

# The effect of oxygen and lead doping on electrical and optical properties of high $T_c$ $\text{GdBa}_2(\text{Cu}_{1-x}\text{Pb}_x)_3\text{O}_\delta$ compound superconductors

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A systematic study of the electrical and infrared properties of the high critical temperature,  $T_c$ , compound superconductor  $\text{GdBa}_2(\text{Cu}_{1-x}\text{Pb}_x)_3\text{O}_\delta$  has been performed. Resistivity and a.c. susceptibility measurements show a significant drop in  $T_c$  when copper is replaced by lead in the range  $0.005 \leq x \leq 0.025$ . Infrared measurements show that the conductivity of the compound increases with the increase in lead concentration. For undoped samples, all the Restrahlen vibrations, common to these materials, are present in the infrared reflectance spectra. As the concentration of lead is increased, a shift of the phonon modes, as well as broadening of the  $150 \text{ cm}^{-1}$  phonon mode, is observed. Also the Restrahlen vibration around  $410 \text{ cm}^{-1}$  present in the normal material starts to disappear. This  $150$  mode is attributed to a change in the oxygen concentration, and is shown to be correlated with the critical temperature.

## 1. Introduction

It is established that the  $T_c$  of YBCUO is not significantly varied on replacing Y by other rare earth ions [1–5]. In the present day study of high  $T_c$  superconductors, a fact accepted by major theoretical models is that the Cu–O planes and Cu–O chains are crucial for superconductivity in HTSC 123 compounds. Any change in the Cu–O planes or chains caused either by changes in the oxygen contents or by the partial substitution of Cu by any magnetic or non-magnetic ions, is expected to bring major changes in the properties of the high  $T_c$  superconductors [6, 7]. In the case of HTSC copper oxides, mixed valency ( $\text{Cu}^{2+/3+}$ ) is created within the compound by charge transfer (hole transfer) from Cu–O chains in Y-123 and Bi–O and Tl–O layers in Bi and Tl cuprates (the so called “hole reservoirs”). Whenever this charge transfer process is suppressed, as for example reducing the oxygen content by Cu–O chains in Y-123, or by substitutions Ca by Y in Bi/Tl-2212,  $T_c$  is reduced drastically and the substance changes from a metallic to insulating or semiconducting state [8, 9]. The mechanism responsible for high temperature superconductivity in Cu–O based systems has still remained an open question. It is understood that the oxidation state of copper plays an important role in determining the nature of superconductivity [10]. The charge distribution in the structure could be disbalanced by imbalancing the conducting Cu–O planes. Recently, various magnetic ions, such as Fe, Co and Ni, have been substituted in place of Cu in YBCUO compounds [10]. A rapid drop in  $T_c$  was observed on increasing the concentra-

tion of the above ions in the compound. Some of the substitutions, such as Fe in YBCUO, have revealed that the structure of the compound also changes from orthorhombic to tetragonal [11].

It is believed that the substitution of a mixed valance element on the copper site may induce valance transition, thereby modifying the band structure and the overall structure of the material.

In this paper an investigation of the infrared spectroscopy, as well as the electrical properties, of  $\text{GdBa}_2(\text{Cu}_{1-x}\text{Pb}_x)_3\text{O}_\delta$  ceramic superconductors is reported. The effect of non-magnetic ions of mixed valent PbO on these properties has been systematically studied. Compositional as well as oxygen concentration induced changes in critical temperature, a.c. susceptibility and infrared properties of these compounds will be presented and discussed.

## 2. Experimental procedure

Powder of appropriate amounts of  $\text{Gd}_2\text{O}_3$ ,  $\text{BaCO}_3$ , CuO and PbO were grounded mechanically to obtain high homogeneity. Oxides with a nominal metal ion composition  $\text{GdBa}_2(\text{Cu}_{1-x}\text{Pb}_x)_3\text{O}_\delta$ , with  $x = 0.005$  and  $0.025$ , were prepared as follows.

After extended manual grinding of a 5 g mixture of each sample, the stoichiometric mixtures were heated for 20 h at a temperature of  $920^\circ\text{C}$ , the synthesized cuprates were pressed into pellets of 1 cm diameter and 2 mm thickness. The pellets were heated at a rate of  $2^\circ\text{C min}^{-1}$  to  $920^\circ\text{C}$  under flowing oxygen at the rate of  $100 \text{ cm}^3 \text{ min}^{-1}$ . After annealing for 30 h at the

above temperature, the samples were cooled to 600 °C under the oxygen flow. At this temperature, the samples were held for 10 h in the continuous oxygen flow and then cooled down to room temperature at the rate of 1 °C min<sup>-1</sup>. The weight changed due to the evolution of CO<sub>2</sub>, indicating that the oxygen concentration in pure sample reaches closer to 6.90, whereas in the doped samples it was 6.76 and 6.68, respectively.

The oxygen stoichiometries were estimated from systematic weighing at every stage of heating and grinding treatment. However, accuracy is not better than ±0.1, since it is obtained from several weight differences; also the dryness of reactants could not be controlled carefully. All the values were calculated from the weight change under the assumption of completed CO<sub>2</sub> evolution. This assumption is based on the infrared reflectance measurements; no carbonate related features were seen in the reflectance spectra of these compounds. Previously, such features have been observed in 123 HTSC superconductors, indicating that carbonate was not decomposed completely [12].

Electrical resistivity measurements were performed using four probe technique. The a.c. susceptibility measurements were performed in the temperature range 20–300 K using a Quantum cryostat and lock-in amplifier equipped with an internal oscillator, which was set to 20 KHz, with a sensitivity of 100 mV, and a voltage amplitude of 0.7 V.

The infrared reflectance measurements were performed at near normal incidence using two different ranges. The ultra violet (u.v.) visible and near infrared measurements were performed with a Cary 2300 spectrophotometer. The far infrared and mid infrared measurements were performed, using a Bruker Fourier transform interferometer.

### 3. Results and discussion

#### 3.1. Electrical measurements

Measurements in the normal state show small changes in resistivity and a.c. susceptibility for the present range of doping, i.e. 0.005 ≤ *x* ≤ 0.025. However, in the superconducting state, as can be seen from the graph of resistance versus temperature shown in Fig. 1, it is clear that the resistance of the undoped samples falls sharply to zero at a transition temperature of 86 K. For another two samples, when Cu is substituted by lead, the transition becomes larger and *T<sub>c</sub>* is reduced to a lower value than that of the pure sample. Table I displays the compositional dependence of the critical temperature for GdBa<sub>2</sub>(Cu<sub>1-x</sub>Pb<sub>x</sub>)<sub>3</sub>O<sub>7</sub>.

The temperature dependence study of the a.c. susceptibility allows one to estimate *T<sub>c</sub>*, as well as the superconducting volume of the high *T<sub>c</sub>* ceramic superconductors. Measurements of a.c. susceptibility are limited to one field for powdered samples; this is because the contacts between the grains in the case of powder are very poor, and hence the observed diamagnetic shielding is mainly due to bulk intragrain superconductivity and is less dependent on the small changes in the applied field. In the normal state the change in susceptibility is small, whereas in the case of

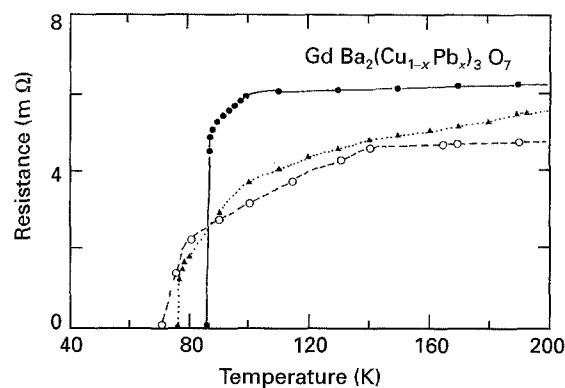


Figure 1 Resistance as a function of temperature for the GdBa<sub>2</sub>(Cu<sub>1-x</sub>Pb<sub>x</sub>)<sub>3</sub>O<sub>7</sub> system. For *x* equals: (●) 0.00, (▲) 0.005 and (○) 0.025.

TABLE I Compositional dependence, *X*, of *T<sub>c</sub>* in GdBa<sub>2</sub>-(Cu<sub>1-x</sub>Pb<sub>x</sub>)<sub>3</sub>O<sub>7</sub>

<i>X</i>	0.00	0.005	0.025
<i>T<sub>c</sub></i> four probe, K	86.0	76.0	71.0
A.c. susceptibility, K	86.5	76.5	71.0

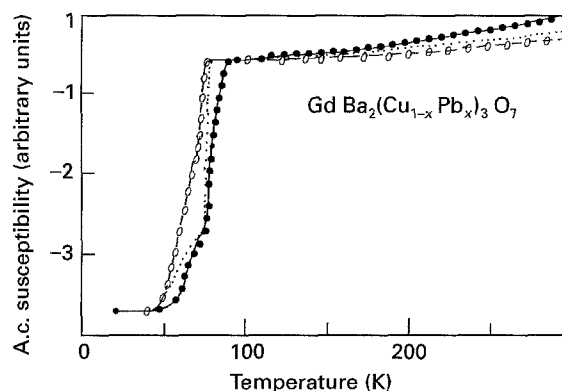


Figure 2 Temperature dependence of a.c. susceptibility of the GdBa<sub>2</sub>(Cu<sub>1-x</sub>Pb<sub>x</sub>)<sub>3</sub>O<sub>7</sub> system. For *x* equals: (●) 0.00, (○) 0.005 and (□) 0.025.

the superconducting state all three samples show a temperature dependence as shown in Fig. 2. These measurements confirm the value of *T<sub>c</sub>* obtained using the four probe technique.

Introduction of mixed valent lead in place of Cu is expected to create charge imbalance which may modify the Cu<sup>3+</sup>/Cu<sup>2+</sup> ratio, since Cu<sup>3+</sup> has a larger paramagnetic moment than Cu<sup>2+</sup> [13]. Susceptibility measurements were carried out in the temperature range 300–20 K. There is a small decrease in normal state susceptibility above 100 K for the doped sample as compared to the parent material. Moreover, susceptibility acquires a moderate temperature dependence and can be fitted to a Curie–Weiss term and temperature independent term. Decrease in the Curie constant on lead substitution indicates a decrease in the paramagnetic moment, which indicates a corresponding decrease in the Cu<sup>3+</sup>/Cu<sup>2+</sup> ratio. Since *T<sub>c</sub>* is very sensitive to this ratio, reduction in the ratio could be responsible for the reduced *T<sub>c</sub>* in the doped samples.

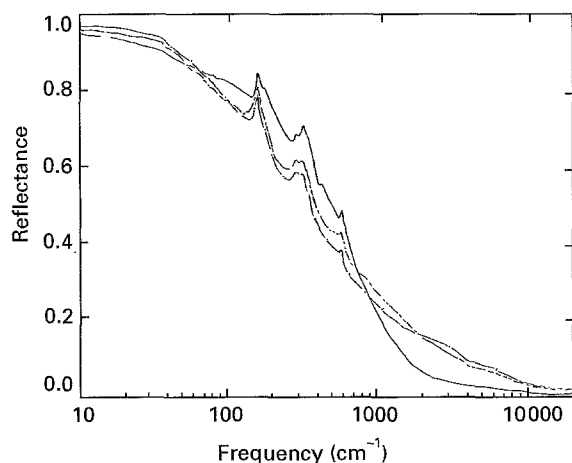


Figure 3 Infrared reflectance spectra of  $\text{GdBa}_2(\text{Cu}_{1-x}\text{Pb}_x)_3\text{O}_\delta$  ceramic superconductors. (—)  $\text{GdBa}_2\text{Cu}_3\text{O}_7$ , (---)  $\text{GdBa}_2(\text{Cu}_{1-x}\text{Pb}_x)_3\text{O}_7$  ( $x = 0.005$ ), (-·-·)  $\text{GdBa}_2(\text{Cu}_{1-x}\text{Pb}_x)_3\text{O}_7$  ( $x = 0.025$ ).

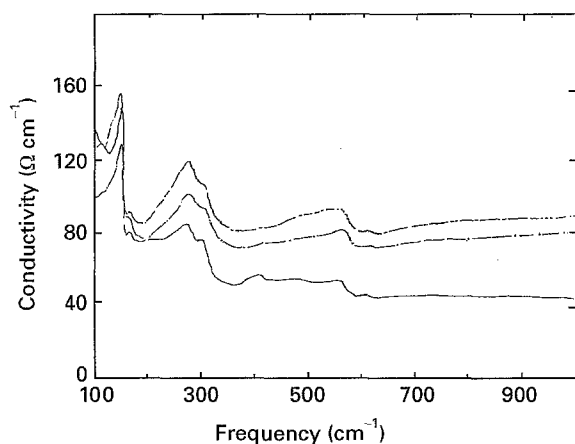


Figure 4 Frequency dependent conductivity of  $\text{GdBa}_2(\text{Cu}_{1-x}\text{Pb}_x)_3\text{O}_\delta$  ceramic superconductors: (—)  $\text{GdBa}_2\text{Cu}_3\text{O}_7$ , (---)  $\text{GdBa}_2(\text{Cu}_{1-x}\text{Pb}_x)_3\text{O}_7$  ( $x = 0.005$ ), (-·-·)  $\text{GdBa}_2(\text{Cu}_{1-x}\text{Pb}_x)_3\text{O}_7$  ( $x = 0.025$ ).

### 3.2. Infrared measurements

The infrared reflectance spectra of  $\text{GdBa}_2(\text{Cu}_{1-x}\text{Pb}_x)_3\text{O}_\delta$  in the normal state measured at ambient temperatures are shown in Fig. 3. Above  $1000\text{ cm}^{-1}$  the reflectance of doped samples is large as compared to the pure sample, and decreases smoothly with increasing frequency. While much can be learned from direct observation of the reflectance spectra, it is customary to study a more fundamental quantity, like conductivity,  $\sigma(\omega)$ , from which one can analyse the infrared response of oxide superconductors. To obtain the conductivity, a Kramer–Kronig relation was applied to the reflectance data of Fig. 3. Fig. 4 shows the real part of the frequency dependent conductivity spectra for the three samples.

The factor group analysis of high  $T_c$  superconductor  $\text{YB}_2\text{Cu}_3\text{O}_7$  predicts 21 infrared phonons in these materials, i.e.  $7\text{B}1\text{u} + 7\text{B}2\text{u} + 7\text{B}3\text{u}$ . In the present study only seven phonons were observed parallel to the  $c$ -axis. This is believed to be a result of highly anisotropic conductivity in this material; out of 21 modes, only seven modes ( $7\text{B}1\text{u}$ ) are observed. These

are the ones having dipoles oscillating parallel to the  $c$ -axis [14–18]. These modes are less effectively screened than those of  $(7\text{B}2\text{u} + 7\text{B}3\text{u})$  polarized in the high conductivity  $a$ – $b$  plane, which prevents phonon modes polarized along the  $a$  and  $b$  crystal axes from interacting with the infrared electric field.

It has also been observed that when the oxygen concentration in the  $\text{YB}_2\text{Cu}_3\text{O}_\delta$  compound varies from six to some higher value, the mode around  $150\text{ cm}^{-1}$  becomes narrow. The minimum width of the  $150\text{ cm}^{-1}$  mode is obtained when the oxygen concentration reaches seven, and at this concentration the  $T_c$  of YBCUO is maximum. It is also true that reduction in the oxygen concentration due to doping at the Cu site will broaden the  $150\text{ cm}^{-1}$ , and  $T_c$  will reduce.

The mode around  $150\text{ cm}^{-1}$  is due to Cu–O chains, as confirmed by neutron scattering measurements [19]; also the  $150\text{ cm}^{-1}$  mode is due to O(1)–Cu(1)–O(1) translation along the  $c$ -axis [20]. On doping, a change in mode strength and shift in frequency takes place for the  $150\text{ cm}^{-1}$  mode, which indicates that Pb goes to the Cu(1) site.

For a well ordered  $\text{YBa}_2\text{Cu}_3\text{O}_7$  compound the Cu–O chain is very long. Hence, a fairly uniform narrow distribution takes place in the vibrational frequency. In the present case, on doping the sample with Pb at the Cu(1) site, it appears that the oxygen concentration of the doped samples is reduced as estimated in Section 3.1. This results in a redistribution of the Cu–O chain, which in turn causes a redistribution in the vibrational frequency, and hence a dispersion in the phonon mode.

Comparing the infrared absorption band for all three samples in Fig. 4, one observes that the mode around  $150\text{ cm}^{-1}$ , which has the highest oscillator strength in the infrared conductivity spectrum, arises from the systematic Cu–O vibration [14]. On doping, the mode becomes broader and shifts slightly to a lower frequency, the shift in the frequencies for  $150\text{ cm}^{-1}$  and all other modes is listed in Table II. A dielectric response function equation [21, 22] was used to estimate the oscillator strength, the centre frequencies and the damping of these samples. It was found, on doping, that the oscillator strength of the  $150\text{ cm}^{-1}$  mode of the parent sample reduces from 5.36 to 5.00, indicating that the mode strength is reduced. The shift in the centre frequencies as calculated by the dielectric model is almost the same as listed in Table II. The broadening and shifting of this mode could be due to alteration of the oxygen constant from seven to lower values, as discussed in Section 3.1. This observation is supported by the decrease in  $T_c$  for doped samples.

It has been shown [20] that the orthorhombic lattice of  $\text{YBa}_2\text{Cu}_3\text{O}_7$  exhibits two well resolved modes near  $300\text{ cm}^{-1}$ . A similar pattern is observed in the conductivity spectra of the present samples. The doublet around  $300\text{ cm}^{-1}$ , which is due to the Cu–O plane bending mode, is also affected by lead substitution. The shift of the doublet at 274 and  $300\text{ cm}^{-1}$  could be induced by changes in the ionic radius caused by lead substitution, which influences Cu–O in-plane

TABLE II Compositional dependence of the phonon centre frequencies,  $\nu_j$ , measured from conductivity spectra obtained by Kramer–Kronig analysis

GdBa <sub>2</sub> Cu <sub>3</sub> O <sub>7</sub> $\nu_j$ (cm <sup>-1</sup> )	GdBa <sub>2</sub> (Cu <sub>0.995</sub> Pb <sub>0.005</sub> ) <sub>3</sub> O <sub>7</sub> $\nu_j$ (cm <sup>-1</sup> )	GdBa <sub>2</sub> (Cu <sub>0.975</sub> Pb <sub>0.025</sub> ) <sub>3</sub> O <sub>7</sub> $\nu_j$ (cm <sup>-1</sup> )
1	150.00	148.50
2	182.26	182.75
3	273.39	275.29
4	300.40	300.40
5	409.37	412.74
6	555.47	557.00
7	611.40	611.40

vibrations. The phonon mode around 410 cm<sup>-1</sup>, which is ascribed to the Cu–O bending mode [19], is highly affected by doping. As the concentration of lead increases, the strength of the mode decreases gradually. This indicates that Pb penetrates in the Cu–O planes and chains and decreases electron phonon interaction, thereby decreasing the superconductivity of the sample. All observed phonons and their compositional dependencies are listed in Table II. The phonon centre frequencies for all the phonon modes for the pure sample agrees with those published in the literature.

#### 4. Conclusions

From these measurements one can conclude that

1. When mixed valent Pb is substituted for Cu in 123 compound the  $T_c$  of the compound is reduced. The drop in  $T_c$  is attributed to the change in Cu<sup>3+</sup>/Cu<sup>2+</sup> ratio, and also due to the reduction in oxygen concentration, which is indicated by broadening of the 150 cm<sup>-1</sup> mode on doping.

2. The infrared spectra of the pure and doped samples exhibit all the allowed phonon, having dipoles oscillating parallel to the *c*-axis, in these types of material. These observations indicate that the structures of all the samples do not change within the present level of doping.

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Received 2 February  
and accepted 11 May 1995