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## Investigations on the IR spectra of $\text{YBa}_2\text{Cu}_3\text{O}_x$ and $\text{BiSrCaCu}_2\text{O}_x$

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**Abstract.** The assignments for the IR peaks in  $\text{YBa}_2\text{Cu}_3\text{O}_x$  were supported by the correlation between the variations of frequencies of IR peaks with lattice constants. The intensities of two peaks at  $410\text{ cm}^{-1}$  ( $P_4$ ) and  $360\text{ cm}^{-1}$  ( $P_5$ ) were found to vary with the intensities of peaks at  $636\text{ cm}^{-1}$  ( $P_1$ ) and  $590\text{ cm}^{-1}$  ( $P_2$ ), respectively. The IR spectra of  $\text{BiSrCaCu}_2\text{O}_x$  with different oxygen contents were also studied and assignments for the peaks have been suggested.

### 1. Introduction

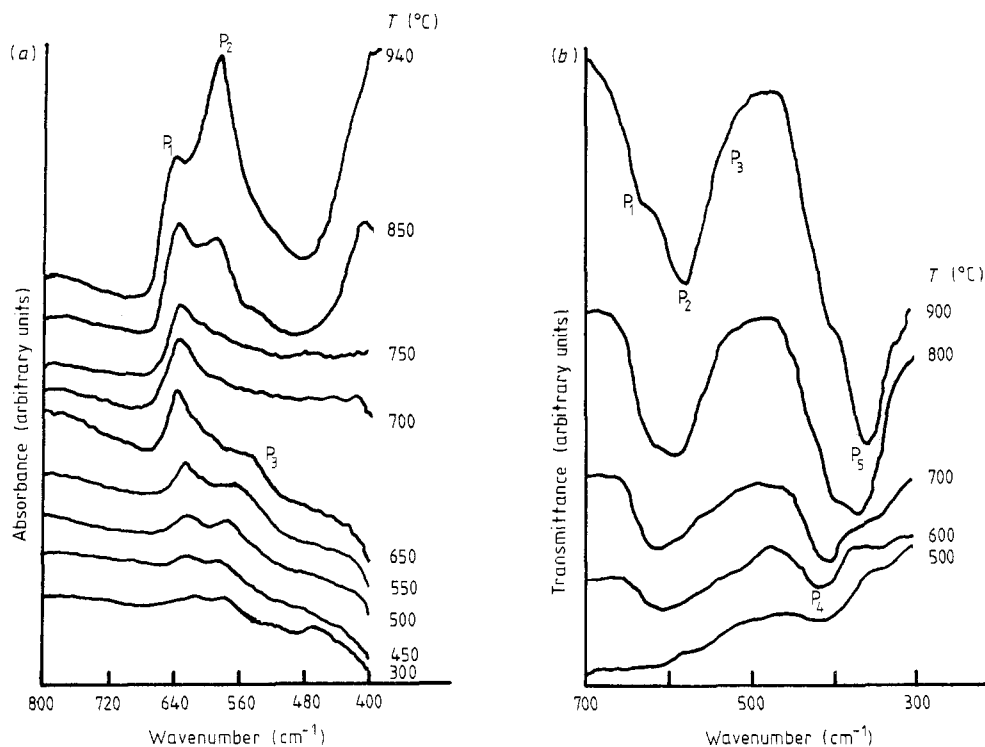
IR spectroscopy has been widely used as a powerful technique for the investigation and characterisation of the high- $T_c$  superconductors. It is shown that the IR spectrum of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  varies with oxygen content  $x$  and reveals changes of frequency and intensity for some peaks [1–10]. In a previous paper [3], we have reported that there are three peaks within the frequency range of  $800\text{--}400\text{ cm}^{-1}$  shown as  $P_1$  ( $620\text{--}642\text{ cm}^{-1}$ ),  $P_2$  ( $590\text{ cm}^{-1}$ ) and  $P_3$  ( $540\text{--}585\text{ cm}^{-1}$ ). Assignments for the peaks were also suggested. At present, however, there is considerable disagreement in the literature for assignments of these peaks [1–3, 8, 9]. For the Bi–Sr–Ca–Cu–O system, there have been to our knowledge no reports concerning the IR spectra of materials with different oxygen contents.

In this work, we studied the IR spectra and lattice constants of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  quenched from different temperatures. Some correlation was found between the variations of peak frequencies and lattice constants. The intensity variations of two peaks at  $410\text{ cm}^{-1}$  ( $P_4$ ) and  $360\text{ cm}^{-1}$  ( $P_5$ ), which have been reported in literature as one peak, show correlation with that of  $P_1$  and  $P_2$ , respectively. We also studied the IR spectra of  $\text{BiSrCaCu}_2\text{O}_x$  with different oxygen contents and assignments for the peaks are discussed.

### 2. Experimental procedure

The sample preparation and annealing treatment procedures can be found in a previous paper [3]. The lattice constants were measured using x-ray powder diffraction analyses.

Bi–Sr–Ca–Cu–O samples were prepared by solid-state reaction using  $\text{Bi}_2\text{O}_3$ ,  $\text{SrCO}_3$ ,  $\text{CaCO}_3$  and  $\text{CuO}$  with nominal composition  $1:1:1:2$  ( $\text{Bi}_1\text{Sr}_1\text{Ca}_1\text{Cu}_2\text{O}_x$ ). The mixed



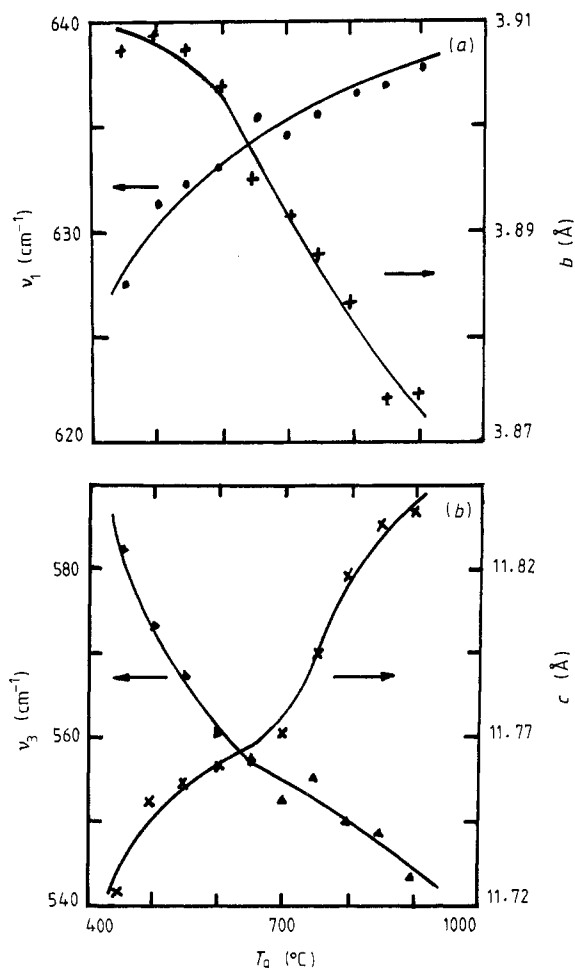
**Figure 1.** The IR spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  quenched at various temperatures; (a), measured by Fourier-transform spectrometer; (b), measured by grating infrared spectrophotometer.

powder was ground thoroughly and calcined at 820  $^{\circ}\text{C}$  for 20 h. The calcined powder was then pressed into pellets and sintered at about 882  $^{\circ}\text{C}$  for 48 h followed by annealing at 800  $^{\circ}\text{C}$  for 48 h in air. The sample showed a sharp superconducting transition at about 110 K and eventually reached zero resistance at 95 K. Hydrogen treatment was performed at about 300  $^{\circ}\text{C}$  for different durations in order to induce oxygen vacancies in the structure.

The sample powder was mixed with potassium bromide (KBr) and pressed into pellets for IR measurements. For the frequency range 4900–400  $\text{cm}^{-1}$ , a Fourier-transform IR spectrometer (Nicolet 7199C) was used. In order to show the IR peaks with frequencies lower than 400  $\text{cm}^{-1}$ , a Perkin-Elmer 577 grating infrared spectrophotometer was also employed.

### 3. Results

Shown in figure 1 are the IR spectra of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  quenched from different temperatures. As no peaks emerge in the frequency range 4900–800  $\text{cm}^{-1}$ , we only show the IR spectra within the frequency range 800–300  $\text{cm}^{-1}$ . It can be seen that there are five peaks shown as  $P_1$  (620–642  $\text{cm}^{-1}$ ),  $P_2$  (590  $\text{cm}^{-1}$ ),  $P_3$  (540–585  $\text{cm}^{-1}$ ),  $P_4$  (410  $\text{cm}^{-1}$ ) and  $P_5$  (360  $\text{cm}^{-1}$ ). The intensity of  $P_1$  increases with increasing quenching temperature and its frequency shifts to higher values; the intensity of  $P_3$  undergoes obvious change but its frequency shifts to lower values;  $P_2$  appears in the spectrum of 700  $^{\circ}\text{C}$  quenched sample and grows rapidly becoming the dominant feature; both  $P_4$  and  $P_5$  increase in



**Figure 2.** Variation of frequencies  $\nu$  and lattice constants with quench temperature  $T_q$ . (a)  $P_1$  peak and lattice constant  $b$ . (b)  $P_3$  peak and lattice constant  $c$ .

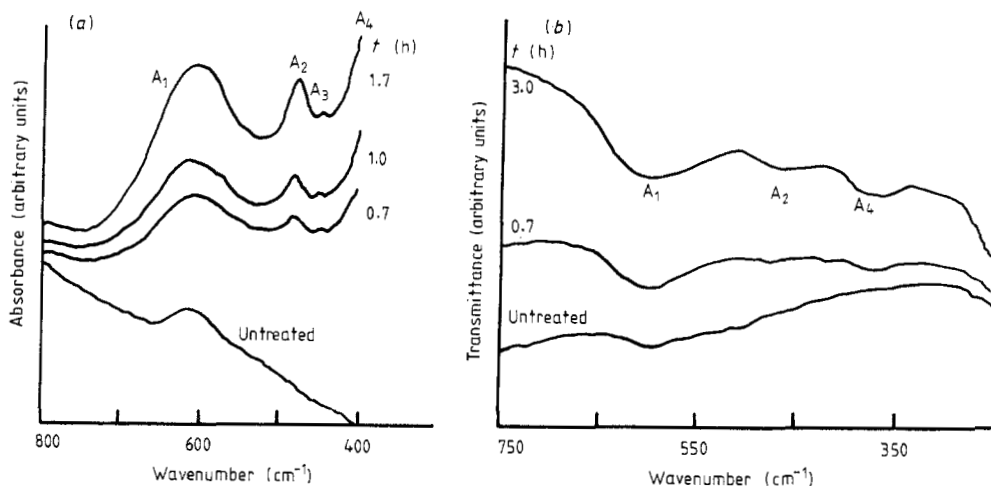
intensity but  $P_5$  appears only in the IR spectra of samples quenched above 700 °C. The intensity variations of  $P_4$  and  $P_5$  show correlations with those of  $P_1$  and  $P_2$ , respectively.

The variations in frequency of  $P_1$  and  $P_3$  and the lattice constants  $b$  and  $c$  with quenching temperature are shown in figure 2. It shows that the frequency of  $P_1$  increases with decreasing lattice constant  $b$  and the frequency of  $P_3$  decreases with increasing lattice constant  $c$ .

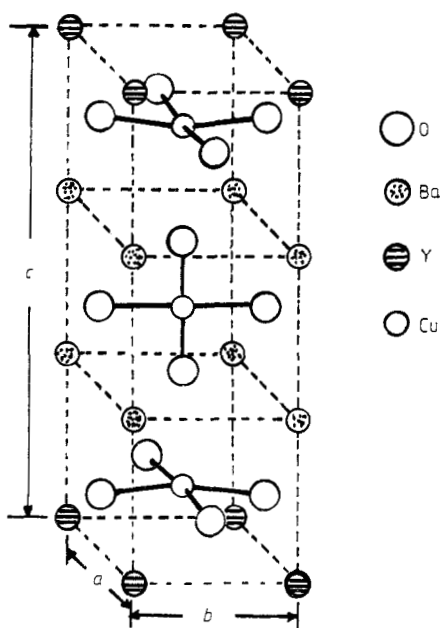
The IR spectra of  $BiSrCaCu_2O_x$  before and after hydrogen treatment at 300 °C for different durations are shown in figure 3. There is only one peak at 610  $\text{cm}^{-1}$  ( $A_1$ ) in the IR spectrum of  $BiSrCaCu_2O_x$  before hydrogen treatment. After hydrogen treatment, three other peaks appear at 475  $\text{cm}^{-1}$  ( $A_2$ ), 450  $\text{cm}^{-1}$  ( $A_3$ ) and 370  $\text{cm}^{-1}$  ( $A_4$ ) in addition to the  $A_1$  peak. The intensities of the four peaks all increase with increasing duration of hydrogen treatment.

#### 4. Discussion

It is generally understood that the frequency of IR peak depends on the bond length of the oscillator. With bond length decreasing, the vibration frequency increases. Figure 2 shows that the frequency of  $P_1$  increases and the lattice constant  $b$  decreases with



**Figure 3.** IR spectra of  $\text{BiSrCaCu}_2\text{O}_x$  before and after hydrogen treatment for different durations; (a), measured by Fourier-transform spectrometer; (b), measured by grating infrared spectrophotometer.



**Figure 4.** The crystal structure of orthorhombic  $\text{YBa}_2\text{Cu}_3\text{O}_7$ .

increasing quench temperature. As the lattice constant  $b$  is proportional to the Cu–O bond length in the 1D Cu–O chains (see figure 4), it is reasonable to assign  $P_1$  to the Cu–O stretching vibration in the 1D Cu–O chains (for the tetragonal phase, it is the Cu–O bond in planes between Ba–Ba layers) [3]. Figure 2 also shows that the frequency of  $P_3$  decreases and lattice constant  $c$  increases with increasing quench temperature. This behaviour is very similar to that of  $500\text{ cm}^{-1}$  peak in the Raman spectrum of  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , which also shifts to lower frequency values with increasing quench temperature [6, 8, 11–15]. Because the  $500\text{ cm}^{-1}$  Raman peak has been unanimously assigned to the O–Cu–O symmetric stretching vibration (Raman active) along the  $c$  axis [1, 6, 8, 11–19], it is

appropriate to attribute  $P_3$  to the O–Cu–O antisymmetric stretching vibration (IR active) along the  $c$  axis [1, 3].  $P_2$  has been unanimously assigned to the Cu–O stretching vibration in the 2D Cu–O planes [1–3]. It is noted that the intensity variations of  $P_4$  and  $P_5$  show correlations with those of  $P_1$  and  $P_2$ , respectively. To our knowledge,  $P_4$  and  $P_5$  have been reported in the literature as one peak at  $360\text{ cm}^{-1}$  [2, 4]. According to their frequencies and intensity correlations with that of  $P_1$  and  $P_2$ , we assign  $P_4$  and  $P_5$  to the bending modes of Cu–O of the  $ab$  planes between Ba–Ba layers and Y–Ba layers, respectively.

For  $BiSrCaCu_2O_x$ , we have shown in a previous paper [20] that oxygen vacancies can be induced in its structure without the structure being destroyed by hydrogen treatment. These oxygen vacancies have considerable influence on the superconducting characteristics and unit cell volume. As is shown in figure 3, there are four IR peaks. Based on knowledge of the IR spectra of  $La_{2-x}Sr_xCuO_4$  and  $YBa_2Cu_3O_x$ , we tentatively assign the IR peaks of  $BiSrCaCu_2O_x$  as follows. The  $A_1$  and  $A_2$  peaks were assigned to the Cu–O and Bi–O stretching vibrations of the Cu–O and Bi–O planes, respectively, because the intensity of in-plane vibration mode is sensitive to the transition from metal to semiconductor [1, 4, 21], these being similar to the  $P_1$  and  $P_2$  peaks in  $YBa_2Cu_3O_x$ . Also the frequencies of  $A_1$  and  $A_2$  are consistent with the bond lengths of related oscillators such as Cu–O ( $1.91\text{ \AA}$ ) and Bi–O ( $2.71\text{ \AA}$ ) [22] (for the structure of the Bi–Sr–Ca–Cu–O system, see reference [22]). The  $A_4$  peak was attributed to the bending modes of Cu–O and Bi–O of the Cu–O and Bi–O planes, these being similar to the  $P_4$  ( $410\text{ cm}^{-1}$ ) and  $P_5$  ( $360\text{ cm}^{-1}$ ) peaks in the IR spectrum of  $YBa_2Cu_3O_x$ .  $A_3$  is always present in the semiconductor  $BiSrCaCu_2O_x$ , but to attribute an assignment to it will require further investigation. The symmetric stretching vibration of oxygen in the Bi–O–Cu–O–Bi chain along its  $c$  axis (Raman active) has been found in the Raman spectrum of Bi–Sr–Ca–Cu–O at about  $480\text{ cm}^{-1}$  [22, 23], but we do not observe its IR partner in the IR spectrum, i.e. the antisymmetric stretching vibration of oxygen in Bi–O–Cu–O–Bi (IR active) along its  $c$  axis. It may be that it lies hidden in the  $A_1$  peak due to the large linewidth of  $A_1$ .

In summary, we have further studied the IR peaks in  $YBa_2Cu_3O_x$ . The assignments for  $P_1$ ,  $P_2$  and  $P_3$  peaks in a previous paper were supported. A new peak ( $P_4$ ), together with another peak ( $P_5$ ) were also assigned according to their frequencies and intensity correlations with  $P_1$  and  $P_2$ .  $P_4$  and  $P_5$  were assigned to the bending vibrations of the Cu–O bond of the Cu–O planes between Ba–Ba layers and between Y–Ba layers, respectively. We also studied the IR spectrum of  $BiSrCaCu_2O_x$  and observed four peaks.  $A_1$  and  $A_2$  were assigned to the stretching vibration of Cu–O and Bi–O of the Cu–O and Bi–O planes, respectively;  $A_4$  ( $370\text{ cm}^{-1}$ ) was attributed to the bending vibrations of Cu–O and Bi–O of the Cu–O and Bi–O planes;  $A_3$  ( $450\text{ cm}^{-1}$ ) needs further investigation.

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