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The mechanical and structural properties of $Y_1Ba_2Cu_3O_{7-x}$ superconductors

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Mechanical losses spectroscopy of two superconducting $Y_1Ba_2Cu_3O_{7-x}$ samples ($T_c = 93$ K) measured at 5, 10, 20 and 30 MHz revealed four peaks. As the frequency of measurement was increased, the peaks shifted to higher temperatures. The relaxation process was found to have an activation enthalpy of 0.188, 0.092, 0.209 and 0.314 eV with an attempt frequency, f_0, equal to 2.46×10^{15}, 5.95×10^{10}, 1.64×10^{14}, and 7.82×10^{13} Hz for P_1, P_2, P_3 and P_4 peaks, respectively. The mechanism responsible for these relaxation peaks is discussed. The infrared spectra of some of these compounds provide evidence for oxygen rearrangement on going from tetragonal to orthorhombic phase. X-ray diffraction analysis shows that these compounds correspond to a single phase which is an orthorhombic perovskite structure.

1. Introduction

There has been a tremendous interest in the field of superconductivity in oxide systems ever since superconductivity in the 30 K range in a multiphase oxide system, La–Ba–Cu–O, was reported by Bednorz and Muller [1]. The electronic structures of these materials are extremely sensitive to oxygen concentration [2] and there is evidence that, for a given oxygen concentration, the distribution of oxygen atoms over available sets of sites in the structure may be important [3]. Neutron diffraction experiments [4] have shown that superconducting $Y_1Ba_2Cu_3O_7$ has an oxygen-deficient orthorhombic perovskite structure, and that as a sample is heated it progressively loses oxygen atoms from sites on the Cu–O chains parallel to the *b*-axis, while those oxygen atoms remaining on these sites experience increasing thermal disorder perpendicular to the Cu–O bond.

Mechanical loss studies in $YBa_2Cu_3O_7$ using different frequencies were carried out by many researchers using different frequencies [5–8]. More experiments are needed using the same sample measured at different frequencies to understand the mechanism responsible for the superconductivity, in particular, peaks at a temperature near the T_c. In order to gain further information about these superconducting oxide systems, we have studied their structural, superconducting and spectroscopic properties, as well as the mechanical and elastic properties which include the velocity of sound, V_l, in the temperature range from 77–300 K using very high ultrasonic frequencies, i.e. 10–30 MHz.

2. Experimental procedure

The $Y_1Ba_2Cu_3O_7$ samples used in this study were prepared by the standard solid-state reaction in the form of pressed ceramic pellets. Room-temperature powder X-ray diffraction patterns were obtained using CuK_α radiation, which showed that these compounds were nearly single phase. The infrared absorption spectra of these samples were determined by a Nicolet DX-spectrophotometer in the wave number range 400–4600 cm^{-1}.

A conventional pulse-echo technique was used at frequencies 10 and 30 MHz to measure the ultrasonic attenuation [9]. A short pulse of longitudinal waves was introduced into the sample by means of an X-cut quartz crystal. The same transducer acted as receiver for the reflected echoes (nearly seven echoes). Pure bees honey was used for the acoustic coupling between the transducer and the specimen.

Typical experimental decaying of the ultrasonic pulses at a very low temperature of 79 K and at room temperature is shown in Figs 1 and 2. The ultrasonic attenuation is calculated by taking the ratio of successive pulses.

3. Results and discussion

The resistance versus temperature of $Y_1Ba_2Cu_3O_{7-x}$ compound was observed at the critical temperature of 92.5 K as shown in Fig. 3. The powder X-ray diffraction pattern of $YBa_2Cu_3O_{7-x}$ is shown in Fig. 4. It has a tripled unit cell along the *c*-axis. The lattice parameters calculated are $a = 0.383\,45$ nm, $b = 0.388\,10$ nm and $c = 1.153\,005$ nm. The structure is a variant of the perovskite unit cell with ordered yttrium and barium cations as shown in Fig. 5. Yttrium and barium ions are ordered along the *c*-axis to give the triple unit cell.

The substantial difference in the ionic radii of yttrium and barium (0.102 nm and 0.142 nm, respectively for eight-fold coordination) causes the ordering of cations at the A site of the (AA_2) Cu_3O_{9-x} defect

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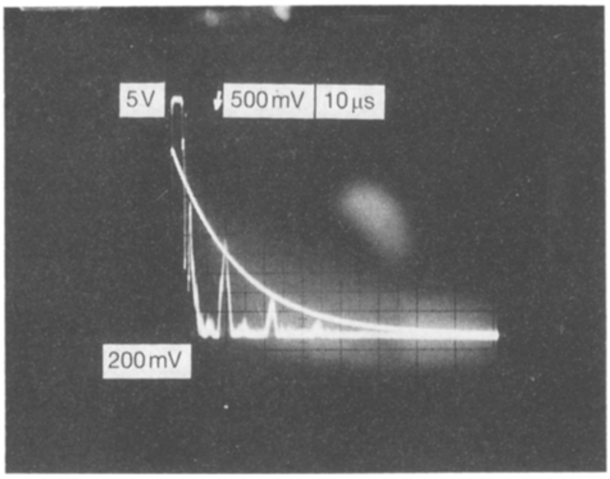

Figure 1 Exponential decay pattern for superconductor YBCO at low temperature ($T = 79$ K) obtained at 10 MHz frequency.

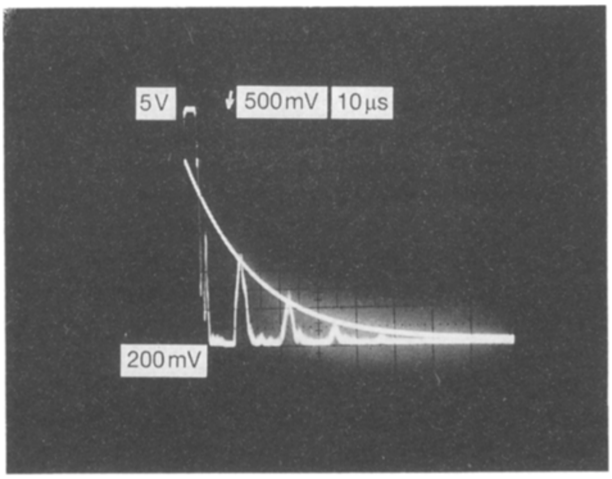

Figure 2 Exponential decay pattern for superconductor YBCO at room temperature obtained at 10 MHz frequency.

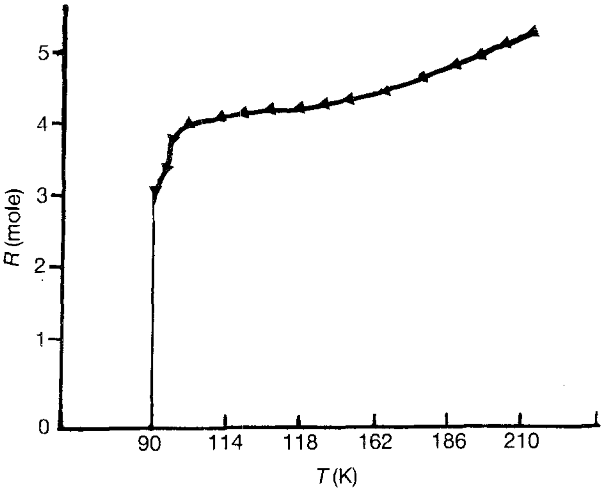

Figure 3 Resistance as a function of temperature of the $Y_1Ba_2Cu_3O_{7-x}$ sample.

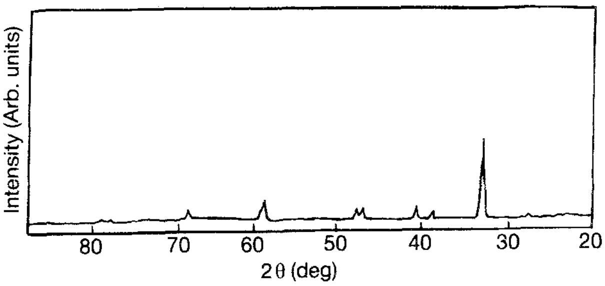

Figure 4 X-ray diffraction of $Y_1Ba_2Cu_3O_{7-x}$ sample.

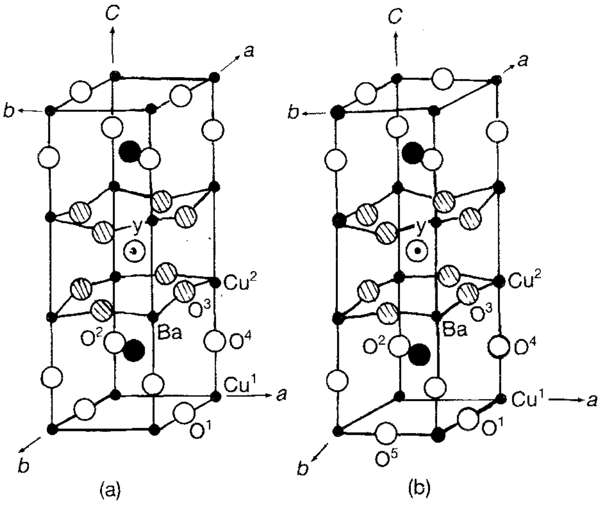

Figure 5 Crystal structure of $YBa_2Cu_3O_{7-x}$; (a) orthorhombic; (b) tetragonal – as can be seen, the O (5) position is not occupied in (a).

perovskite structure. Owing to the oxygen deficiency ($x = 2$) in the formula, the yttrium-ion adopts an eight-fold coordination, whereas barium will be in a ten-fold oxygen coordination. Another notable feature of the structure is that there are no oxygens in the plane containing yttrium. Similarly, in the ordered orthorhombic structure, the O(5) positions are vacant. That is, the orthorhombic symmetry arises due to the presence of a unique oxygen atom, O(1), ordered on one of the crystallographic axes (*b*-axis). Owing to the oxygen deficiency in Y-123, there exists mixed valency in copper and the nominal chemical formula can be written as $YBa_2Cu_2^{2+}Cu_1^{3+}O_7$. Because of existence of two closely related structure types (namely ordering of two O(1) or O(5) oxygens, leading to the interchange of *a* and *b* axes), twinning is a common phenomenon in 123 materials. Only orthorhombic phases are found to have several twinnings as can be expected. The twinning in Y-123 thus occurs when the material transforms from tetragonal to the orthorhombic structure on cooling during synthesis. Our values for the lattice constants are comparable with those obtained by others [10]. Fig. 6 shows the infrared spectra for $Y_1Ba_2Cu_3O_7$ compound in the region 400–900 cm^{-1} for (a) orthorhombic superconducting sample (SC) and (b) tetragonal nonsuperconducting (NSC) sample. It is clear from Fig. 5a that the SC sample shows highly degenerate, very broad vibrational modes.

In NSC (Fig. 6b) two additional distinct vibrational modes at about 600 and 650 cm^{-1}, not present in the SC, are observed. A plausible explanation could be as follows. The additional feature in our NSC samples may be due to oxygen re-arrangement which is consistent with the results obtained by others [11]. Figs 7 and 8 shows four peaks in the ultrasonic attenuation versus temperature (P_1, P_2, P_3 and P_4) of the two

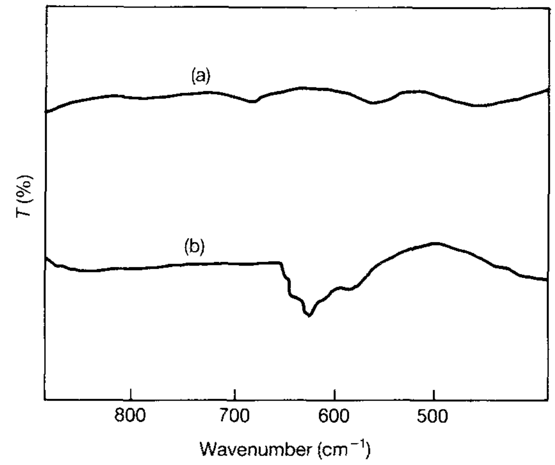

Figure 6 Infrared spectra for (a) superconducting sample (SC), and (b) non-superconducting (NSC) for $YBa_2Cu_3O_{7-x}$ compound.

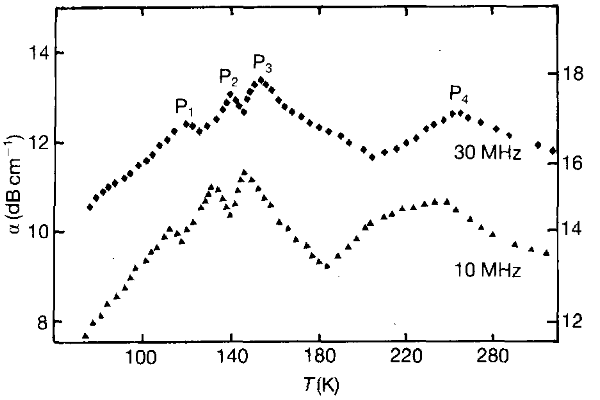

Figure 7 The ultrasonic attenuation of $YBa_2Cu_3O_{7-x}$ (sample 1) as function of temperature at (▲) 10 MHz (◆) 30 MHz

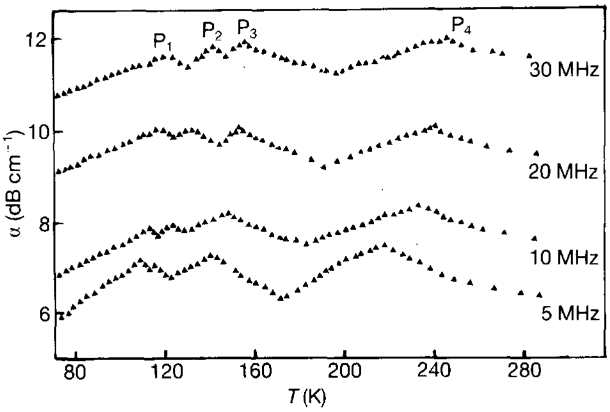

Figure 8 The ultrasonic attenuation of YBCO (Sample 2) as function of temperature at frequencies of 5, 10, 20 and 30 MHz.

YBCO specimens (Samples 1 and 2, respectively). In the first sample P_1, P_2, P_3 and P_4 occur at 113, 122, 147 and 232 K when measurements are taken at 10 MHz frequency but they occur at temperatures 119, 140, 154, and 244 K when measurement is done at 30 MHz. In the second YBCO sample, the peaks occur at temperatures slightly larger than those found in the first sample when measured at similar frequencies (10 and 30 MHz) with an increase of nearly 1.5%. However, the relaxation strengths of P_1, P_2, P_3 and P_4 in the first sample are larger than those found in the second sample. This may be due to the grain size (< 2 μm) being smaller in the first sample than the second (< 6μm). Anderson *et al.* [12] found that the grain size affects the strength of the relaxation peaks and their temperatures. One more interesting observation is that in both samples the relaxation strength decreases as the frequency increases. Also the separation between P_1 and P_2 was 5 K at a frequency of 5 MHz, 10 K at 10 MHz, 15 K at 20 MHz and finally 22 K at 30 MHz. Thus if the measurement is carried at kilohertz and hertz frequencies, P_1 and P_2 will be integrated. More interesting, the ratio between the height of P_1/P_2 is equal to nearly 1.2 at 5 MHz while it is nearly 1 at 10 MHz and the ratio decreases at 30 MHz frequency, i.e. 0.8. This means that at kilohertz frequencies, P_1 may be larger than P_2 and at hertz frequencies the P_1 height will be substantially larger than P_2. The results of Weller [13] to a certain extent agree with our conclusion. The shift in temperature of the peaks with the frequency increment indicates that these peaks are thermally activated relaxation processes. For such a process the relaxation time usually varies with the temperature according to the Arrhenius relationship $\tau = \tau_0 \exp(W/kT)$, where τ_0 is a constant and W is the activation enthalpy for the process. The peak occurs when the product of the angular frequency, ω, and the relaxation time, τ, is equal to unit and hence $\omega = \tau_0^{-1} \exp(W/kT_m)$. Fig. 9 shows the relation between the peak temperature and the frequency from which we can calculate the value of W and f_0 ($= \tau_0^{-1}/2\pi$). The values of W and f_0 i.e. the frequency of vibration of a particle in one of the wells [12] for the two YBCO specimens, are listed in Table I.

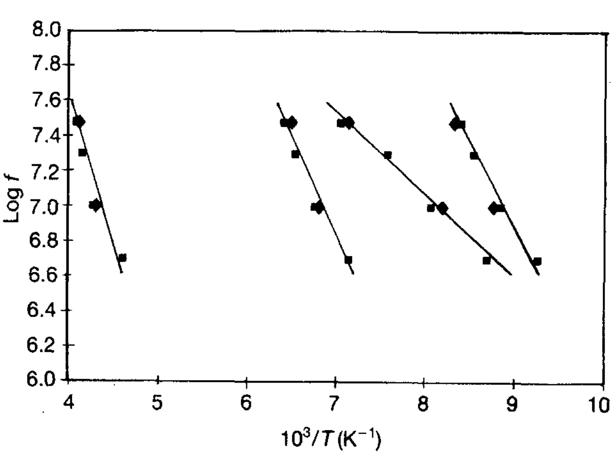

Figure 9 Plot of the logarithmic frequency versus the reciprocal of the peak temperature for (◆) Specimen 1, (■) Specimen 2.

Yusheng *et al.* [14] also reported a group of weak peaks at 160–180 K (T_{P_1} in their notation) and at temperatures from 250–270 K (T_{P_2}) which agrees with our work. Also, the room-temperature longitudinal sound velocity, v_l, was reported by them as 4.2 km s^{-1} while in the present work it is nearly 4.6 km s^{-1} (we have deleted v_l values for the first sample because the time base for the oscilloscope was not calibrated). If we take the average values of P_1, P_2 and P_3 at the frequency of 10 MHz in the present work, we will find

TABLE I The peak temperatures measured at different megahertz frequencies in two superconductor YBCO specimens. Calculated values of activation parameters (W and f_o) plus longitudinal velocity are included.

Sample	Peak	T_m (K)				W (eV)	f_0 (Hz)	V_l (m s^{-1})
		5 MHz	10 MHz	20 MHz	30 MHz			
1	P_1		113		119	0.212	2.88×10^{16}	
	P_2		122		140	0.090	5.18×10^{10}	
	P_3		147		154	0.307	3.31×10^{17}	
	P_4		232		244	0.447	5.20×10^{16}	
2	P_1	108	114	117	120	0.188	2.46×10^{15}	4886
	P_2	115	124	132	142	0.092	5.95×10^{10}	4875
	P_3	140	148	153	156	0.209	1.64×10^{14}	4844
	P_4	217	234	241	245	0.314	7.82×10^{13}	4774

that there is a complex peak occurring at 1.4 T_c in both samples (Samples 1 and 2) and not at $2T_c$ as reported by Yusheng *et al.* [14] as they use three types of superconductors (LSCO, YBCO and BSCCO). This difference may be attributed to the difference in the grain size and probably the thermal treatment of the specimens. Our specimens were calcinated and sintered at a temperature of 840 °C while in Yusheng *et al.*'s work it seems to be between 900 and 1100 °C.

We believe that P_1, P_2 and P_3 are complex peaks which may be attributed to thermally activated atomic jumps (probably over distances appreciably less than the interatomic distances [13]). The broad peak, P_4, is frequently observed in all YBCO [8, 14]. Laerman [15] states that twin boundaries in YBCO could be a likely candidate for the relaxation entities. It could be concluded that this peak is caused by the lattice readjustment or instabilities, due to the ordering of the oxygen atoms and of close relation to the high T_c. This observation is consistent with our infrared measurements. Internal friction or mechanical spectroscopy of a sample is very sensitive to their structure and also to the mechanism of the relaxation. Careful study will provide useful information about the structural defect and its relation to superconductivity. The effect of neutron and gamma radiation on superconductors of different types (YBCO and BSCCO) is at present under study. Preliminary results show that the heights of the relaxation peak increases as the radiation (i.e. neutron and gamma) increases. Using the internal friction experiment, we have found that in BSCCO the number of the relaxation peaks is larger than those found in the YBCO, indicating that the structural defects in these two specimens are different.

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