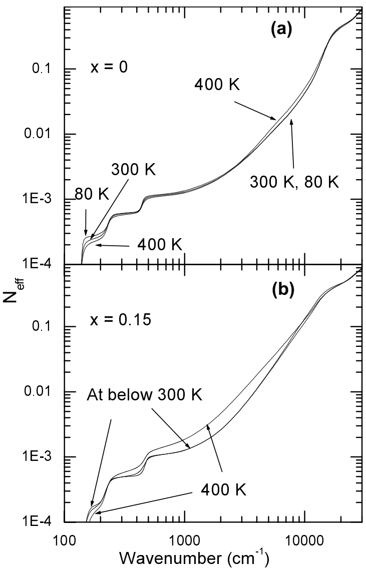

Fig. 3. Spectral weight (N_{eff}) of (a) $x = 0$ and (b) $x = 0.15$, obtained from integration of the ϵ_2 using finite energy f-sum rule.

Fig. 2 shows ϵ_2 of both samples obtained by K. K. analysis of reflectivity spectra. For $x = 0$, a single peak observed in ϵ_2 at ≈ 15400 cm^{-1} (at IR band frequency) is extensively reported and is attributed to a transition of Bi 6s electrons from a filled Bi^{3+} subband to an empty Bi^{5+} one. However, for $x = 0.15$, the behavior of ϵ_2 shown in fig. 2-b is unusual. At 300 K, $\epsilon_2 \approx 1$ at $\approx$ 1000 cm^{-1} increases to ≈ 3.5 at ≈ 4500 cm^{-1} followed by relatively slow increase to ≈ 5 at ≈ 9000 cm^{-1}. A peak corresponding to IR band appears at ≈ 12900 cm^{-1}, at frequency lower than that in case of undoped sample. On comparison, for $x = 0$, $\epsilon_2 \approx 1$ at ≈ 1000 cm^{-1} remains almost unchanged up to ≈ 8000 cm^{-1}.

For $x = 0.15$, we observe a significant temperature dependence of ϵ_2 as shown in fig. 2-b. At 400 K, $\epsilon_2 \approx 3$ (≈ 1 at 300 K) at ≈ 1000 cm^{-1}, at first, rises sharply, followed by a slow increase, and remains larger than that at 300 K up to ≈ 9000 cm^{-1}.The IR band appears at the same energy but peak intensity lowers. This seems as if , on increasing temperature, ϵ_2 at frequency of the IR band decreases and is transferred to the lower frequency region. This indicates the presence of more IR peaks at frequency below the one corresponding to IR band.

This speculation is strongly supported by spectral weight calculation of total IR transition (N_{eff}) that gives the effective number of carriers per Bi atom contributing to the infrared transition is shown in fig. 3. We notice that N_{eff} of $x = 0$ sample does not show appreciable temperature dependence. However, significant temperature dependence of N_{eff} is seen in $x = 0.15$ sample (fig. 3-b). At 400 K, N_{eff} remains large to much lower frequency ≈ 250 cm^{-1} (≈ 12000 cm^{-1} in $x = 0$) where it crosses the one at lower temperature. This indicates that in potassium doped sample N_{eff} shifts towards lower frequency region as temperature increases.

N_{eff} seems to be transferred to the peaks present at lower frequency. These peaks correspond to some new excitations among the bound states created by hole doping in CDW gap. Recently, Bischofs et al [4] presented a model for lightly doped $BaBiO_3$ where they suggested the formation of such bound states inside the peierls gap as a result of hole doping. Also at higher temperature, some carriers are thermally excited to some higher energy states. Excitation from these thermally excited band to either some other allowed states inside peierls gap or empty Bi^{5+} band may be the possible reason for the rise of ϵ_2 with increasing temperature.

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