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Physical properties of $YBa_2Cu_3O_{7-x}$ superconductor sintered at different temperatures

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$YBa_2Cu_3O_{7-x}$ ceramics prepared by sintering at 920 and 1030° C were studied in some detail. Although samples prepared at 920° C had lower density, they had larger transport critical current at 77 K. A correlation between the transport critical current and the magnetic field dependence of the second maximum in the imaginary part of the initial susceptibility was found and discussed. According to our results samples prepared at higher temperature had larger but (in spite of almost ideal density) poorly connected grains.

1. Introduction

It is well known that the critical currents (J_c) of the ceramic $YBa_2Cu_3O_{7-x}$ superconductors compare very poorly with those of the homogeneous [1] (single crystal) compound. The comparison between the values of J_c obtained [2] from magnetization and I–V relation has shown that in larger magnetic fields ($\geqslant 200$ Oe at 4.2 K) ceramic superconductors behave as an assembly of practically disconnected grains. However, the intrinsic properties of the (isolated) grains are comparable to those of single crystals. Therefore the possibility of an improvement in the intergrain links may ultimately decide the future of the large scale applications (wires, etc.) of these and possibly all other high-temperature (oxide) superconductors.

The other problem arises from the strong anisotropy of the YBaCuO single crystals. Therefore, the practical polycrystalline material will have to have oriented grains. However the oriented grains alone may not solve the problem of intergrain links.

Apparently there are several parameters which may affect the intergrain connections in a ceramic material. In addition to the microstructure (texture, porosity, grain sizes and their distribution) the segregation at the grain boundaries (impurities, different phases or even different stoichiometry of the same phase) may seriously affect the superconducting properties of these materials.

For a given material the sintering temperature will have the strongest influence on all the above parameters and hence on the intergrain connections. In what follows we report the results of the detailed study of the properties of YBaCuO ceramics prepared from the same initial powder by sintering at widely different temperatures (920 and 1030° C). These temperatures were selected because they represent the lowest and the highest practical sintering temperatures (below 920° C the sintering is too slow whereas above 1000° C rapid decomposition of the compound occurs).

2. Sample preparation and experimental techniques

The YBaCuO compound was prepared by the conventional solid state reaction method. The starting powders were CuO, Y_2O_3 and $BaCO_3$. Ytrium oxide, Y_2O_3, was obtained by precipitation with NH_4OH from ytrium acetate, $Y(CH_3COO)_3$. The stoichiometric proportion of the powders was thoroughly mixed in an agate mortar with ethanol.

In order to get closer contact between reactants, the mixed power was pressed into pellets and calcined. The material was crushed and pressed into pellets again before any new calcination or final sintering took place. This was done again to achieve a better chemical homogeneity.

The pellets were calcined at 800, 900 and 920° C for 6 h in an open air atmosphere, followed by slow cooling to room temperature. Some final (920° C) calcined pellets were used as first samples (C) for our measurements.

The resulting calcined material (C) was sintered at 920° C for 8 h in an atmosphere of flowing oxygen. The samples were then slowly cooled (4 h) to 500° C in the same oxygen atmosphere and annealed for 6 h followed by slow cooling to room temperature (material S).

A portion of material S was resintered (without crushing) at 1030° C for 3 h in an flowing oxygen atmosphere and slowly cooled (1 K min^{-1}) to 450° C. At 450° C additional annealing in oxygen was carried out for 24 h followed by cooling to room temperature giving new material, R.

Differential thermal analysis (DTA) measurements

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were made using Perkin Elmer 1700 DTA instrument. DTA was used to follow and guide all stages of sample preparation indicating its degree of calcination, solid state reaction.

The densities of our pellets (measured both by the mass to volume ratio and with the Archimedes method) where 4.2, 4.7 and 6.0 g cm^{-3} for calcined (C) sintered (S) and resintered (R) samples, respectively. We noted that even prolonged sintering at 920° C gave rather porous samples ($\leqslant 0.74$ of the ideal density, D_0) whereas sintering at 1030° C gave very dense samples (0.94 of D_0).

The samples for the electrical and magnetic measurements were cut from the pellets in a rectangular shape with typical dimensions 1.5 mm × 1 mm × 10 mm. The same samples were used for all measurements (of other properties). The resistivity was measured with a standard a.c. method and with current of 0.1 mA r.m.s. The critical transport current was measured with a pulse method using a single sinusoidal pulse (2 sec period) at 77 K only. The limit of the voltage detection in that case was $\leqslant 10^{-6}$ V.

The a.c. susceptibility was measured with the high sensitivity set up described earlier [3]. The frequency used was 28.4 Hz and a.c. magnetic fields down to 1.5 mOe were employed. Separate parallel coil enabled simultaneous application of the d.c. field. The magnetic fields were parallel to the length of the sample so that the demagnetizing factor was negligible (a few per cent). Both the imaginary and real part of the initial susceptibility were recorded simultaneously.

3. Results and discussion

DTA measurements on YBaCuO material showed that the $BaCO_3$ compound disappeared completely after the second calcination. This was monitored through absence of endothermic reaction starting at around 803° C due to α–β first order phase transition in $BaCO_3$. DTA results on fully reacted material (Fig. 1) showed peritectic decomposition [4, 5] occurring intensively above 1000° C although even at 900° C some kind of endothermic reaction (like melting) took place which was probably due to presence of $BaCuO_2$ or Ba_2CuO_3 phase. As can be seen in Fig. 1, resintered samples (R) had a larger fraction of these nonwanted phases. In spite of the expected melting of some newly formed phases at higher sintering temperatures (1030° C) our carefully prepared samples remained apparently solid, keeping their shape during sintering. Moreover oxygen desorption and absorption [6, 7] as well as orthorhombic–tetragonal transition of YBaCuO were monitored by DTA, but not shown here.

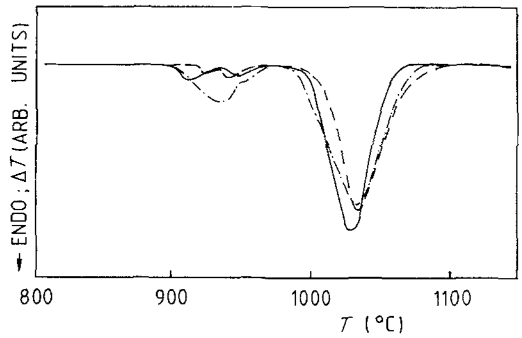

Figure 1 Typical DTA curves (40 K min^{-1}) for our $YBa_2Cu_3O_{7-x}$ samples (C calcined in air at 920° C, S sintered in oxygen at 920° C and R resintered in oxygen at 1030° C). (——) C; (- - -) S; (—·—·) R.

The resistivity of our samples, normalized to their own room temperature values are shown in Fig. 2. The room temperature resistivities were 3.42, 1.85 and 2.0 mΩ · cm for C, S and R samples, respectively.

As expected the room temperature resistivities of oxygen annealed samples (S, R) were lower than that for the sample sintered in air (denoted as calcined, C), but that for R (resintered at 1030° C) was higher than that for S (sintered at 920° C). Higher resistivity of sample R probably indicates some decomposition of the 1 2 3 phase, as will be discussed later. The rate of the resistivity decrease on lowering the measuring temperature increased very rapidly going from C to R. The corresponding ratios (r) of the room temperature resistivity to that at 93 K were 1.4, 2.2 and 3.3 for C, S and R samples, respectively. The value of r for sample R was identical to that for the a–b plane of $YBa_2Cu_3O_{7-x}$ single crystals [1] but the corresponding resistivity was several times larger than that for the single crystals. The resistive superconducting transitions of our samples are shown in some detail in the inset to Fig. 2. We noted a somewhat lower transition temperature for sample C and the step like transitions both for C and S. The step like transitions can be associated either with inhomogeneity or with a particular weak link structure. However the absence of these steps does not mean the absence of the weak intergrain links in the sample. Full widths of resistive transitions were 4, 3 and 1 K for C, S and R samples, respectively. Except in the extreme cases the resistive superconducting transitions in ceramic superconductors are notoriously insensitive to the volume effects [8] (zero resistance state can be achieved while the major fraction of the volume is still nonsuperconducting). In contrast to that the initial magnetic susceptibility measurements are very sensitive to the volume effects [9] and can yield the volume fraction of the superconductivity (diamagnetism) in the sample.

In Figs 3 and 4 we show the real and imaginary parts of the initial susceptibility ($\chi = \chi_r + i\chi_i$) of our samples in the temperature range 78–92 K. Figure 3 demonstrates the sensitivity of the diamagnetic transition of the granular (ceramic) superconductor on the applied a.c. field. Therefore in order to compare the widths of the diamagnetic transitions in different samples one has to find out the lower limit for the a.c. field below which the width and the shape of the transition do not depend on the magnitude of the exciting a.c. field. For our samples the limiting field was about 15 mOe r.m.s. The transitions of all three samples in this field are shown in Fig. 4. We noted an almost perfect diamagnetic shielding at 78 K ($\chi_r \simeq -0.9$). The full widths of diamagnetic transitions were 8, 4 and 5 K for samples C, S and R, respectively. In contrast to samples C and S which exhibited a typical two-step pattern in χ_r associated

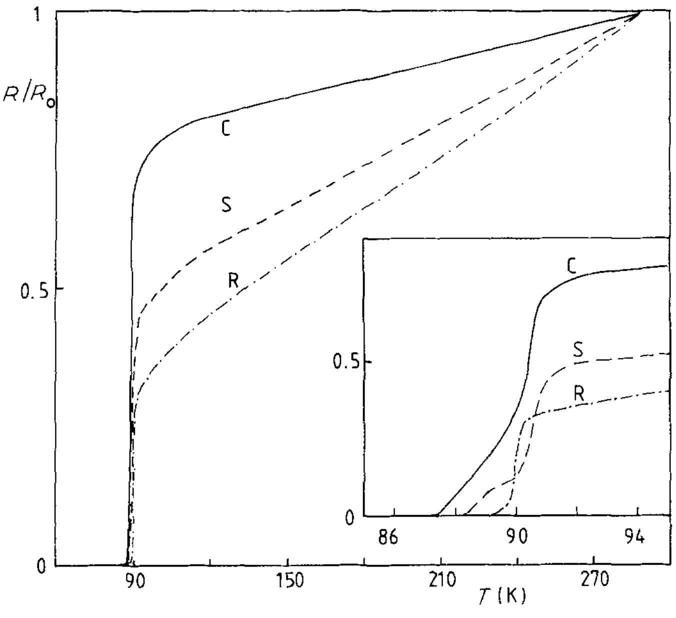

Figure 2 Normalized resistivity (to its own room temperature values R_0) of calcined (C) sintered (S) and resintered (R) $YBa_2Cu_3O_{7-x}$ samples. Inset shows expanded temperature scale around superconducting transition temperature.

with the intra and intergrain diamagnetic shielding [10] sample R showed a very narrow intragrain step and a small tail-like intergrain shielding. At the same time the intergrain (bulk) diamagnetic shielding was the strongest for sample S. The differences in the diamagnetism of our samples were seen more clearly by inspecting the imaginary parts of the initial susceptibility, also shown in Fig. 4. The imaginary susceptibility represents the a.c. loss and is therefore in a superconductor associated with the field penetration in the material. In a ceramic superconductor the grains are usually small and at the same time sizeable magnetic field is required to penetrate fully in them. Therefore the maximum in χ_i associated with the loss in single grains (or clusters of well connected grains) is seen only in higher a.c. or d.c. fields [10, 11]. In contrast to that even small field strongly perturbs the assembly of the weak intergrain links and hence produces sizeable a.c. loss (χ_i). This expected behaviour was apparently well obeyed both for samples C and S. The difference between those two samples was that the intergrain peak for sample S was higher, narrower and shifted to higher temperature indicating better coupling between the grains in that sample. In contrast to samples C and S the sample R showed both intra and intergrain peak in χ_i. Furthermore these peaks were relatively small and of about the same size indicating very large but poorly connected (in a superconducting sense) grains. Indeed the inspection by the optical microscope confirmed the presence of much larger grains in sample R. Taking into account the relationship between χ_i and the magnetisation [12]

$$\chi_i = \int_0^{2\pi} M \mathrm{d}H/\pi H_0^2,$$

where $H = H_0 \sin \omega t$, one can make a prediction for the ratio of the critical currents (proportional to hysteresis) in two superconductors of the same shape measured in the same field if the temperatures of their peaks in χ_i coincide. Since these conditions were roughly met for the intergrain peaks in χ_i for samples S and R we can predict that the critical transport

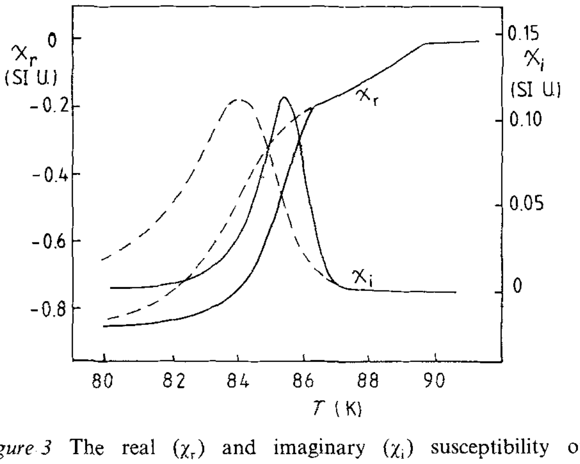

Figure 3 The real (χ_r) and imaginary (χ_i) susceptibility of $YBa_2Cu_3O_{7-x}$ samples C (calcined in air) in two different a.c. fields. (——) 0.015 Oe; (– – –) 0.15 Oe.

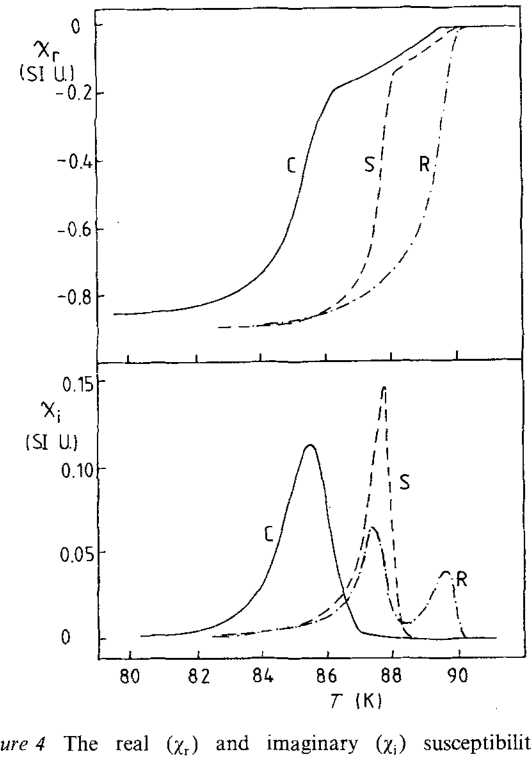

Figure 4 The real (χ_r) and imaginary (χ_i) susceptibility of $YBa_2Cu_3O_{7-x}$ C, S and R samples in 0.015 Oe a.c. field.

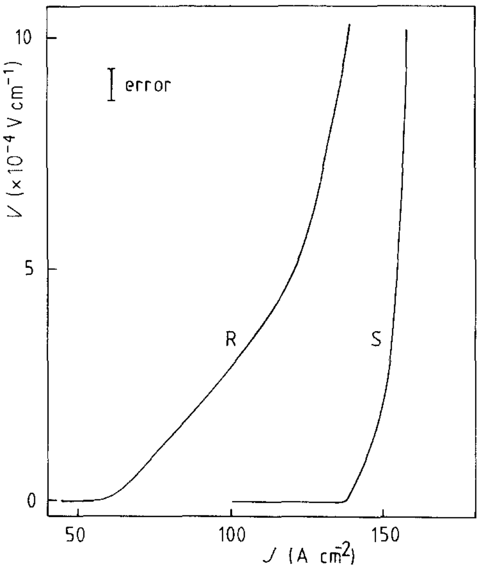

Figure 5 V–I curves for critical current of $YBa_2Cu_3O_{7-x}$ sintered (S) and resintered (R) samples.

current would be just over twice the size in sample S than in sample R at the same temperature.

Figure 5 showed the results of the critical current measurements in samples S and R at 77 K (liquid nitrogen). The ratio of these currents was 2.15, close to that of the ratio of the intergrain peak heights in these two samples. Considering the critical currents in our samples we noted that the electric field of 10^{-5} V cm^{-1} (limit of our resolution) corresponds to resistivity about seven times smaller than that of a pure copper at liquid nitrogen temperature. It is also interesting to note the unusual step-wise V–I relation for sample R. We regard this as support to our claim that sample R could be regarded as an assembly of good and large, but rather poorly coupled grains. Since that sample had almost ideal density the reason for that should probably be sought in the partial decomposition or phase separation at the grain boundaries. The fraction of the decomposed (other phase) material seem however to be rather small considering almost perfect diamagnetism of our sample in low field at 77 K. The alternative explanation is rather strong unfavourable grain orientation which seems to us unlikely for the sintered sample.

Before concluding this section we wish to emphasize the potential of the investigation of the imaginary susceptibility for the determination of the critical transport currents in high temperature superconductors. In particular, according to Bean's model of the critical states [13] there is a relation between the field of full penetration (B_p) and the critical current, $B_p = \mu_0 J_c r$, where r is radius of a long cylindrical sample and J_c is the critical current. Since there must be a definite relation between the $B_0 = \mu_0 H_0$ (the maximum applied field) and B_p for a given sample one can in principle by monitoring the temperatures of the peak in χ_i at different fields (H_0) deduce the dependence of the critical current on temperature. Therefore, for larger $\Delta H_0/\Delta T$ (peak) dependence [10] one can expect a larger critical current at the given temperature. This was indeed confirmed for our samples S and R, the average slope of H_0 against T (peak in the temperature range 88–78 K was 2.2 times larger for samples S than that for sample R.

4. Conclusion

The influence of the very different sintering temperatures (920 and 1030° C) on the normal state and superconducting properties of polycrystalline $YBa_2Cu_3O_{7-x}$ samples has been investigated. As expected sintering at 1030° C produced the samples with an almost ideal density whereas the porosity of the samples sintered at 920° C was $\geq 26\%$. In spite of very different densities some properties of these samples such as the fraction of the diamagnetic shielding at 77 K and the room temperature resistivities were practically the same. Different sintering temperatures however produced rather different microstructures; whereas the sample sintered at 920° C, had a fine granular structure, sintering at 1030° C provoked an excessive growth of the individual grains. These microstructural differences manifested themselves very clearly in the behaviour of the initial susceptibility. In addition the initial susceptibility (its imaginary part in particular) was used to deduce the quality of the intergrain coupling and to obtain a prediction for the ratio of the critical currents in two samples. The direct measurements of the critical transport currents at 77 K confirmed that prediction. The critical current of the sample sintered at 920° C was about 2.2 times larger than that sintered at 1030° C. It is tentatively suggested that the smaller critical current in a sample sintered at 1030° C was due to incipient decomposition of the 1 2 3 phase at the grain boundaries.

Although larger, the critical current of the sample sintered at 920° C is still some orders of magnitude too small for the large scale applications of superconductivity. Our impression is that such improvement in the current carrying properties of these low density small grained ceramics is unlikely.

On the other hand a dense ceramic with a larger grain of good quality could be achieved by sintering at higher temperature. If during this process the incipient decomposition and the segregation of the impurity phases at the grain boundaries can be avoided these ceramics may become better candidates for the large scale applications of superconductivity. A detailed investigation of this possibility is now in progress.

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