Evidence for a structural change in TSMG Y123 at 225 K

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Abstract

This paper reports on an ultrasonic study at 85 kHz and 485 kHz of melt-textured Y123 (YBa2Cu3Oy) where a possible structural change has been identified in the 220 K region. Work on oxygenated and partially deoxygenated samples has shown that the change is associated with oxygen in the samples and that the activation energy for the process is 110 meV. The conclusions are based on a qualitative and quantitative description of ultrasonic attenuation and ultrasonic velocity changes in the material as a result of slow thermal cycling and quenching experiments. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

With the development of high-temperature superconductors (HTSs), it is important to characterise the materials as well as possible. This has prompted the present study into melt-textured Y123 (YBa2Cu3Oy) which is now receiving much more attention than previously prepared sintered samples, particularly as the melt-textured samples show the most promise for practical applications. Previous ultrasonic work by ourselves [1–3] and others [4–8] has shown the potential of ultrasonic techniques for investigating relaxation processes and structural changes in HTSs. Recently, we have identified a structural change in Bi2212 in the 160 K region associated with the movement of oxygen in the structure [2,3].

2. Experimental

The samples were prepared from a powdered mixture of the high-purity oxides of Y, Ba and Cu in the molar ratio of 1.8:2.4:3.4 with 0.5% by weight of Pt. This molar ratio allows for an additional 40% of the Y211 phase which results in larger grain size and high-Jc. The powders were calcined at 890°C for 10 h and ground with an alumina mortar and pestle before being pressed into 40 mm diameter disks at 200 MPa. The disks were heated to 1150°C for 30 min to achieve a semimelt of the Y211 before cooling to the seeding temperature of 1030°C. The top seeding melt growth (TSMG) was achieved using a...
single crystal of composition of Sm123:Sm211 in the ratio of 5:2. Finally for oxygenation, the samples were annealed in flowing oxygen with cooling from 450°C to 300°C at a rate of 1 K/h before being held at 300°C for 100 h. The presence of the Y211 was a complicating factor in the ultrasonic experiments and this was investigated using pure sintered samples of Y211. This matter is discussed in Section 3.2 below.

The ultrasonic equipment is based on a regenerative system [9] where a sample bar approximately 30 mm in length is attached to an X-cut 85 kHz quartz transducer 33 mm in length with a cross-section of 6 mm × 3 mm which is similar to the sample. Transducers of differing cross-sections have also been used. The length of the sample is adjusted so the composite bar vibrates at a frequency of approximately 85 kHz. Experiments were also conducted on the same composite bar at the second overtone of 480 kHz. Measurements of internal friction (IF) based on transducer drive voltage (< 3 V rms) and current and velocity changes determined from the composite bar frequency were made during temperature cycling at 1 K/min and temperature-quenching experiments. Experiments were performed in He, as an exchange gas, at 1 atm. The melt-textured samples had the c-axis perpendicular to the length of the bar so the ultrasonic vibrations were in the ab-plane.

3. Results

3.1. Oxygenated and sintered Y123

Internal friction and frequency results for a sintered Y123 sample are presented in Fig. 1 for comparison with the later melt-textured results. The IF results for sintered samples are well-known and reviewed elsewhere [4,8]. Samples of Y123, between 80 K and room temperature, are characterised by three IF peaks in the 115 K, 130 K and 240 K regions. The lower temperature peaks have been identified as relaxation peaks where the 130 K peak has been shown to depend on chain oxygen content [6]; however, the 115 K peak is less dependent on this oxygen. The broad 240 K peak has been thought to be due to a structural change [4] but has not been studied extensively. The frequency measurements in sintered samples have shown a noticeable change in slope in the 240 K region and thermal hysteresis has been observed below this temperature.

3.2. Oxygenated melt-textured Y123

Results for oxygenated melt-textured Y123 are shown in Fig. 2. The previously reported peaks are evident; however, there are significant differences. The 115 K and 130 K peaks are still present although the 130 K peak is higher than in the sintered sample possibly due to changes in the chain oxygen level.

The most significant change is the apparent movement of the 240 K peak to the 220 K region with considerable sharpening, particularly on the low temperature side and the greatly increased height of the peak. The frequency data show a distinct change in slope centred on the 220 K region with a reduction in slope by a factor of approximately 2 below 220 K.
Thus, the sample undergoes considerable stiffening below 220 K. Within experimental limits, the hysteresis previously reported is not obvious in the melt-textured samples. This is consistent with the results of Pal-Val et al. [7]. Internal friction and modulus results, based on earlier work with Bi2212 [1–3], indicated a possible structural change in the 220 K region, first from the shape of the IF peak and second from the change in slope of the modulus data. These arguments will be developed later. The IF data in Fig. 2 also show a small peak in the 180 K region. It is concluded that this peak is due to the presence of Y211. Experiments on pure sintered Y211 displayed a distinct IF peak in this region. Results on Y211 indicate that the presence of the Y211 in the TSMG Y123 did not influence the interpretation of results in this paper.

To investigate a possible relationship between the changes in the modulus and IF data, we plotted the rate of change of frequency as a function of temperature, averaged over 5 K temperature intervals. The results shown in Fig. 3 reveal a close qualitative agreement between this data and the IF results of Fig. 2, reflecting the presence of a common underlying process in Y123.

To verify that the 220 K IF peak was not a relaxation peak, experiments were performed at 485 kHz with the same composite bar as used in the 85 kHz experiments. Results shown in Fig. 4 indicated that the peak was independent of frequency. As relaxation peaks change with frequency, the 485 kHz experiments provide further evidence for the structural change at 220 K. A possible temperature shift within the experimental limits of temperature measurement would imply an activation energy of at least 3 eV which is unacceptably high.

3.3 Oxygen-deficient melt-textured Y123

Ultrasonic experiments were conducted on a range of Y123 samples with differing oxygen levels. Fully oxygenated samples were annealed in flowing oxygen under differing conditions to reduce the oxygen level. Of particular interest was the slightly deoxygenated $\delta = 0.2$ sample. This sample was heated to 600°C over 3 h, maintained at that temperature for 1 h, cooled to 530°C over 3 h, maintained at that temperature for 48 h and allowed to cool to room temperature in the oven. According to Jorgensen et al. [10], the resulting oxygen level is approximately 6.8, i.e., $\delta = 0.2$. Samples were not quenched to room temperature in the final step to avoid creating cracks in the bar.

Results of IF and frequency measurements are shown in Fig. 5 using similar scales to Fig. 2. Comparing the results with those for the fully oxygenated sample in Fig. 2, it can be seen that the 220

![Fig. 3. Temperature rate of change of velocity (frequency) as a function of temperature in oxygenated melt-textured Y123. Results show a similar form to the ultrasonic attenuation in Fig. 2. The rate of temperature change is averaged over 5 K intervals.](image)

![Fig. 4. Changes in ultrasonic attenuation at 480 kHz in oxygenated melt-textured Y123 in the 220 K region. Within experimental error, the values of the peak temperature at 85 kHz (Fig. 2) and 485 kHz are the same, indicating that the peak is not a relaxation peak.](image)
K IF peak and the change in slope at 220 K have virtually disappeared. We would conclude that the 220 K peak is a characteristic of highly oxygenated samples. This indicates that the peak is related to long-range ordering in the oxygen chains. This long-range structure is subsequently destroyed when small amounts of oxygen are removed, creating shorter-chain structures.

4. Investigating the 220 K region

In order to further investigate the 220 K peak, quenching experiments were performed on a fully oxygenated sample where the sample was held between 220 K and 230 K until the IF stabilized and then the sample was quickly cooled to temperatures between 180 K and 210 K. This was done to investigate the dynamic behaviour of the atomic species causing the IF peak. The quenching and temperature stabilization took about 3 min, so measurements were taken after this time. The temperature was measured with a control thermocouple inserted in a ‘dummy’ sample which was very close to the composite bar. Other experiments showed that such temperature measurements were valid. Both samples were in a 2 cm diameter thin brass tube which was temperature controlled via a resistance wire heater wound non-inductively along the tube with a control thermocouple in close thermal contact with the wire and the tube. The results of typical IF and frequency recovery in Fig. 6 show a recovery time of the order of 500 s. When the results are plotted on a logarithmic scale in Fig. 7, an exponential form of recovery is indicated. Expressing the recovery in the form:

$$\Delta(t) = \Delta(0) \exp\left(-C(T) t\right).$$

the values of the decay constants $C(T)$ were obtained as a function of temperature, $T$, from the slopes of the graphs in Fig. 8 where $\Delta(t)$ is the logarithmic decrement (IF), $t$ is the time and $\Delta(0)$ the initial damping.
The temperature dependence of the decay constants can be expressed in the form:

\[ C(T) = C_0 \exp\left(-E/kT\right), \tag{2} \]

where \( E \) is the activation energy, \( C_0 \) the attempt frequency and \( k \) the Boltzmann constant. When a series of \( C(T) \) values were placed on an Arrhenius plot as shown in Fig. 8, the slope indicated an activation energy for the recovery process of approximately 110 meV.

Alternatively, Eq. (2) can be expressed in terms of the relaxation time, \( \tau \):

\[ \tau = \tau_0 \exp\left(\frac{E}{kT}\right). \tag{3} \]

Although temperature following quenching was kept to within 1 K, it is noted that the temperature stability, as reflected in the values plotted in Fig. 8, is the limiting factor in accurately determining the activation energy. The overall trend of the increasing decay times with decreasing temperature is obvious.

An alternative analysis of changes immediately below the 220 K region can be obtained by considering the form of the IF changes in the thermal cycling data between 180 K and 210 K. Below 180 K, the IF values are affected by the 130 K peak. Considering

[Fig. 8. An Arrhenius plot of the decay constants for a number of experiments similar to those presented in Figs. 6 and 7. The slope of a line of the best fit indicates an activation energy for the recovery process of approximately 110 meV. It is noted that there is considerable scatter in the experimental points.]

the IF as due to a general relaxation process of the form:

\[ \Delta = KN\omega\tau/(1 + \omega^2\tau^2), \tag{4} \]

where \( \omega \) is the angular frequency, \( \tau \) the relaxation time, \( K \) a constant and \( N \) the number of defects. It is evident experimentally that \( \omega\tau \gg 1 \) so Eq. (4) reduces to:

\[ \Delta = KN/\omega\tau. \tag{5} \]

Eq. (5) assumes a constant number of defects; however, if the number of defects is of the form:

\[ N = N_0 \exp\left(-E/kT\right), \tag{6} \]

and is increasing as the temperature is increasing from 180 K to 210 K, then this factor needs to be included in Eq. (5). Thus, the IF as a function of temperature becomes:

\[ \Delta = (KN/\omega\tau_0) \exp\left(-2E/kT\right). \tag{7} \]

When the experimental results were plotted as in Fig. 9, a straight line relation was observed. Substituting the slope in Eq. (7), again yields an activation energy of 110 meV, supporting the results from the quenching experiments.

5. Conclusions

Results of ultrasonic attenuation and velocity (frequency) experiments at 85 kHz and 480 kHz
provide strong evidence for a structural change in oxygenated melt-textured Y123 in the 220 K region. The structural change was shown to be dependent on the chain oxygen within the material with the active species being associated with an activation energy of 110 ± 20 meV. This result is similar to the reported activation energy for the 130 K peak [4] and is consistent with chain oxygen zig-zag vibration. The structural rearrangement stiffens the material below 200 K, indicating the incorporation of the chain oxygens into more rigid and well-defined positions.

Above 220 K, the chain oxygens are able to move more within the structure which is reflected in the greater temperature dependence of the velocity through the softening of the material.

As the 220 K ultrasonic features are only present at high oxygen levels, it is proposed that the structural change is associated with long-range ordering in the CuO chains. At lower temperatures, it is known that the chain oxygens form a zig-zag pattern. One explanation of the structural change is that above 220 K, the zig-zag structures transform into linear chains. It is the transition between the two structures which results in the IF peak as the oxygens become more mobile in transition from one structure to another.

The general shape of the IF peak can be interpreted in terms of a three-stage process. Below 220 K, peak small linear chain regions start to form with the boundary region between the two structures contributing significantly to the IF. As the temperature is increased, the regions start to overlap. This results in a decrease in IF above the peak as the overall contribution of the boundary region between the two structures decreases. Finally at higher temperatures, only the high-temperature structure is present. This structure has higher IF than the low-temperature structure. It is noted that results of pyroelectric [11,12], piezoelectric [12] and specific heat [13] experiments support our proposal for the structural change in Y123 in the 220 K region. These results were explained in terms of the ferroelectric nature of the copper oxide planes.

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References