Physica C 173 (1991) 337–341
North-Holland

Critical current density, reversible and irreversible magnetization in $YBa_2Cu_4O_8$ and $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$

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Received 31 August 1990

DC magnetic measurements on the high-T_c superconductors $YBa_2Cu_4O_8$ (124, $T_c=80$ K) and $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ ($T_c=87$ K) are reported. The irreversible lines of 124 and ceramic $YBa_2Cu_3O_7$ (123) are quite similar. The results show that there is no significant difference between the critical currents of the 124 phase and those of the 123 phase. Conversion of 124 into 123+CuO does not change the grain size of the material but enhances its critical current density.

Bulk samples of the high-T_c superconductor $YBa_2Cu_4O_8$ (hereafter referred to as 124) have recently been synthesized by various groups and by different methods. Morris et al. [1] synthesized bulk 124 samples by a high-oxygen-pressure technique. These samples exhibited a superconducting transition at around 80 K. Cava et al. [2] were successful in synthesizing the 124 phase in a powder form under one atmosphere oxygen pressure by utilizing a catalyst such as alkali-metal carbonates. X-ray [3–4] and neutron [5] diffraction studies revealed that the 124 structure is closely related to $YBa_2Cu_3O_7$ (designated 123 below), but with one additional Cu–O structure chain in the unit cell. Each unit cell contains two Cu–O chains and this leads to a much longer c lattice parameter of 27.24 Å and a smaller orthorhombicity (0.8% in 124 phase, 1.8% in 123 phase). Furthermore, the 124 compound has excellent thermal stability of its oxygen content up to 800°C, the well-known tetragonal–orthorhombic phase transition of the 123 structure at high temperature is absent, and no twins are observed in the 124 phase. Recent work [6] has indicated that the addition of Ca in the 124 phase increases T_c to 87 K. However, no further data have been available to date to analyze the mechanism for the increase of T_c by Ca substitution in the 124 compound.

Measurements on well-characterized single-phase 124 of the electrical resistivity, magnetization and the field dependence of the critical current density J_c at 4.2 K have already been published [7]. There is little information however, on the irreversibility line of the 124 compound and on the temperature dependence of J_c for pure and Ca doped 124 samples, and for the 123 phase obtained by decomposition of 124 [8]. From a technical point of view, these properties have great significance in the high-T_c compounds.

In the present paper, we present a detailed study of the reversible and irreversible properties of the 124 ceramic system with $T_c=80$ K. In general, we find that the magnetic behavior of this system is very similar to that found in ceramic 123 compounds. In addition, we present the temperature dependence of J_c for the 124 compound and compare its behavior with that obtained for Ca doped 124 and 123 systems. Formation of 123 phase by decomposition of 124 leads to a significant increase of J_c. This conversion process is interesting because the starting compound, as well as the end product, are superconductors and the conversion is not dependent on

the addition of elements that are not compatible with superconductivity.

$YBa_2Cu_4O_8$ were prepared by solid state reaction stoichiometric mixtures of the constituent oxides, following the procedure described recently by Pooke et al. [9]. The stoichiometric mixtures, with an addition of 0.2 mol $NaNo_3$, were prereacted as a loose powder for 30 min at about 600°C. The powders were then pressed into pellets, reacted at 815°C for 12 h in flowing oxygen, and then ground. This procedure was applied at least four times. The best materials are obtained when the samples are quenched from 815°C to ambient temperature, then heated again to 800°C and furnace-cooled under flowing oxygen to room temperature. The X-ray diffraction patterns reveal essentially phase-pure materials. Least-squares refinement of the crystallographic unit cells yielded $a=3.833$ Å, $b=3.873$ Å and $c=27.19$ Å for pure 124; $a=3.837$ Å, $b=3.862$ Å and $c=27.24$ Å for the Ca doped sample, in complete agreement with refs. [6,9].

The microstructure of the sintered materials was investigated by JOEL JFM 35 scanning electron microscope (SEM) observation. An energy dispersive X-ray spectrometer (EDS) Link system 860 attached to the SEM was used to determine the chemical composition.

The DC susceptibility measurements on a solid ceramic piece were carried out in a 155 PAR vibrating sample magnetometer VSM and a commercial SHE SQUID magnetometer in various fields of 10 Oe $< H <$ 20 kOe. The irreversibility line [10] was measured by the conventional procedure: The sample was zero-field-cooled (ZFC) to a low temperature, a field H was applied, and the magnetization of the shielding branch was measured as a function of temperature. The sample was then field-cooled (FC) from above T_c in a field H and the Meissner branch was measured. The field-dependent temperature T_{irr} is the temperature where a relative deviation of 1% between the ZFC and FC branches is observed.

Figure 1 shows the surface morphology of $YBa_2Cu_4O_8$ (124) sample detected using a SEM. The sample has a granular structure with a typical grain size of 2–3 μm. The picture shows smooth and uniform surfaces. The EDS analysis indicates that the bulk contains the stoichiometric composition of Y, Ba and Cu without additional phases. The composition was found to be uniform from grain to grain.

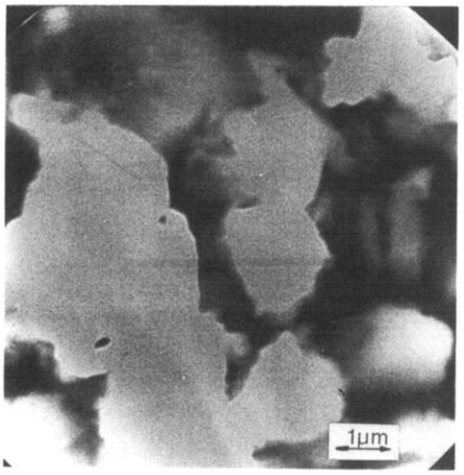

Fig. 1. SEM photograph showing the grain structure and voids in $YBa_2Ca_4O_8$. The scale bar marks 1 μm.

Superconducting diamagnetic transitions were studied on a VSM by measuring the temperature dependence of the Meissner susceptibility after cooling in constant fields of 30–40 Oe. Typical curves are shown in fig. 2. $YBa_2Cu_4O_8$ (124) exhibits Meissner flux expulsion at 81 K and no sign of the presence of the 123 phase is observed around 92 K. From the magnitude of the diamagnetic moment and assuming that the density of the sample is 6 g/cm^3, we deduce (without correcting for the demagnetization factor), a Meissner fraction [11] of approximately 23% at 4.2 K. For the Ca doped sample T_c is increased to 87 K.

The thermal stability of the 124 superconductor is much better than that of 123, since oxygen is neither lost nor gained during heating or cooling [1,2]. In order to confirm this finding, we heated a piece of 124 sample at 815°C for about two hours, then quenched the material to liquid nitrogen temperature. The superconducting properties of the quenched sample were retained, and the most striking phenomenon is that T_c for the quenched sample (labelled as q124 in fig. 2) is increased by about 2 K.

An example of the temperature dependence of the magnetization of $YBa_2Cu_4O_8$ in both FC and ZFC modes with a magnetic field of 50 Oe is shown in fig. 3. Also shown is the temperature dependence of the remanent magnetization obtained by turning off the

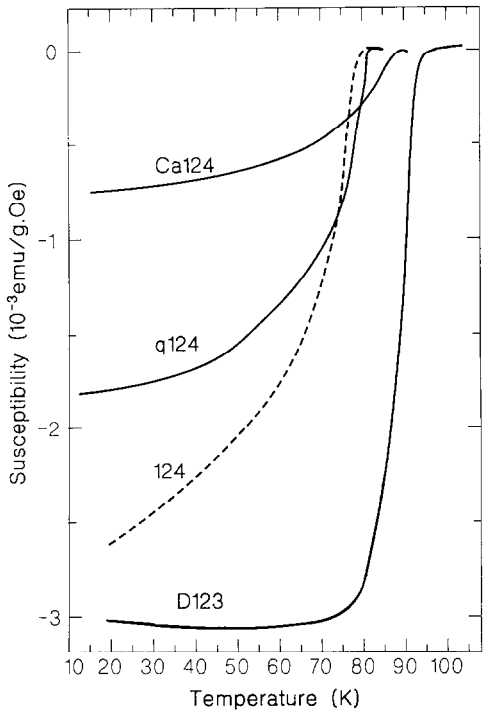

Fig. 2. Temperature dependence of the Meissner signal at 30–40 Oe for $YBa_2Cu_4O_8$ (124), $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ (Ca124), for 124 material quenched from 815°C (q124), and for 123 sample obtained by decomposition of 124 (D124) (see text).

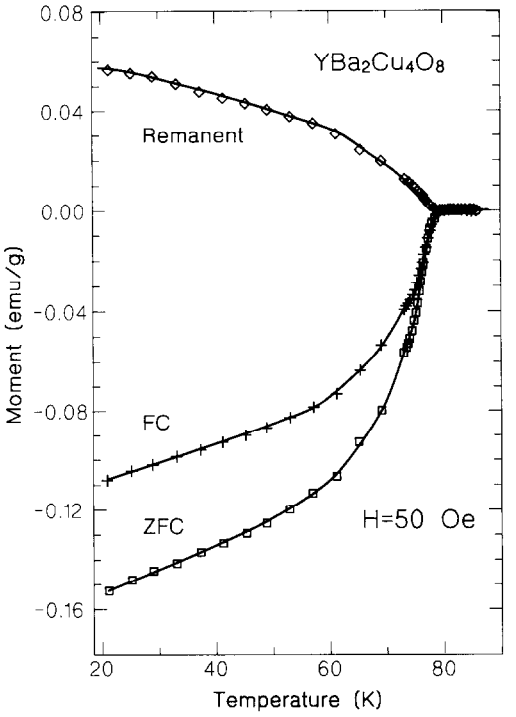

Fig. 3. ZFC, FC and remanent magnetization curves for $YBa_2Cu_4O_8$ at 50 Oe.

applied magnetic field after a FC process to low temperature. Similar curves were measured for various fields, up to 20 kOe. Above a field-dependent temperature T_{irr}, the ZFC and FC curves coincide, exhibiting a reversible region. The field dependence of T_{irr} is shown in fig. 4 in the form of a field versus reduced temperature phase diagram. For comparison, the irreversibility line for a ceramic 123 is also shown in fig. 4. The overall qualitative picture of these two curves is quite similar.

With the purpose of acquiring information about the critical current density J_c of pure 124 and Ca doped samples, we have measured the magnetic hysteresis up to 14 kOe (see fig. 5) at several temperatures following the methodology proposed by Kim et al. [12] and on the basis of Bean's approach [13]. In the Bean model $J_c(H) \propto \Delta M$, where ΔM is the difference in the magnetization measured at the same magnetic field H, when it is increasing or decreasing. $J_c(0)$ (in units of A/cm^2) is obtained from the remanent magnetization M_{rem} (in Gauss): $J_c = 30M_{rem}/R$ where R is a typical particle diameter. Note that the length scale is that of the grains, not the geometrical length scale, reflecting the break of intergrain links in the high-field limit of the hysteresis loop [14–16]. From M_{rem} obtained at 4.2 K and using an average size of 2 μm for the grains (see fig. 1), we get $J_c = 7.5 \times 10^5$ A/cm^2 for pure 124 and 4.0×10^5 A/cm^2 for the Ca 124 samples. The magnitude of J_c for 124 phase compares well with that reported by Jin et al. [17] and much higher than the J_c obtained in ref. [7]. Figure 6 summarizes the temperature dependence of M_{rem} for the 124 and Ca doped 124 samples. For comparison, fig. 6 also shows the temperature dependence of M_{rem} obtained for the 123 sample where the average size of grains is ~10 μm. At 4.2 K and $H=0$, the calculated $J_c = 6 \times 10^5$ A/cm^2 is roughly of the same magnitude as that for bulk 124 compound, consistent with the similar irreversibility lines of the 124 and 123 compounds mentioned above (fig. 4).

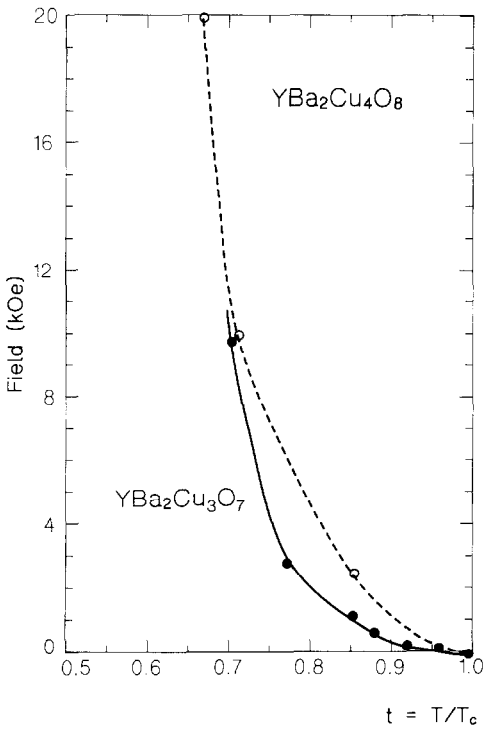

Fig. 4. The irreversibility line T_{irr} for $YBa_2Cu_4O_8$ (124) (dashed line) and ceramic $YBa_2Cu_3O_7$ (123). The reduced temperature $t \equiv T_{irr}/T_c$ is shown.

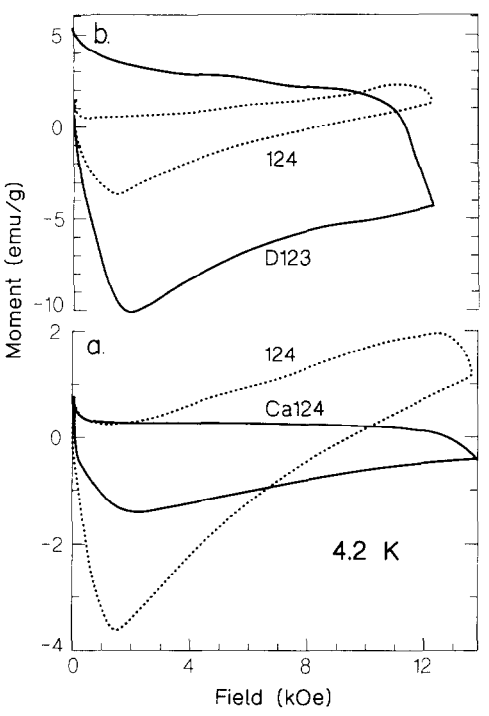

Fig. 5. (a) Magnetic hysteresis curves at 4.2 K for $YBa_2Cu_4O_8$ (124) and $Y_{0.9}Ca_{0.1}Ba_2Cu_4O_8$ (Ca124).
(b) Magnetic hysteresis curves at 4.2 K for pure 124 and for $YBa_2Cu_3O_7$ (D123) decomposed from 124.

The most informative experiments involve measurements of the $M(H)$ hysteresis loops at various temperatures. Figure 5(a) demonstrates the low temperature (4.2 K) cycles for 124 and Ca doped 124 samples. Two features are readily observed in the figure: (i) The applied field position of the minimum in the virgin curves is almost unshifted; and (ii) ΔM for a given field is much larger in the pure 124 sample. $M(H)$ at various temperatures (4.2–75 K) was measured for both samples, and M_{rem} values are exhibited in fig. 6 as a function of temperature. Qualitatively the two curves exhibit the familiar fast decrease of M_{rem} with temperature found in other high-T_c superconducting materials [18,19]. However, it is apparent from fig. 6 that M_{rem} values for pure 124 are higher than those of Ca doped 124. For a wide range of temperatures M_{rem} is proportional to $T^{-\alpha}$ with a similar α (1.6) for both materials. Direct measurements of $J_c(T)$ are of course essential to verify this relation.

The conversion of 124 to 123 was studied extensively by Morris et al. [8]. They found that at ambient pressure, the time scale is only a few minutes at elevated temperatures. We heated a piece of 124 material for 2 min at 920°C, and then quenched the sample to liquid nitrogen temperature. The sample was annealed at 500°C under flowing oxygen for a few hours and cooled slowly to ambient temperature. X-ray diffraction measurements show that only the characteristic peaks of the 123 phase and the lines corresponding to CuO are present. T_c of the material is 92 K and fig. 2 presents the Meissner FC signal measured at 40 Oe (labelled as D 123). The absence of a diamagnetic signal at 80 K also indicates that the conversion to 123 is completed. The surface morphology of D123 detected by a SEM show that the average size of the grains in the 123 phase remains 2 μm. This value is smaller by approximately a factor of 5 than the typical grain size in a 123 phase prepared in a conventional manner.

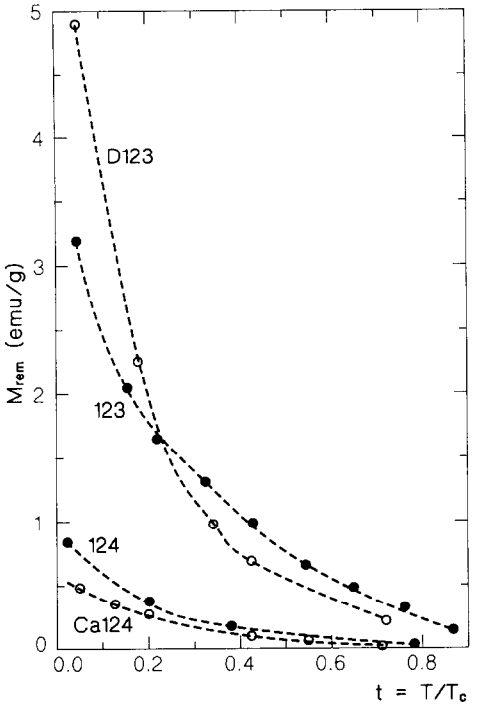

Fig. 6. Remanent magnetization M_{rem} as a function of the reduced temperature for 124, Ca124, 123 and D123 samples.

The most striking phenomena related to D123 are shown in fig. 5(b) and fig. 6. Figure 5(b) illustrates typical magnetic hysteresis curves at 4.2 K for 124 and D123. (The 124 curves in fig. 5(a) and (b) correspond to the same measurement but on different scales.) M_{rem} values obtained at various temperatures are shown in fig. 6. Since the length scale of grains for 124 and D123 is practically unchanged, a huge increase in J_c is obtained. For example, at 4.2 K and $H=0$, $J_c=4.5\times10^6$ A/cm^2. Direct measurements of $J_c(T)$ are of course essential to verify these phenomena.

The phase stability boundaries of the 123 and 124 phase at various oxygen pressures at high temperatures have shown that conversion of 124 into 123+CuO phases occurs at low oxygen pressures [8]. The enhanced J_c in the converted D123 sample is probably due to flux pinning by small inclusions of nonsuperconducting CuO within the superconducting 123 grains converted from 124. In fact, the most important use for the 124 compound ($T_c=80$ K) may be as a precursor for the preparation of 123 with small grain sizes. After synthesis of single phase 124, subsequent short thermal treatment in air would remove enough oxygen to cause the 124 to convert into 123 plus excess CuO, and to produce CuO islands and highly strained local regions, both of which may act as flux pinning centers.

Acknowledgement

This research was supported by Grant No. 3198189 from the Ministry of Science and Technology.

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