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Kramers–Kronig analysis of the reflectance spectra of Pb-doped Bi-4334 type glass and the corresponding glass-ceramic superconductor

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Abstract. The room temperature reflectance spectra in UV–VIS–NIR region (energy range of 0·6 to 6·2 eV) for glassy, partially crystalline and its fully crystalline superconducting ceramic phases of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ have been studied by Kramers–Kronig (KK) analysis. A comparative study of the energy loss function $[-\mathrm{Im}(1/\varepsilon)]$ and the absorption coefficient $[\alpha(E)]$ has been done. Excitons in the superconducting phase hitherto evidenced by the authors are located in the polarizable layers of the superconducting cuprate and their implications for superconductivity have been pointed out. An estimate of the optical band gap energy (E_g) has also been made from the linear fit of α^2 vs. E curve for the superconducting phase. Jezierski's method of R-extrapolations in the higher energy has been used to show that both methods yield results that agree quantitatively and can be relied upon.

Keywords. Optical reflectivity; superconductivity; exciton.

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The glassy precursors for high T_c superconductors like $Bi_{4-n}Pb_nSr_3Ca_3Cu_4O_x$ ($n = 0\cdot1$–$1\cdot0$) are important for its possible applications in making superconducting wires/tapes, thick films etc. [1–5a]. These precursor glasses also show some interesting electric and dielectric properties [2], not exhibited in other transition metal oxide glasses which do not become superconducting in their respective crystalline (ceramic) phases. Thus the study of optical properties of these glasses and the corresponding superconducting glass-ceramics appears to be interesting. To the best of our knowledge, no such comparative analysis of the reflectance spectra of the glassy precursors and the corresponding superconducting glass-ceramic has been done so far.

In the present paper we report, for the first time, results of Kramers–Kronig (KK) analysis of the room temperature reflectivity spectra (in the photon energy range 0·6–6·2 eV) of the as-quenched glassy phase and the corresponding partially and fully crystalline phases of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$. Optical parameters like the energy loss function $[-\mathrm{Im}\{1/\varepsilon(E)\}]$ and the absorption coefficient $\alpha(E)$ have been calculated for all the three phases. In our previous communication [6] we have discussed the results of KK analysis of the superconducting phase only where we have shown evidences of the existence of Wannier excitons in Bi-based superconducting cuprates. In this brief report, apart from a comparative analysis of the three subsequent phases of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$, we have discussed the mode of excitonic absorption and

the corresponding energy band gap. We have also tried to locate possible positions of the exciton peaks and discuss their role in bringing about superconductivity in these layered cuprates. At the end, we have briefly discussed the different aspects regarding the choice of high energy ($E \geqslant 6{\cdot}2$ eV) extrapolating functions used by other researchers, needed to carry out the KK analysis. This is important because the artificial R-extrapolation never gives the exact value of the phase (θ) which agree with the experimental reflectance curve and so there is always an experimental error in the values of optical constants in the experimental range calculated by the KK analysis.

The preparation technique of the Pb doped Bi–Sr–Ca–Cu–O glasses and the corresponding glass-ceramic have been discussed in detail elsewhere [7]. The glassy and the partially-crystalline phases of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ are semiconducting whereas the glass-ceramic phase (having mostly 2212 phase) is superconducting with $T_{co} \sim 72$ K [7]. The reflectivity measurements have been performed on the Pb doped Bi–Sr–Ca–Cu–O systems for all its three subsequent phases discussed above, separately, with a UV–VIS–NIR spectrophotometer (Hitachi U3410) in the spectral range of 200–2200 nm at 297 K and at normal incidence.

The basic principles involved to carry out KK analysis and its fruitful application to extract different optical parameters of a physical system have been discussed in detail in our previous communication [6]. It is seen that the low energy ($E \leqslant 0{\cdot}6$ eV) extrapolation function used by us has been consistent with reproducible data for different high T_c superconducting oxides. But in the higher energy range ($E \geqslant 6{\cdot}2$ eV) several approaches like Philipp–Taft formula [8] or Jezierski formula [9] or Roessler formula [10] have been used. We feel that as there are more than one method for high energy extrapolation it needs an examination as to how well they can be relied upon to yield comparable data. We approach the problem in the following way:

According to Philipp–Taft formula one has, $R(E) = R(E_b)(E_b/E)^A$ where, E_b is the upper limit of the energy range used and A is a constant where the continuity condition for $R(E)$ at $E = E_b$ is included explicitly. Jezierski used the following formula for $R(E)$ viz.

$$R(E) = R(E_b)(E_b/E)^{\gamma} \quad \text{for} \quad E \geqslant E_b, \tag{1}$$

where, $\gamma = [A_1(E_b/E)^{B_1} + A_2(E_b/E)^{B_2} + 4]$. The values of B_1 and B_2 are chosen arbitrarily from the consistency conditions and A_1, A_2 are determined from a set of equations. We have applied this formula to evaluate $\alpha(E)$ for the superconducting phase with typical values of $B_1 = 0{\cdot}5$ and $B_2 = 10$ following the arguments of Jezierski. The values A_1 and A_2 are then obtained by fitting (1) to the data points in the range of 5–6·2 eV by the least squares method and then refining these values of A_1 and A_2 by the parameter search programme.

Figures 1a–c describes the behaviour of the measured reflectance $R(E)$ for the respective three phases of the Pb doped Bi–Sr–Ca–Cu–O system. The reflectance spectra for the superconducting $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ having predominant Bi-2212 character resembles that obtained by Terasaki *et al* [11] for single crystal of Bi–Sr–Ca–Cu–O (2212 phase). The bands around 1·8 eV have been identified as due to Cu–O charge transfer excitations [6]. Furthermore, from figures 1a–c one observes that for

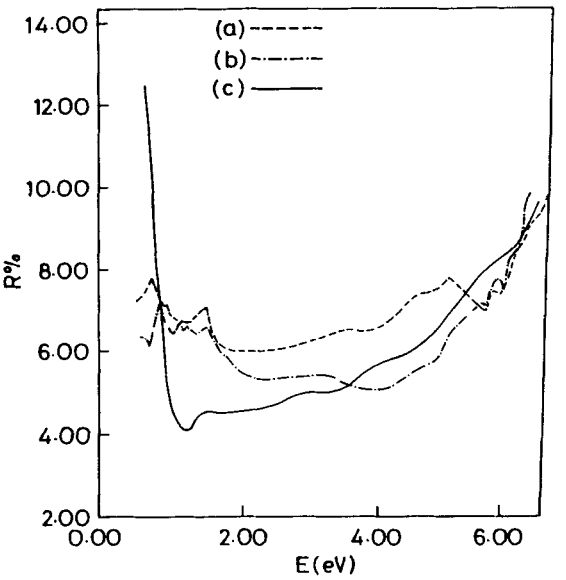

Figure 1. Optical reflectance ($R\%$) vs. photon energy (E) in the range of 0·6–6·2 eV for (**a**) glassy, (**b**) partially crystalline and (**c**) the ceramic superconducting phase of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$, (c) is from ref. [6].

$E \geqslant 4$ eV, all the three phases of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ have comparable reflectances, in contrast to their behaviour at lower energies where the superconducting sample only shows a strong decrease in reflectivity between 0·6 and 1·0 eV, followed by a minimum. This indicates that some sort of absorption process is taking place in the NIR range ($E \sim 1$ eV) only in the superconducting phase of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$.

Figure 2 (inset) shows the plot of $-\mathrm{Im}\{1/\varepsilon(E)\}$ vs. E for the superconducting glass-ceramic phase of the present Pb doped Bi-system showing a sharp "plasmon" peak in the lower energy region ($\sim 1\cdot0$ eV) which could be assigned to the excitations from O–2p to Cu–3d (upper Hubbard) state [6]. Furthermore, it is interesting to note that the plasmon-minimum (which is believed to be characteristic for a-b response of high T_c superconductors) is clearly present in the reflectivity spectrum (figure 1) of the superconducting phase only, as expected [i.e. around 1 eV]. Figure 2 (inset) also apparently suggests that among the various layers (Cu–O, Bi–O, Sr–O, etc.) gradually formed in the fully crystalline superconducting phase of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$, not all of them have any direct contribution to superconductivity. Otherwise absorption would not have been that weak below 5 eV, indicating that only the carriers of the conducting CuO_2 layers participate in such low energy excitations. Rao [12] had studied in detail the structure of Bi-based superconducting cuprates which has established that Bi–O and Sr–O layers possibly have no direct correspondence to superconductivity in Bi-based compounds. Then those layers just behave like dielectric (polarizable) layers having the properties of an insulator.

Strikingly, the energy loss functions ($-\mathrm{Im}\{1/\varepsilon(E)\}$) for the semiconducting glassy and partially annealed Pb doped Bi–Sr–Ca–Cu–O systems have exhibited a negligible

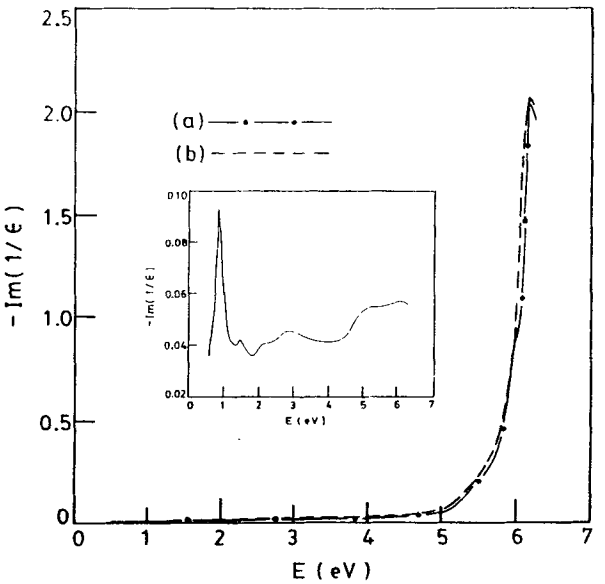

Figure 2. Plot of loss function $[-\mathrm{Im}\{1/\varepsilon(E)\}]$ vs. E for (**a**) semiconducting glassy phase and (**b**) partially crystalline phase of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$. Inset: Plot of loss-function $[-\mathrm{Im}\{1/\varepsilon(E)\}]$ vs. E for the superconducting ceramic phase of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ (from ref. [6]). The sharp peak around 1.0 eV is likely due to excitations of O–2p to Cu–3d states.

loss for a wide range of energy ($\sim$0·6–4·5 eV) and no plasmon peak has been observed in the low energy range (figure 2). This may be attributed to the fact that in the semiconducting glassy or partially crystalline phases of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ the charge carriers are in localized states [7] and hence enough free carriers are not available to give rise to plasma oscillation. Here one must note that the normal state behavior of the superconducting phase of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ is metal-like with a larger number of free carriers.

Figure 3a–c shows the variation of the absorption coefficient (α) with photon energy for the three phases of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$. It is important to note that both the glassy and partially crystalline phases have an absorption tail common to other amorphous or quasi-crystalline semiconductors, whereas the ceramic superconducting phase has pronounced peaks around 1·5 eV and it was proposed that the peaks correspond to an excitonic absorption [6]. In this context it will be relevant to mention that if one looks at the plot of α vs. E for CuO, one of the basis ingredients in all high T_c cuprates, one observes presence of absorption peaks at 1·0, 1·3 and 1·5 eV which could be associated with Wannier excitons formed between the holes at O site and the electrons at Cu site. Now recalling the fact that our system being a layered cuprate superconductor in the glass-ceramic phase, one might expect excitons, if they are formed, will be of Cu–O type.

Now the question is, if at all excitons are there, where they can be? The answer lies in the fact that the present system in its glass-ceramic phase is predominantly a Bi-2212 layered cuprate superconductor and transport measurement on single crystal

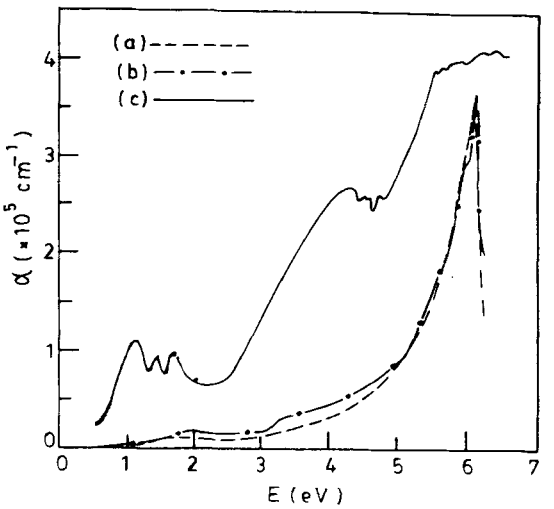

Figure 3. Variation of absorption coefficient $\alpha(E)$ with E for (**a**) glassy phase, (**b**) partially crystalline phase and (**c**) superconducting ceramic phase of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$.

of Bi-2212 has revealed high anisotropy of resistivity between the directions parallel and perpendicular to the c-axis indicating presence of both dielectric and metallic layers [13]. Thus it is plausible that those dielectric layers may sustain excitons and free carriers in the metallic layers are responsible for conductivity. In this context it is worthwhile to mention that Ghosh *et al* [14] have shown the existence of excitons at room temperature in the dielectric (polarizable) layers of a polycrystalline $YBa_2Cu_3O_x$ superconductor from a similar point of view. It is also quite obvious that the main difference in the spectra of the superconducting $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ and its non-superconducting glassy and partially crystalline phases is the presence of exciton bands around 1·5 eV in the former compound and is almost absent in the latter two. The cause may be speculated by considering that for amorphous/quasi-crystalline materials, the presence of a large number of carriers in the localized states would screen the formation of a sufficient number of hole-electron pairs or excitons so that the probability of excitonic interaction will be largely reduced. However, it may be argued that CuO displays the same exciton band structure but is not superconducting. CuO is an insulator and there are not enough carriers to be paired. Recent reflectance and transmittance studies [15] have also not revealed any excitonic absorption. There should not only be enough carriers to be paired but the system should sustain excitons if the latter should play any part in bringing about superconductivity or an enhancement of transition temperature. Gradual annealing of the as-quenched glassy precursors to a fully crystalline superconducting system, increases the conductivity [7] so that the glass-ceramic phase of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ is metal-like. However, elaborate investigations by other methods are necessary before coming to a definite conclusion about the presence of an exciton and its consequences in Bi-based superconductors.

An estimate of the value of optical band gap (E_g) for the superconducting phase of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ can also be made from the spectral analysis. It is well known

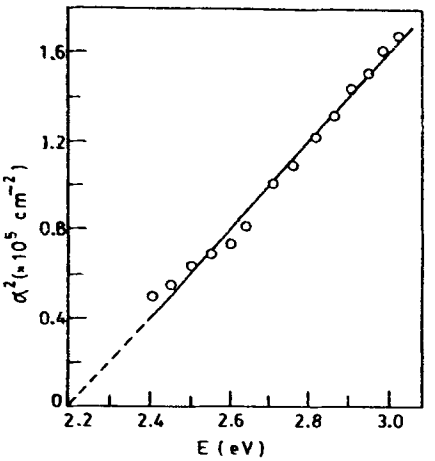

Figure 4. Plot of α^2 vs. E for the ceramic phase of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$. A good linear fit indicates that the allowed transition is direct.

that if valence band and conduction band extrema are located at $k = 0$ and the bands are parabolic in the region, then for direct allowed transition, $\alpha(E) \propto (E - E_g)^{1/2}$ and for indirect allowed transition, $\alpha(E) \propto (E - E_g)^2$ where $E = \hbar w$. For the superconducting phase one finds that the plot of $[\alpha(E)]^2$ vs. E (figure 4) is a better linear fit than that of $[\alpha(E)]^{1/2}$ vs. E. This indicates that the allowed transition is direct and E_g is found to be 2·20 eV. Both of these findings agree well with the results of similar observation made by other researchers [13, 16] for different high T_c cuprates.

As further check on our results we have calculated the effective number of carriers, $N_{eff}(E)$ for the superconducting phase using the relation

$$N_{eff}(E) = (m/2\pi^2e^2)\int_0^E E' \mathrm{Im}[\varepsilon(E')]\mathrm{d}E', \tag{2}$$

which is found to be nearly 7 up to 6 eV. This agrees well with that obtained by Nucker *et al* [17] for Bi-2212 superconducting system.

Finally we discuss the use of R-extrapolation at higher energy as mentioned earlier. Figures 5a and 5b respectively show the plots of absorption spectra with incident photon energy in the range 0·6–6·2 eV for the superconducting sample only (as a typical example) using the method as discussed earlier and the method of Jezierski [9] for high energy extrapolation. These two plots indicate that even in the absence of additional information such realistic extrapolation formulae yield results which agree with each other and can be relied upon.

In conclusion, we note that the reflectance spectra for the as-quenched semiconducting glassy and the partially crystalline phases of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ are distinct from its corresponding completely crystalline superconducting phase in the range close to 0·6 eV. Superconducting phase exhibits a plasmon peak at around 1·0 eV which is caused by the excitation of charge carriers of O–2p and Cu–3d states. Interestingly no such plasmon peak is observed for the glassy and partially annealed phases of

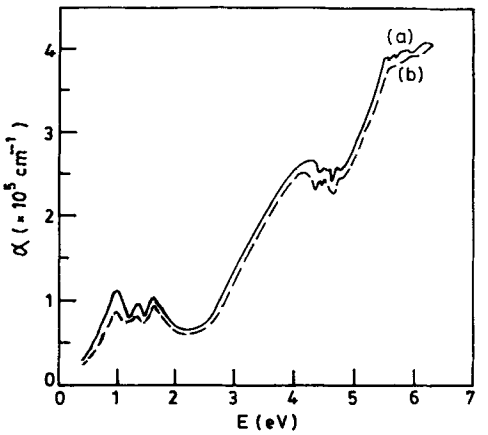

Figure 5. Plot of α vs. E for the superconducting $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ by (**a**) our method discussed above and (**b**) by the method of Jezierski.

$Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$. The cause of the appearance of absorption peaks at around $E \sim 1{\cdot}5$ eV in superconducting $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ has been discussed in the light of a possible excitonic absorption with excitons being sustained by the insulating layers of the present Bi-based superconducting glass-ceramic. However, thorough investigation of the structure of the DOS near Fermi surface would be necessary to ascertain our speculation as to why the formation of excitons is apparently not favoured in the glassy and partially crystalline phases of $Bi_{3\cdot9}Pb_{0\cdot1}Sr_3Ca_3Cu_4O_x$ as seen from our experimental results. Nevertheless, the present investigation reasonably suggests that superconductivity in layered cuprates might be brought about when excitons in the polarizable layers and carriers in the conducting layers are both present in sufficient numbers. We have also discussed the applicability of the Jezierski method of R-extrapolation formulae in the higher energy range which can be successfully adopted to perform KK analysis.

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