

**ELECTRICAL AND INFRARED STUDY OF
Bi₂Sr₂Ca₁Cu₂O₈ IN SEMICONDUCTING,
SUPERCONDUCTING CERAMIC AND
SUPERCONDUCTING GLASS CERAMIC STATE**

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ABSTRACT

We have studied the electrical and infrared properties of Bi₂Sr₂Ca₁Cu₂O₈ compound in three states. Electrical and IR measurements show that the pure powder state sample is a semiconductor, the ceramic Bi₂Sr₂Ca₁Cu₂O₈ sample prepared after annealing at 820°C for 240 hours shows a T_c of 85 K, whereas Bi₂Sr₂Ca₁Cu₂O₈ sample prepared through glassy route, i.e. melting at 1250°C and annealing at 820°C for 240 hours shows a drop of T_c by 5 K. The infrared spectra of superconducting ceramic and glass ceramic states in the available frequency range of measurement reveals the presence of three phonons. Since the vibrational mode around 595 cm⁻¹ is due to CuO₂ layers and as the CuO₂ layers are responsible for T_c in the ceramic superconductors, any change in these layers will affect the T_c. The shifting of the 595 cm⁻¹ mode towards lower frequencies in the glass ceramic due to different preparation process, indicates that there is a change in CuO₂ layers resulting in a change of T_c, which is confirmed by Four probe dc measurements.

INTRODUCTION

The bismuth base cuprates $\text{Bi}_2\text{Sr}_2\text{Ca}_x\text{Cu}_y\text{O}_8$ (where $x = 1, 2$, and $y = 1, 2, 3$) belongs to a class of high temperature superconductors having T_c in the range 80-110 K depending on the phase of the compound. These compounds have no rare earth atoms as in YBCO [1-2]. It has been established [3-4] that there are three superconducting phases i.e. the (2201) phase having $T_c \sim 80$ K, the (2212) phase with T_c equal to 85 K and finally the (2223) phase where the T_c approaches 110 K. The (2212) phase has been extensively studied due to its easy formation and strong correlation between the hole concentration and the critical temperatures (T_c) which has been demonstrated by various substitution studies [6-7]. The 2223 and 2201 phases are difficult to synthesize as a single phase.

A close correlation between the vibrational behavior of the semiconducting and isomorphous superconducting $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ is expected because of the similarity of their crystalline structure.

The role of phonons and other low energy excitations in the mechanism of high T_c superconductivity is currently a central issue. In the present study, we intended to compare the vibrational modes of the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ compound in the semiconducting, ceramic superconducting and glass ceramic superconducting states.

EXPERIMENTAL PROCEDURE

The bulk polycrystalline samples of nominal composition $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_x$ were prepared using starting materials such as Bi_2O_3 , SrCO_3 , CaCO_3 and CuO of 99.99% purity. Mixed powders were ground in an agate mortar. A portion of grounded powder was pressed into pellets of 3 mm thickness and 1 cm diameter. Two pellets were made of the above dimension. One of the pellets was placed into a furnace and heat treated for 240 hours at 800°C. The untreated

pellet is marked as sample III, the heat treated pellet is marked as sample I. The remaining powder was calcined at 800°C for 10 hours in air. The calcined mixture was melted in a covered alumina crucible at 1050°C for 1 hour in an electric furnace. The melt was quenched rapidly on a stainless steel plate and pressed quickly by another steel block, resulting in a disk of 2 mm thick. This glass ceramic disk was placed into the furnace and heat treated for 240 hours at 800°C. This glass ceramic sample is marked as sample II. Resistivity measurements were made on all the three samples using standard Four probe technique. During the measurements each sample was cooled to 20 K using closed-cycle cryocooler. The resistivity of sample III decreases slightly as the temperature is reduced and then starts increasing as the temperature is further lowered indicating the semiconducting behavior.

RESULTS AND DISCUSSIONS

Fig. 1 represents the resistivity temperature dependence for sample I, II and III. The resistance of sample I starts decreasing as the temperature reaches 100 K and it falls to zero at 85 K. For sample II the room temperature resistance is higher as compared to I. For sample II, the zero resistance is obtained at 80° K which indicates that in glass superconductor i.e. sample II, the superconducting volume is reduced and hence in turn the T_c of the sample drops, which is a consequence of different preparation processes. From Fig. 1, we also observe that there is a large difference between the electrical resistivity of sample III as compared to I and II, which shows the resistivity behaviour of an amorphous and a semiconducting state. Below 160 K the resistivity of sample III is very high whereas the resistivity of sample I and II is zero, below 80 K.

Infrared spectra of the pellets were taken using Nicolet Spectrometer equipped with DTGS detector and CsI beam splitter. Spectra were measured in the range of 200 to 4500 cm^{-1} with a resolution of 4 cm^{-1} . Samples used for IR measurement were not polished in order to avoid any contamination. The absolute reflectance of the sample was determined by comparison with the

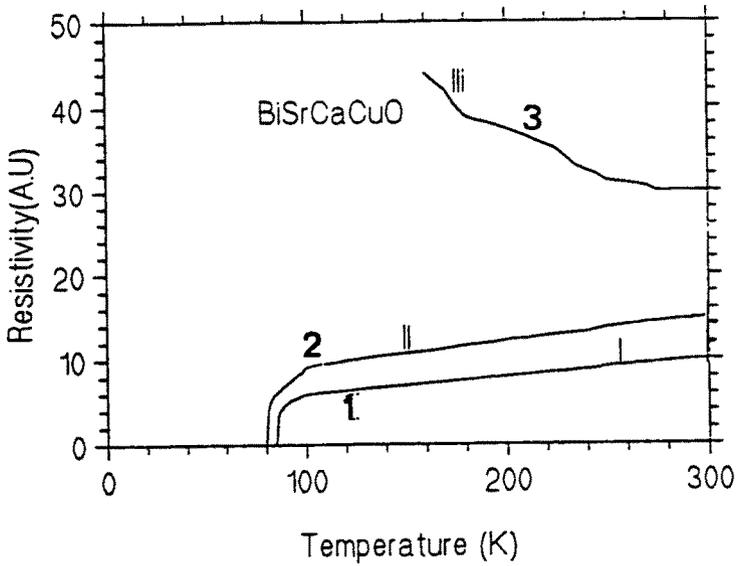


Figure 1 : Resistivity as a function of temperature for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ in three different states.

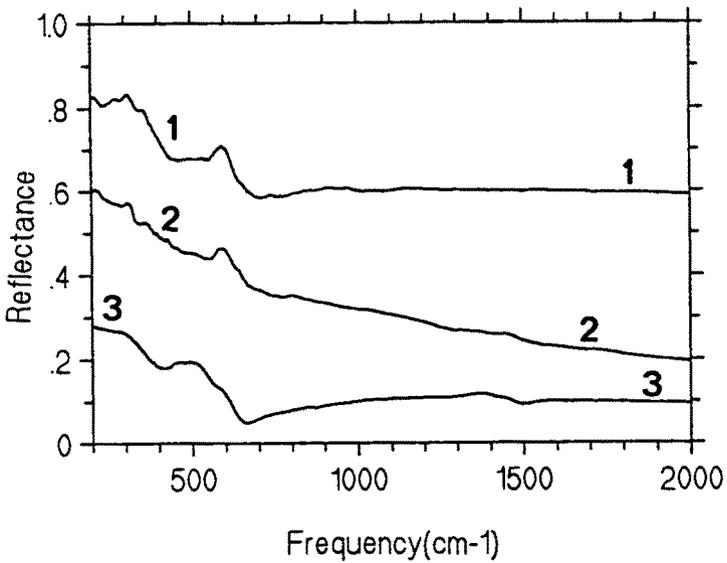


Figure 2 (a) : Detail IR reflectance spectra for the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ samples.

known reflectivity of an aluminum deposited mirror. The reflectance spectra of samples I, II and III are shown in Fig. 2. For samples I and III, we observe that the reflectance decreases smoothly with increasing frequency and three phonon modes are observed in the present spectral range. The reduced reflectance at high frequency could be due to the scattering from the unpolished surface of the samples. Due to diffuse scattering from the grainy surface of sample I, the spectrum taken against a standard reference mirror was strongly distorted, especially at high frequencies. We observe from Fig. 2 that the reflectance of sample I is quite high both at low and high frequencies. This is because this sample was coated with a thick layer of aluminum film in order to make correction due to the scattering losses.

It is well known that Infrared spectra of amorphous semiconducting material are very similar to those of crystals with the same composition, with the difference that their line width is larger. Since sample I and II are polycrystalline materials, their IR spectra resembles those of semiconducting sample III and the difference in the line width of these samples is obvious i.e. the vibrational mode associated with the untreated sample is very broad as compared to those of sample I and II, as can be seen from Fig. 2.

In order to study the optical parameters of these samples the experimental reflectivity data of fig. 2 was analyzed using Kramer-Kronig routine. First the reflectance $R(\omega) = r^2(\omega)$ is transformed to obtain the phase angle difference $\theta(\omega)$ between the reflected and incident waves.

$$\theta(\omega) = \int_0^{\infty} \frac{\ln R(\omega') d\omega'}{\omega'^2 - \omega^2} \quad (1)$$

The real and imaginary parts of the dielectric functions $\epsilon_1(\omega)$ and $\epsilon_2(\omega)$ are related to the reflectivity $r(\omega)$ and $\theta(\omega)$ through the complex refractive index $(n + i k)$ where :

$$n(\omega) = \frac{1 - r^2}{1 + r^2 - 2r \cos \theta} \quad (2)$$

$$k(\omega) = \frac{2r \cos \theta}{1 + r^2 - 2r \cos \theta} \quad (3)$$

Also the real and imaginary parts of the dielectric functions are related to $n(\omega)$ and $k(\omega)$ as

$$\epsilon_1(\omega) = n^2 - k^2 \quad (4)$$

$$\text{and} \quad \epsilon_2(\omega) = 2nk \quad (5)$$

The optical and dielectric constants are then used to calculate the optical conductivity and the energy loss function.

Fig. 3 represents the real part of the frequency dependent dielectric response functions $\epsilon_1(\omega)$, for all the three samples. We observe that for the superconducting samples $\epsilon_1(\omega)$ is negative at low frequencies. This corresponds to metallic behaviour of the material in the normal state at ambient temperature. As the samples are cooled down below the critical temperature the material transforms from metallic to superconducting states. This observation is confirmed by four probe resistivity measurements. Sample III remains semiconductor at ambient temperature as well as at low temperature. The values of static and high frequency dielectric constant measured by extrapolating to lower and higher frequencies are in agreement with those published in literature [6] measured by A.C bridge method.

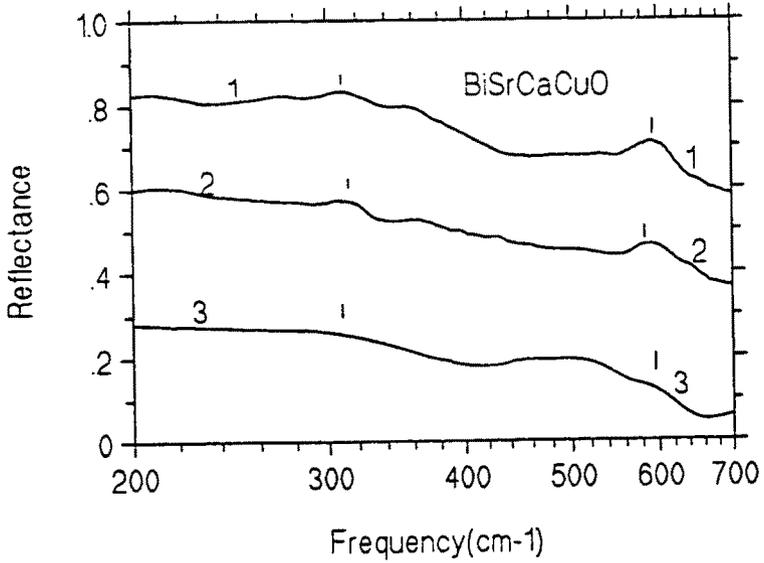


Figure 2 (b) : Phonon vibration in IR reflectance spectra of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ in three different states.

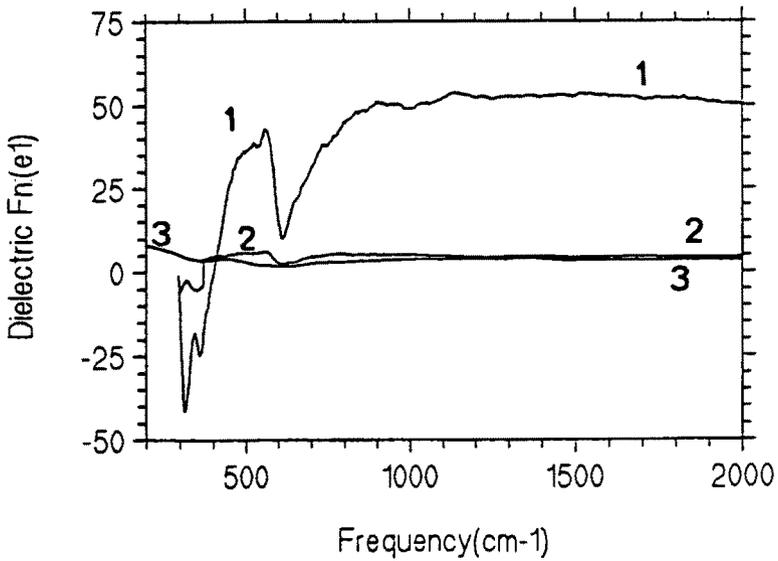


Figure 3 : The frequency dependent real part of dielectric function for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$.

The characteristics of phonon bands in $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ observed in these measurements, are similar to those studied by neutron scattering [8], electron energy loss spectroscopy [10] and tunneling [11].

TABLE 1

Vibrational modes and T_c of $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ compound

Sample No.	Material $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$	T_c K°	Phonons cm^{-1}			
I	Treated Ceramic for 240 hours	85 K	311	358	595	-
II	Treated Glass Ceramic for 240 hours	80 K	311	358	586	-
III	Untreated Powder	-	310	480	585	1450

From IR measurements i.e. from Fig. 2 (a) and Fig. 2 (b), we observe 3 phonon modes in our measured frequency range. The calculations and assignment of vibrational frequencies for $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ are reported in ref. [12-14]. Seven IR active phonon modes are predicted. We observed only three because of the low frequency limitation of our spectrometer. The observed phonon modes are summarized in table 1. The vibrational modes of non-superconducting samples around 310, 480 and 585 cm^{-1} are due to the individual constituents of the $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ compound, where as the mode around 1450 cm^{-1} is due to undecomposed CaCO_3 and SrCa_3 present in the untreated powder sample. After heat treatment the SrCO_3 and CaCO_3 decomposes completely and hence we do not see any mode around 1500 cm^{-1} in the superconducting samples. Following the assignments of ref. [13], the vibrational band around 595 cm^{-1} is assigned to CuO sliding mode. The sliding mode of CuO plane couples with the motion of free carriers and gains anomalously large intensity. Hence the vibrational mode around 595 cm^{-1} which is due to CuO plane has a higher intensity as compared to other

modes as shown in fig. 2 (a) and 2 (b). The phonon mode around 595 cm^{-1} present in sample I shifts to lower frequency in sample II. This indicates that there is a change in CuO_2 layer arising from the various techniques employed in the preparation of the samples [15-16]. The CuO plane plays a major role in the electronic structure of the cuprate superconductor. In $\text{Bi}_2\text{Sr}_2\text{Ca}_1\text{Cu}_2\text{O}_8$ system the transition temperature T_c increases with the number of CuO layers [17-18]. Since CuO_2 planes are responsible for the critical temperature in these materials any change in energy of these modes, as observed in the IR spectra, will bring in a change in their critical temperature. This was confirmed by four probe measurements.

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