Evidence of charge localization from photoinduced infrared absorption in BaBiO₃

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Abstract. Photoinduced infrared activities were studied in BaBiO₃ and the results compared with those of La₂CuO₄ and YBa₂Cu₃O_{6+x}. The spectral range of investigation covered the interval from 50 to 4000 cm⁻¹. Clear evidence of lattice relaxation around the photoinjected charges was observed in the phonon spectral range with the bleaching of IR phonon bands. On the high energy side, we observed the rising edge of a broad electronic absorption. The results give an evidence of the suppression of the charge density wave due to the lattice relaxation around the photoinjected carriers. Moreover the low-energy charge excitation in the near infrared appears as a common characteristic of both layered and three-dimensional high *T_c* superconductors, and may be relevant in the pairing mechanism.

Keywords. Superconductivity; charge density wave; optical properties.

1. Introduction

The widening of the chemical structures that support high *T_c* superconductivity offers an interesting experimental and theoretical opportunity to verify the common characteristics which underlie all the systems and may eventually lead to the understanding of the mechanism of superconductivity.

It has been shown that the photoinjection of electron-hole pairs in La₂CuO₄ (Kim *et al* 1987; Ginder *et al* 1988) and YBa₂Cu₃O_{6+x} (Kim *et al* 1988; Taliani *et al* 1988, 1989) results in the formation of local electronic states which are associated with lattice distortions. These electronic excitations have been indicated as the pairing factors in the mechanism of high *T_c* superconductivity.

In the quest of a general behaviour, we have investigated the semiconducting BaBiO₃ material which is the precursor of the high *T_c* Ba_{1-x}K_xBiO₃ compound (*T_c* = 30 K) (Mattheis *et al* 1988; Cava *et al* 1988). This compound is interesting for the following reasons: (i) is the only one without Cu–O planes, (ii) has no magnetic ions, (iii) is three-dimensional rather than layered and (iv) shows a static charge density wave (CDW) in the insulating phase up to the insulator-metal transition. In this respect it is useful to compare the optical properties of BaBiO₃ with those of the conventional Cu-oxide high *T_c* superconductors by the photoinduced absorption technique.

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2. Experiment

2.1 Sample preparation

Stoichiometric proportions of powdered metal nitrates dissolved in distilled water were employed to synthesize BaBiO_3 by the citrate-polymer route (Wang *et al* 1987). The resulting solution was stirred up and heated to 90°C , and let react. At complete reaction the resulting gel was subsequently decomposed to a solid by heating. The powders were calcined at 450°C and then ground, pressed into pellets, sintered and annealed at 950°C . X-ray diffraction measurements showed that the product was X-ray pure (Thornton and Jacobson 1978).

Pressed pellets were used for the optical spectroscopic experiments. The ceramic was ground and mixed with polyethylene or CsI powders (0.5–4.0 wt%) in an agate mortar and then pressed to obtain optically transparent pellets in the far-IR and mid-IR spectral range respectively.

2.2 Experimental set-up

Absorption spectra and photoinduced absorption (PA) measurements were performed in a cryostat at 10 K by using a modified Bruker FTIR interferometer; an Ar^+ laser was used for photoexcitation at 2.5 eV. Consecutive interferograms of 32 scans each, with laser on and off, were stored for a total number of about 5000 scans in order to achieve an appreciable S/N ratio. The PA spectrum was derived by calculating the $-\Delta T/T$ ratio (i.e. the fractional variation of transmittance due to photoinduction).

3. Results

3.1 Infrared absorption

The absorption spectrum of BaBiO_3 (figure 1) shows four bands in the phonon spectral range.

Figure 1. Infrared absorption spectra of BaBiO_3 . Inset is the monoclinic BaBiO_3 structure.

This is consistent with the monoclinic distortion induced by the coupling of the lattice with a CDW (there are two inequivalent BiO₃ octahedra with the consequent doubling of the cell, see inset in figure 1). This dimerization results in the activation of an acoustic mode in the cubic undimerized structure, that becomes IR-active (TO'₄) because of the consequent folding of the Brillouin zone. Uchida *et al* (1985) proposed the following assignment of the phonons: Ω_1 at 492 cm⁻¹ is the bending mode of the BiO₃ octahedra, Ω_2 at 264 cm⁻¹ is the Bi–O stretching mode, Ω_3 at 155 cm⁻¹ is the TO'₄ mode and the Ω_4 at 104 cm⁻¹ is the external mode (the octahedra are moving as a whole).

3.2 Photoinduced absorption

3.2a Phonon modes: The phonon band at 492 cm⁻¹ assigned at Ω_1 is clearly affected by photoexcitation. This band presents a structured photoinduced bleaching (PB) suggesting that some components of the absorption band are bleached to a different extent. In view of this, we investigated the laser intensity dependence (I_{laser}) of the total bleached area (A_{PB}) where:

$$A_{\text{PB}} = \int_{\Omega_1} (\Delta T/T)_{I_{\text{laser}}} d\Omega.$$

A_{PB} varies proportionally to the square root of I_{laser} as shown in the inset of figure 2. Such a dependence excludes also the possibility of a thermal effect. A decrease of the

Figure 2. Photoinduced absorption spectrum of BaBiO₃ at 10 K of phonon region (continuous line), detailed view of the 500 cm⁻¹ IR band (dashed line). Inset is the laser intensity (mW/cm⁻²) dependence of the effective bleached area of mode Ω_1 .

oscillator strength of this band has been observed by Uchida *et al* (1985) with the increase of Pb doping in BaBiO_3 .

Other bleachings appear in correspondence with the Ω_2 and Ω_3 bands, but we cannot exclude that thermal effects contribute to these features. Nevertheless in the thermal modulation spectra the bleaching of Ω_3 is weaker than the bleaching of Ω_2 contrary to what we observe in PA spectra (see figure 2). From these considerations we tend to believe that the photoinduced bleaching of Ω_3 is intrinsic.

3.2a Charge excitations: In figure 3 the photoinduced spectrum is shown up to 4000 cm^{-1} . A broad absorption envelope with an onset at 1000 cm^{-1} (0.12 eV) increases in intensity towards the high energies and levels off at about 4000 cm^{-1} (0.5 eV). Due to the remarkable oscillator strength underlying the absorption we assign this feature to a dipole allowed electronic transition. This feature corresponds with a photoinduced electronic band with maximum at 0.5 eV observed by photo-modulation spectroscopy (Wei *et al* 1990). The laser intensity dependence at 2800 cm^{-1} is proportional to $I_{\text{laser}}^{1/2}$ as in the case of the Ω_1 phonon band bleaching.

Figure 3. Photoinduced absorption spectrum of BaBiO_3 at 10 K. Inset is the laser intensity (mW/cm^{-2}) dependence of the electronic PA.

4. Discussion

As has been observed in layered cuprate semiconducting precursors of the HTSC materials, photoexcitation of BaBiO_3 leads to the generation of electron-hole pairs and eventually gives rise to a lattice distortion around the photoinjected charges which is accompanied by a modification of the electronic structure.

In the case of BaBiO_3 , where the electronic gap at the Fermi energy is due to the doubling of the unit cell due to the CDW (Mattheiss and Hamman 1983), the photoinjected charges reduce the CDW order parameter inducing a local electronic state within the gap. The photobleaching of the Ω_3 phonon mode, which is made IR-active by the CDW distortion, is also a strong indication of the local suppression of the CDW due to the photoinduced carriers.

In BaBiO_3 , contrary to La_2CuO_4 and $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ where A_g phonon modes are made IR-active, no photoinduced phonon band appears. This is consistent with the fact that the symmetry of the undimerized structure of BaBiO_3 does not allow the activation of any A_g mode in Raman scattering.

It is interesting to notice that both the electronic PA band and the PB of the Ω_1 mode have the same laser power dependence. The power 1/2 dependence is a typical indication of a bimolecular recombination process of the photogenerated species. This implies that the decay rate is proportional to n_{ps}^2 , where n_{ps} is the number of photoexcited species. Considering a generation rate of these species proportional to the laser intensity, we can write the rate equation for n_{ps} as:

$$dn_{\text{ps}}/dt = \alpha I_{\text{laser}} - \beta n_{\text{ps}}^2$$

where α and β are constants. In steady-state conditions ($dn_{\text{ps}}/dt = 0$) the number of photoexcited species is proportional to the square root of the illumination intensity:

$$n_{\text{ps}} = \alpha/\beta I_{\text{laser}}^{1/2}$$

This dependence indicates that the photogenerated carriers recombine in pairs. The behaviour differs from the conventional semiconductors in which the recombination is monomolecular because of its defect-assisted nature and hence the recombination is determined by the density of these defects and not by the density of photoexcited species. Our experimental method allows detection of only long lived photoexcited species, with lifetime in the order of milliseconds. The exclusion of a defect-trapping process indicates that the long lifetime is not due to defect states but rather that the photoexcited species are indeed self-trapped.

This is indicative of a strong interaction between the lattice and charge carriers. The similar square root dependence of the photoinduced charge excitation at 0.5 eV and the phonon bleaching indicates that both these signatures are characteristics of the same photoexcited species. This behaviour is common for several superconducting systems including La_2CuO_4 , $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ and thallium-based perovskites (Foster *et al* 1989) despite the different structures and basic compositions.

In this respect, the strong similarity between the mid-IR absorption derived from reflectivity measurements of the superconductors and the photoinduced absorption of the parent semiconductors is noticeable. The common low-energy photoinduced charge excitation may be relevant for the pairing mechanism.

5. Conclusions

In summary, the photogenerated carriers interact strongly with phonons reducing locally the CDW distortion. This effect is accompanied by the creation of a new electronic state within the optical gap, and the modification of the selection rules of IR phonon absorption. This is a strong evidence of a substantial electron-phonon interaction. In particular, the low energy charge excitation, which is a common feature of all the high temperature superconductors, may play a fundamental role in pairing mechanisms.

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