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Optical study of $RE_{1+x}Ba_{2-x}Cu_3O_6$ (RE = Nd, Sm) and $YBa_2Cu_3O_6$ in the mid infrared range

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Abstract. Infrared reflectance, and transmission measurements as well as Raman scattering have been used to study the $RE_{1+x}Ba_{2-x}Cu_3O_6$ (RE = Nd, Sm) and $YBa_2Cu_3O_6$ absorption bands in the 1100–1500 cm^{-1} infrared range as a function of temperature and beam polarization. In addition to two-phonon absorption between 1100 and 1170 cm^{-1}, we observe excitations around 1400 cm^{-1}, occurring in oxygen rich enclosures within the samples, and assign them to an excitation involving two-phonons plus the 270 cm^{-1} local mode related to Cu-O broken chains. Thus, the previously reported possible magnetic origin of the 1436 cm^{-1} sharp absorption band in $YBa_2Cu_3O_6$ is contested.

PACS. 74.72.Jt Other cuprates – 74.25.Gz Optical properties – 74.25.Ha Magnetic properties – 71.55.Ht Other nonmetals

1 Introduction

Infrared absorption bands common to all materials containing CuO_2 layers have been reported by Perkins *et al.* [1] and Grüninger *et al.* [2]. In addition to the intense absorption band around 2800 cm^{-1}, that Lorenzana and Sawatsky [3] assigned to phonon-assisted bimagnon absorption, crystal field (CF) excitations associated with the rare earth electronic $f-f$ transitions have been observed in the 1000–10000 cm^{-1} range, in the $RE_{2-x}Ce_xCuO_4$ (RE=Nd and Pr) [4–7] and $RE_{1+x}Ba_{2-x}Cu_3O_{6+y}$ (RE = Nd, Sm) [8,9] cuprates. In this paper, we focus our attention on the sharp absorption band observed around 1436 cm^{-1} in $YBa_2Cu_3O_6$ [2], $Y_{1-x}Pr_xBa_2Cu_3O_6$ [10] and $Y_{1-x}RE_xBa_2Cu_{3-y}Zn_yO_6$ [11]. The interpretation of this band has been the subject of intense activity. While first assigned to the optical magnon [2], its magnetic character could not be established in spite of studies under high magnetic fields [10,11], Zinc doping and rare earth substitution [12]. No measurable effect due to the magnetic field has been observed, a fact that, according to Zibold *et al.* [11] and later to Grüninger *et al.* [12], could be attributed to a spin-flop transition in which spins align mainly perpendicularly to the external field [13]. Neutron scattering studies of $YBa_2Cu_3O_{6+y}$ ($y = 0.2$ [14] and $y = 0.15$ [15]) have shown that the optical magnon energy, at $\mathbf{k} = 0$, is around 550 cm^{-1}, putting into question the magnetic character of the 1436 cm^{-1} excitation. Recently, in an optical conductivity study of ^{18}O isotope substituted $YBa_2Cu_3O_6$, Grüninger *et al.* [16] have associated the 1436 cm^{-1} excitation with a combination-tone of a spin excitation of ∼1050 cm^{-1} and a phonon of about 400 cm^{-1}. However, they have also indicated that such an assignment needed to be checked by a careful theoretical analysis.

In order to clarify the origin of the 1000–1500 cm^{-1} range infrared absorption bands and the corresponding excitations in $REBa_2Cu_3O_6$ (RE = Y, Nd and Sm), we have performed infrared transmission and reflection along with micro-Raman scattering measurements in these materials.

2 Experiments

Y and $RE_{1+x}Ba_{2-x}Cu_3O_6$ (RE = Nd with $x = 0.00$, and RE = Sm with $x = 0.00$ and $x = 0.11$) single crystals with deviations from stoichiometry of less than 1% were grown by the self-flux method as described in reference [17] for the yttrium compound and according to references [18] and [19] for RE = Nd, Sm. The samples (typically 1.5×1.5×0.1 mm^3 after thinning) were reduced by annealing in high vacuum at 700 °C for four

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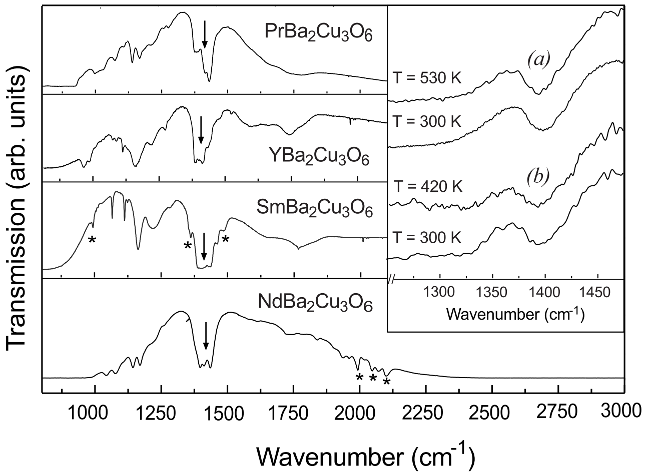


Fig. 1. IR transmission spectra across *ab*-oriented platelets of $REBa_2Cu_3O_6$ (RE = Pr, Y, Sm and Nd) in the 800–3000 cm^{-1} range, at $T = 78$ K. (↓) indicates the absorption bands between 1350 and 1450 cm^{-1}, and (*) designates CF-transitions associated with the Sm^{3+} (Ref. [9]) and Nd^{3+} (Ref. [8]) ions. Inset, IR transmission above and below the Néel temperatures, in (a) $NdBa_2Cu_3O_6$ and (b) $SmBa_2Cu_3O_6$.

days and then checked by X-ray, insuring D_{4h} symmetry. The studied crystals, with their *ac*- or *ab*-planes perpendicular to the incident beam, were mounted in a continuous-flow temperature-regulated helium cryostat for the low temperature experiments and fixed to a heated holder for the measurements above room temperature. 1 cm^{-1} resolution for the infrared transmittance study in the 1100–1500 cm^{-1} range and the infrared reflectance measurement in the 100–700 cm^{-1} range were obtained, using a Fast-Fourier-Transform interferometer (BOMEM DA 3.002) equipped, depending on the spectral range, with either a globar source, a KBr beam splitter and a MCT detector or a globar source, a Mylar Beam splitter and a liquid helium cooled Ge-bolometer. Room temperature Raman back-scattering studies were performed with a LABRAM-800 confocal system equipped with a charge-coupled-device (CCD) detector. A 5 mW 6328 Å He-Ne laser line polarized perpendicular to the *c*-axis, focused to a few microns spot diameter on the sample, was used for excitation.

3 Results and discussions

The absorption bands common to all the $REBa_2Cu_3O_6$ (RE = Pr, Y, Sm and Nd) compounds around 1400 cm^{-1} are presented in Figure 1. As shown in the inset, these absorptions in $NdBa_2Cu_3O_6$ at $T = 530$ K and in $SmBa_2Cu_3O_6$ at 420 K, persist above their Néel temperature [21] with no change of intensity, indicating that a magnetic origin is unlikely.

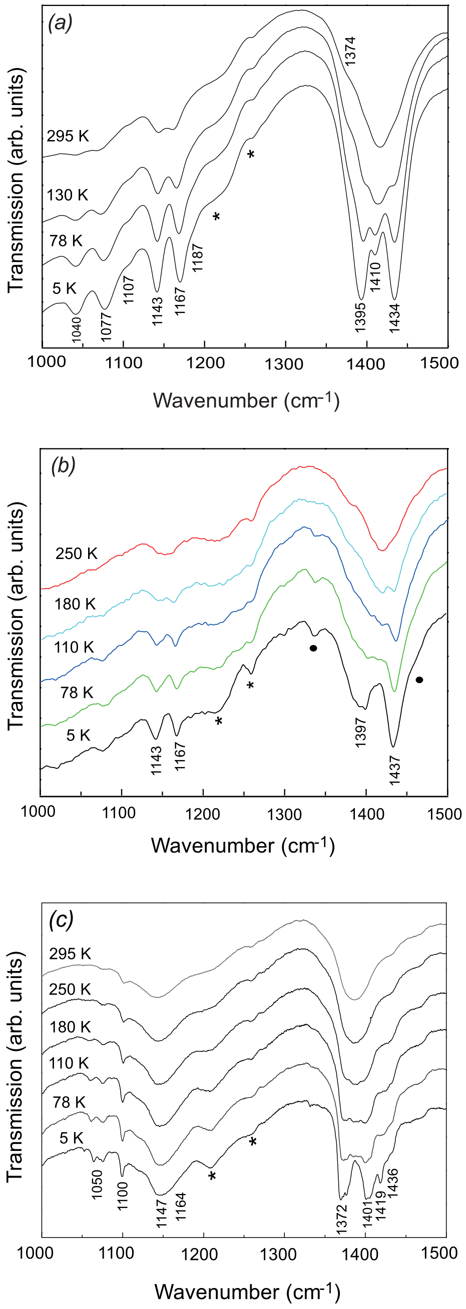


Fig. 2. Transmission spectra in the 1000–1500 cm^{-1} range as a function of temperature across *ab*-oriented platelets of $NdBa_2Cu_3O_6$ (a), $SmBa_2Cu_3O_6$ (b), and $YBa_2Cu_3O_6$ (c), respectively. (*) designates water vapor and KBr absorptions, whereas (•) in (b) corresponds to $^6H_{5/2} \rightarrow {}^6H_{7/2}$ CF-transition, associated with the Sm^{3+} ions.

Figures 2a–c show the infrared transmission measurements of $NdBa_2Cu_3O_6$ (a), $SmBa_2Cu_3O_6$ (b), and $YBa_2Cu_3O_6$ (c) in the 1000–1500 cm^{-1} range with T varying from 295 to 5 K. We observe two-phonon excitations between 1040 and 1187 cm^{-1} and multiple bands around 1400 cm^{-1}, at 1374, 1395, 1410 and 1434 cm^{-1} (a), 1397, 1437 cm^{-1} in (b), and 1372, 1401, 1419 and 1436 in (c), respectively. The absorption bands are better resolved at 5 K and broaden by more than 20% around 295 K. In contrast to the isolated and very narrow 1436 cm^{-1} band, reported by Grüninger *et al.* [2,16], more than three absorption bands are observed around 1400 cm^{-1}.

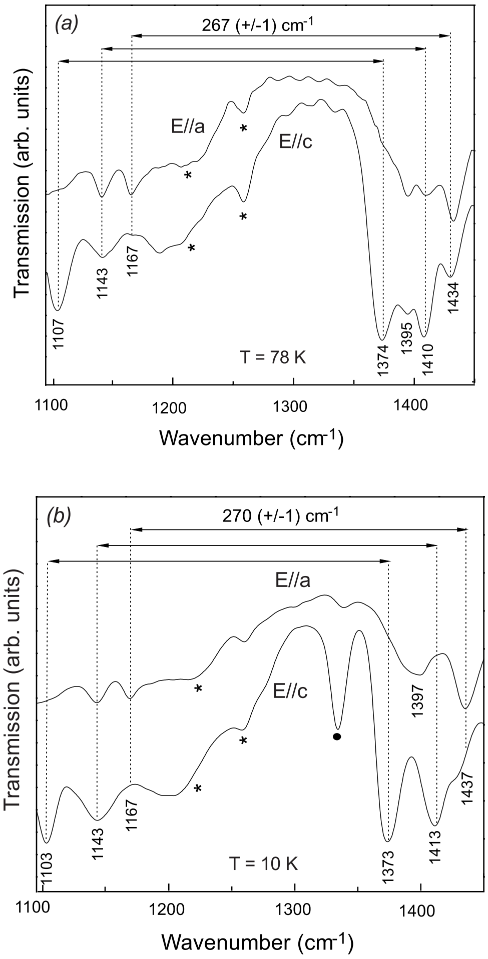


Fig. 3. IR-transmission across *ac*-oriented platelets of (a) $NdBa_2Cu_3O_6$ and (b) $SmBa_2Cu_3O_6$ for two polarizations of the incident beam. Notice the correlation between the three absorption bands in the 1150 and 1400 cm^{-1} regions.

In Figures 3a and 3b, the transmission measurements across *ac*-oriented platelets for the two orthogonal beam polarization modes are presented. In $NdBa_2Cu_3O_6$ (Fig. 3a), the absorption band intensities at 1107, 1143, 1167 cm^{-1} are correlated with the 1374, 1410, 1434 cm^{-1} ones having a constant 267 cm^{-1} energy separation. Similarly in $SmBa_2Cu_3O_6$ (Fig. 3b), an energy separation of 270 cm^{-1} between the 1103/1373, 1143/1413 and 1167/1437 cm^{-1} bands is detected. Furthermore, although the Sm/Ba substitution does not affect the energy separation between the two-phonon excitations and their replica around 1400 cm^{-1} by more than 10 cm^{-1}, a drastic attenuation of the absorption bands at 1382, 1423 and 1453 cm^{-1} is observed in $Sm_{1.11}Ba_{1.89}Cu_3O_6$ (Fig. 4b).

We have also performed far-infrared and Raman experiments on the $SmBa_2Cu_3O_6$ and $Sm_{1.11}Ba_{1.89}Cu_3O_6$ samples. In the Figure 4 inset, reflectivity measurements in the 250–350 cm^{-1} range are presented for both stoichiometric (a) and Sm-rich (b) samples. We note the disappearance of the excitation around 270 cm^{-1} in the substituted material $Sm_{1.11}Ba_{1.89}Cu_3O_6$.

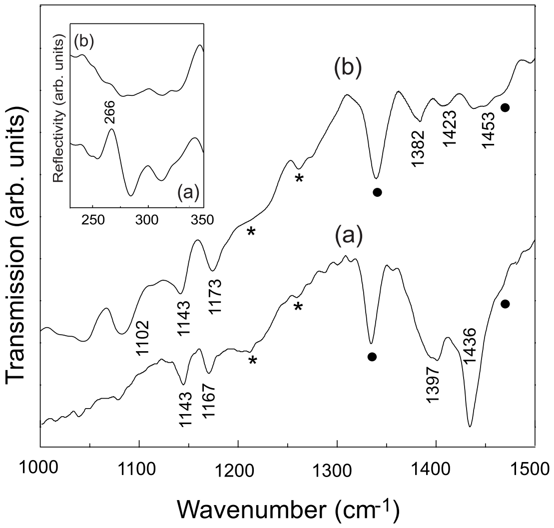
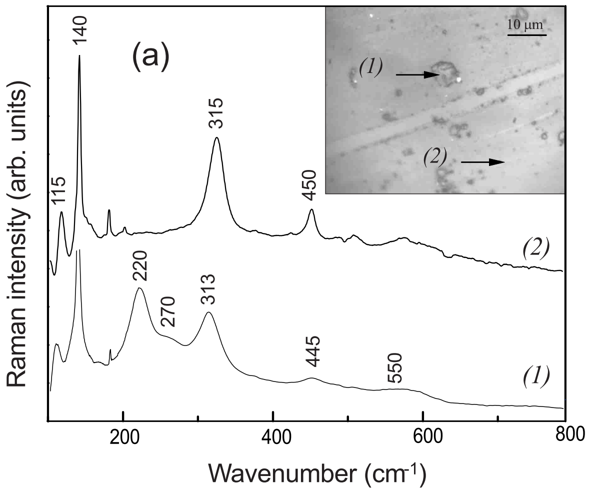


Fig. 4. Transmission spectra across *ab*-oriented platelets of (a) $SmBa_2Cu_3O_6$ and (b) $Sm_{1.11}Ba_{1.89}Cu_3O_6$ in the 1000–1500 cm^{-1} range. (*) designates water vapor and KBr absorptions, and (●) is associated with CF-transitions. Inset, far infrared reflectance in $SmBa_2Cu_3O_6$ (a) and $Sm_{1.11}Ba_{1.89}Cu_3O_6$ (b) samples at $T = 10$ K.

Micro-Raman scattering studies in the 100–800 cm^{-1} range are presented in Figures 5a–b. The experiments were performed in the $z(xx)\bar{z}$ configuration for two different laser beam positions (1) and (2) on the $SmBa_2Cu_3O_6$ and $Sm_{1.11}Ba_{1.89}Cu_3O_6$ samples, as indicated by the arrows in the insets. When the incident beam is focused on a light area (position (2)), we observe the expected [22–28] phonon excitations at 115, 140, 315, and 450 cm^{-1} in $SmBa_2Cu_3O_6$ (5a) and at 140, 313, 445 and 550 cm^{-1} in $Sm_{1.11}Ba_{1.89}Cu_3O_6$ (5b), respectively. In position (1), where the crystal surface presents dark enclosures, we notice two additional excitations at 220 and 270 cm^{-1} in $SmBa_2Cu_3O_6$, and 220 and 280 cm^{-1} in $Sm_{1.11}Ba_{1.89}Cu_3O_6$.

Multiphonon studies in $RE_{1+x}Ba_{2-x}Cu_3O_{6+y}$ materials are rather scarce. We attribute the absorption bands observed in the 1100–1200 cm^{-1} range to two phonon absorption processes associated with the O(4) ion [23–28] and the Cu(1)-O(1) chains [29–31], in agreement with the phonon density of states measurements in $YBa_2Cu_3O_6$ [30].

The constant energy separation between correlated excitations in the 1100–1200 cm^{-1} and 1350–1450 cm^{-1} ranges (Figs. 3a–b) strongly suggests the existence of a coupling between the two-phonon processes and the excitations at 267, 270, and 280 cm^{-1}, in $NdBa_2Cu_3O_6$, $SmBa_2Cu_3O_6$ and $Sm_{1.11}Ba_{1.89}Cu_3O_6$ respectively, that leads to additional absorption bands in the 1350–1450 cm^{-1} range. Attenuation of the infrared reflectivity in the 250–350 cm^{-1} range, as observed in



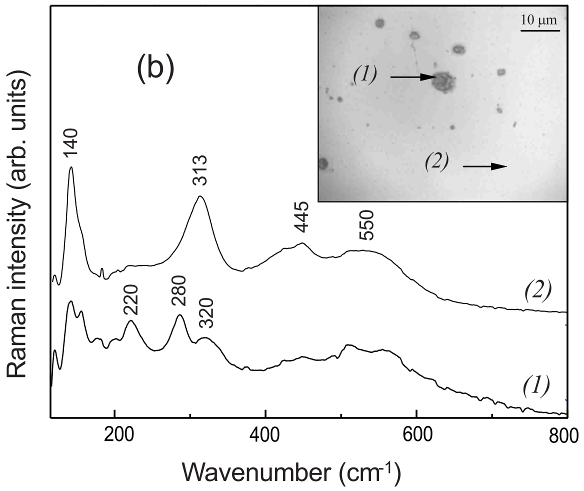


Fig. 5. Micro-Raman measurements at $T = 300$ K, in the $z(xx)\bar{z}$ configuration, in (a) $SmBa_2Cu_3O_6$ and (b) $Sm_{1.11}Ba_{1.89}Cu_3O_6$. In the micrograins of the inset, → locates the positions (1) and (2) where the laser beam is focused. Notice that the 270 (a) and 280 (b) cm^{-1} peaks only appear when the beam is located in the dark regions.

$Sm_{1.11}Ba_{1.89}Cu_3O_6$ (inset Fig. 4) results in weaker absorption bands around 1400 cm^{-1} (Fig. 4), which further confirms the coupling.

The 270 cm^{-1} equivalent excitation has been intensively studied by reflectance methods, where peaks at 277 cm^{-1} in $YBa_2Cu_3O_6$, 285 cm^{-1} in $Nd_{2-x}Ce_xCuO_4$, and 270 cm^{-1} in $Bi_2Sr_2CuO_6$ and $SmBa_2Cu_3O_7$, have been reported [22,26–28,32,33]. This mode could not correspond to the sharp resonance that was observed by neutron scattering in $YBa_2Cu_3O_7$ [34] and attributed to local magnetic fluctuations, since this latter resonance is only observed in superconducting samples with high oxygen content. According to Thomsen *et al.* [26], this excitation is associated with the CuO broken chain local mode, that corresponds to an oxygen excess in the semiconducting $REBa_2Cu_3O_6$ samples, while Calvani *et al.* [32] have pointed out that such a local mode contributes to polaron formation in electron and hole-doped cuprates.

$SmBa_2Cu_3O_6$ and $Sm_{1.11}Ba_{1.89}Cu_3O_6$ micro-Raman scattering measurements identify dark inclusions on the sample surface where the 270 cm^{-1} (Fig. 5a) and 280 cm^{-1} (Fig. 5b) local modes are present. The infrared beam diameter (∼2 mm) probes the average sample absorption, so that the intensity of the absorption bands around 1400 cm^{-1} depends essentially on the average number of dark enclosures in the studied compounds. We interpret the attenuation of the bands around 1400 cm^{-1} in the $Sm_{1.11}Ba_{1.89}Cu_3O_6$ sample as being due to a lower oxygen excess in comparison to $SmBa_2Cu_3O_6$, where more enclosures are observed (Figs. 5a–b).

Grüninger *et al.* [16] have excluded the pure vibrational (multiphonon) character of the 1436 cm^{-1} band in $YBa_2Cu_3O_6$ on the basis of a small frequency shift of this band following ^{18}O isotope substitution. It would be interesting to perform measurements in ^{18}O isotope substituted samples where prior to the infrared transmission study, the isotope substitution in the inclusions is checked and analyzed by Micro-Raman.

4 Conclusion

Infrared transmission, far-infrared reflectance and micro-Raman scattering studies as a function of temperature, polarization and crystal stoichiometry, lead us to conclude that the universal bands observed in the $RE_{1+x}Ba_{2-x}Cu_3O_{6+y}$ materials around 1400 cm^{-1} have non-magnetic origin. They are likely to correspond to a combination, characterized by a relatively strong dipole, of two phonon excitations with a Cu-O broken chain local mode located in the enclosures.

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