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### Studies on Characteristic of Infrared Spectra of Superconductor Bi-Sr-Ca-Cu-O System

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## STUDIES ON CHARACTERISTIC OF INFRARED SPECTRA OF SUPERCONDUCTOR Bi-Sr-Ca-Cu-O SYSTEM

**Key Words:** Infrared Absorption; Optical Density; Sintered;  
Superconductor

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### ABSTRACT

We made the superconductor of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_7$  by the solid state reaction. According to the results of measurement by infrared spectrophotometer with the varying of wave number from 4000 to 400  $\text{cm}^{-1}$ . We discovered three infrared absorption peaks at room temperature, i.e., peak  $A_1$  at 500–550  $\text{cm}^{-1}$ , peak  $A_2$  at 800–840  $\text{cm}^{-1}$  and peak  $A_3$  at 1370–1420  $\text{cm}^{-1}$ . We find that peak  $A_1$  is due to impure phase, peak  $A_2$  is related with the crystal structure and peak  $A_3$  is caused by the vibration of the atom layers of calcium.

### INTRODUCTION

We made the superconductor of  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_7$  by the solid state reaction, with  $T_{\text{ef}}=84.3\text{K}$ ,  $T_{\text{ci}}=112\text{K}$ . The structural analysis showed that the major

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superconducting phase was 2212 phase and the minor was 2223 phase. According to the results of measurement by infrared spectrophotometer with the varying of wave number from 4000 to 400  $\text{cm}^{-1}$ , we discovered three infrared absorption peaks at room temperature, i.e., peak  $A_1$  at 500–550  $\text{cm}^{-1}$ , peak  $A_2$  at 800–840  $\text{cm}^{-1}$  and peak  $A_3$  at 1370–1420  $\text{cm}^{-1}$ . We studied the cause of resistance of these three peaks in detail.

Mosanori et al., who studied the Raman spectra of superconductor of Bi–Sr–Ca–Cu–O system, thought that no Raman peak caused by the vibration of Cu–O plane was observed at the range of wave numbers which were less than 700  $\text{cm}^{-1}$  and the Raman peak occurred at 500  $\text{cm}^{-1}$  was due to impure phase. We think the appearance of peak  $A_1$  has the same reason.

To find the reason of appearance of peak  $A_2$ , we prepared the samples both by fast melting and freezing the superconductor of  $\text{BiSrCaCu}_2\text{O}_y$  ( major phase was 2212 ) without any treatment and by that with the restitution of heat treatment. The results of the experiments of infrared absorption spectra showed that, the superconductor prepared by both sintering and melting with the restitution of heat treatment had a large infrared absorption peak near 1400  $\text{cm}^{-1}$  whereas the sample melted without any treatment did not. Comparing the results of structural analyses by X-ray diffraction, we conclude that the infrared absorption peak near 1400  $\text{cm}^{-1}$  is caused by the vibration of the atom layers of calcium.

At the range of temperatures 150K–270K, we recorded the infrared spectrum of the superconductor and found the frequency and optical density of peak  $A_2$  had a sudden change at 210K–230K, whereas those of  $A_3$  and  $A_1$  did not make any change with temperature. Using the same specimen, we observed the X-ray diffraction patterns at the corresponding temperature range. There was a contraction along the c axis of 2212 phase at 210K–230K. But no change has been found along the a and b axes. That means the sudden change of frequency and optical density of infrared absorption peak  $A_2$  is caused by the distortion of crystal structure of the superconductor.

## EXPERIMENTS AND RESULTS

A lot of research works has been done since the discovery of new high  $T_c$  Bi–Sr–Ca–Cu–O superconductor at the beginning of 1988. The studies of infrared absorption spectra and Raman spectra of high  $T_c$  superconductor are generally focused on the wave numbers which are less than 700  $\text{cm}^{-1}$ , and there are only a small amount of studies of Raman spectra of Bi–Sr–Ca–Cu–O system. We measured the infrared absorption spectra of Bi–Sr–Ca–Cu–O system at the room temperature and low temperature and also gave the structural analyses of X-ray diffraction patterns at low temperatures.

We obtained the superconductor of Bi–Sr–Ca–Cu–O system by solid state reaction, the nominal cation ratio of which is  $\text{Bi} : \text{Sr} : \text{Ca} : \text{Cu} = 1 : 1 : 1 : 2$ , with

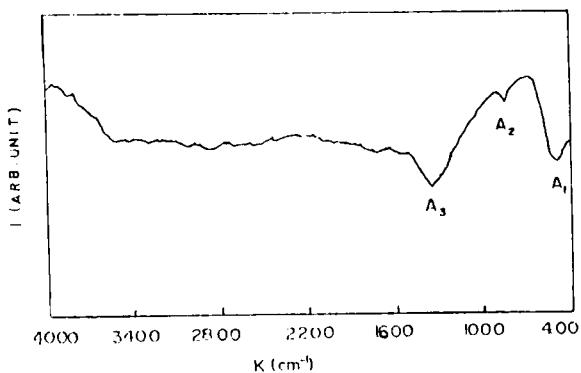


Fig. 1 The infrared absorption spectrum of the superconducting sample at room temperature.

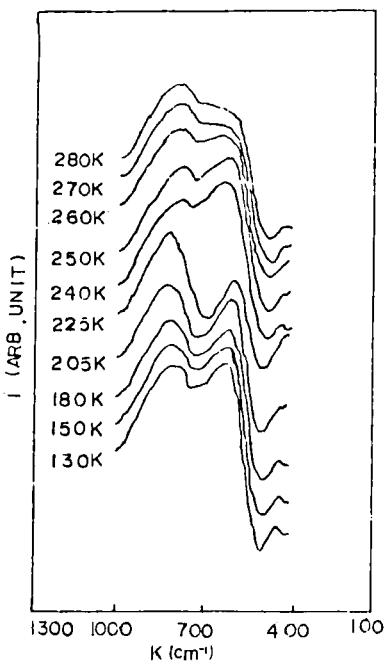


Fig.2 The infrared absorption spectra from 150K to 270K.

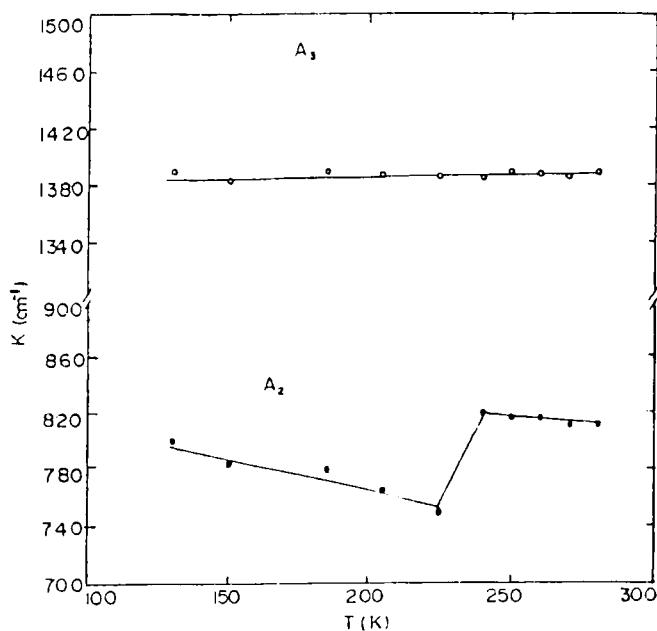


Fig.3 The variation of the frequency of peak A<sub>2</sub> and A<sub>3</sub> with temperature.

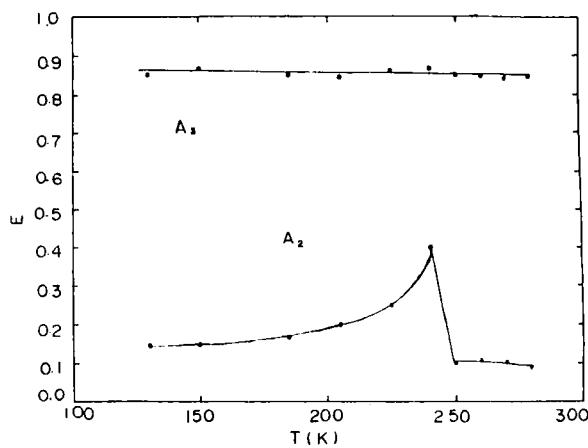


Fig.4 The variation of the optical density of A<sub>2</sub> and A<sub>3</sub> with temperature.

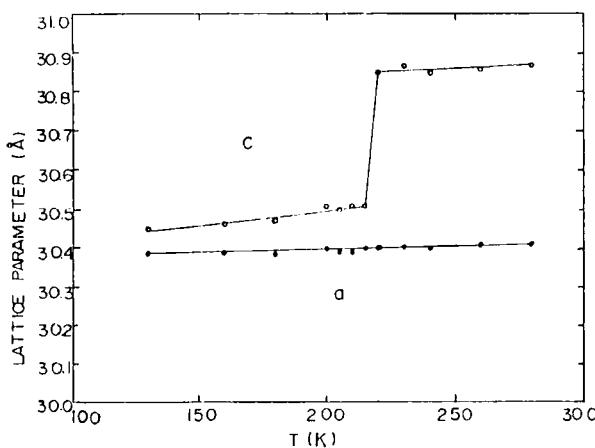


Fig.5 The variations of lattice parameters of the 2212 phase with temperature.

the superconducting transition temperature  $T_{\text{cf}} = 84.3\text{K}$  and  $T_{\text{ci}} = 112\text{K}$ . the structural analysis of X-ray diffraction pattern showed that the major phase was 2212 phase with minor 2223 phase.

We recorded the infrared absorption spectrum of the superconductor sample at room temperature with the varying of wave numbers from  $4000$  to  $400\text{ cm}^{-1}$ , as shown in Fig. 1. From the figure we can tell there are three infrared absorption peaks, i.e., peak  $A_1$  at  $500$ – $550\text{ cm}^{-1}$ , peak  $A_2$  at  $800$ – $850\text{ cm}^{-1}$  and peak  $A_3$  at  $1370$ – $1420\text{ cm}^{-1}$ . Mosanori et al., who studied the Raman spectra of superconductor of Bi–Sr–Ca–Cu–O system, thought that no Raman peak caused by the vibration of Cu–O Plane was observed at the range of wave numbers which were less than  $700\text{ cm}^{-1}$  and the Raman peak occurred at  $500\text{ cm}^{-1}$  was due to impure phase.

In order to find the reason of resistance of peak  $A_2$  and  $A_3$ , we measured the infrared absorption spectra and analyzed the structure of the superconductor by X-ray diffraction at the range of the temperatures  $150\text{K}$ – $270\text{K}$ . The infrared absorption spectra from  $150\text{K}$  to  $270\text{K}$  are shown in Fig.2. According to the results of the measurement we show the variations of the frequency and optical density ( $E = \lg I_0 / I$ ) of peak  $A_2$  and  $A_3$  with temperature in Fig. 3 and Fig. 4 respectively. In the figures it is obvious that there is a sudden change of the frequency and the optical density of peak  $A_2$  at  $210\text{K}$ – $230\text{K}$  but the frequency and optical density of peak  $A_3$  do not vary with temperature, presented as a straight line. The

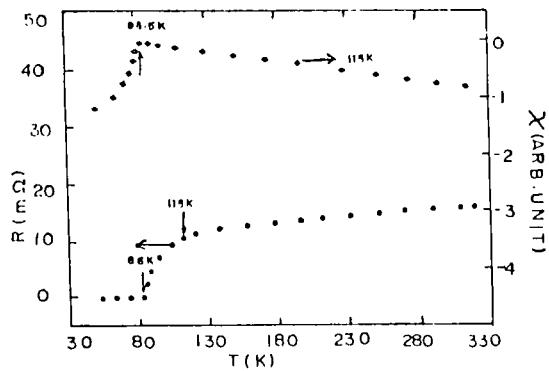


Fig.6 The resistance of sample C at the low temperatures.

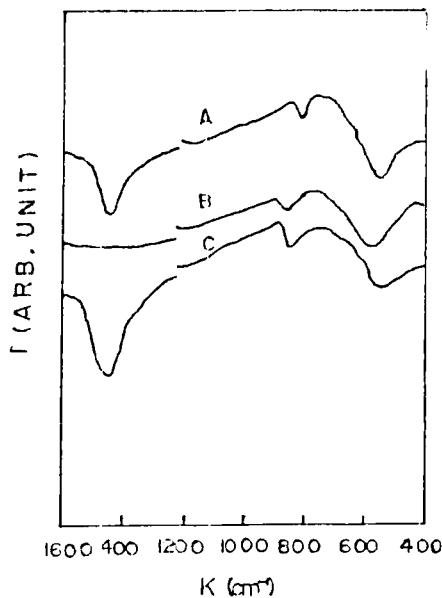


Fig.7 The infrared absorption spectra of samples A, B, C.

results of the X-ray diffraction are shown in Fig.5. The figure shows that there is a 1% contraction of 2212 phase along *c* axis at 210K–230K and no evident change along *a* and *b* axes. Y. S. He et al. measured the supersonic decay of Bi–Sr–Ca–Cu–O system at low temperatures and also found the sudden change at 200K–230K. So we can draw the conclusion the there is really a distortion of crystal structure of Bi–Sr–Ca–Cu–O system occurred at 210K–230K. From the above we conclude that the sudden change of the frequency and the optical density of infrared absorption peak  $A_2$  is due to the distortion along *c* axis. The energy of peak  $A_2$  (about 0.1 eV) is equivalent to that of optical phonon. According to the fact that  $A_2$  is related with the longitudinal optical phonon, i.e., polarized phonon. It is under the further study whether there are relations between the longitudinal optical phonon and the vibration of Cu–O atom plane.

To find the reason of resistance of peak  $A_3$ , We made the  $\text{BiSrCaCu}_2\text{O}_y$  (nominal cation ratio) sample (A) superconducting at the liquid nitrogen temperature range. By fast melting in the vacuum arc furnace we obtained the sample B melted which presented as semiconductor at the liquid nitrogen temperature range. We got the sample C after the restitution of heat treatment in which oxygen was flowing at 800°C. Fig.6 shows the results of the measurements of the resistance at the low temperatures of sample C. The results of infrared absorption measurements of samples A, B, C are shown in Fig.7. The results of analyses by X-ray diffraction show the major phase of sample A and C is that of 2212 with  $a = 5.41\text{ \AA}$   $b = 5.43\text{ \AA}$   $c = 30.6\text{ \AA}$  and the major phase of sample B is that of 2201 with  $a = 5.41\text{ \AA}$   $b = 5.43\text{ \AA}$   $c = 24.6\text{ \AA}$ . Fig.6 shows the sample C superconducts at liquid nitrogen temperature range with  $T_{\text{cf}} = 86\text{ K}$   $T_{\text{ci}} = 115\text{ K}$ . Fig.7 shows both sample A and C have a infrared absorption peak near  $1400\text{ cm}^{-1}$  whereas sample B do not.

The analyses show the structural phase transformation 2212 $\leftrightarrow$ 2201 takes place near the melting point of  $\text{BiSrCaCu}_2\text{O}_y$ , while fast melting is performed. That is to say that the atom layers of calcium in the unit cell of 2212 phase disappear and 2212 phase has become that of 2201 while melting; the atom layers of calcium are embeded in the unit cell again and 2212 phase is formed with the restitution of heat treatment. Comparing the results of structural analyses by X-ray diffraction and those of infrared absorption peak near  $1400\text{ cm}^{-1}$  is caused by the vibration of the atom layers of calcium. In a word the atom of calcium has prominent influence on the phase transformation at high temperature and the superconductivity of the Bi–Sr–Ca–Cu–O system.

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