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Microstructural, electrical and magnetic properties of $NdBa_2Cu_3O_{7-\delta}$ prepared from BaO_2

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$NdBa_2Cu_3O_{7-\delta}$ was synthesized in oxygen from a stoichiometric mixture of Nd_2O_3, BaO_2 and CuO between 890 and 1070 °C. The resulting material was composed of small crystals of $NdBa_2Cu_3O_{7-\delta}$ (2 to 10 μm) and of $BaCuO_2$ as a secondary phase. The effect of the synthesis temperature on the normal-state resistivity, the critical current density and the magnetic susceptibility was investigated. The highest J_c values (175 A cm^{-2}) were measured in samples treated between 1010 and 1050 °C.

1. Introduction

Among all the processes employed to produce $YBa_2Cu_3O_{7-\delta}$ superconductors, the solid-state reaction is the most often used. In this process, Y_2O_3, CuO and $BaCO_3$ powders are mixed and calcined near 950 °C to form $YBa_2Cu_3O_{7-\delta}$. One of the most important disadvantage of this technique is the difficulty of obtaining complete decomposition of the carbonate, which tends to stay at the grain boundaries where it hampers the passage of current between superconducting grains. One way to minimize the residual carbonate is to substitute BaO_2 for $BaCO_3$ [1]. This method has been successfully used to synthesize $YBa_2Cu_3O_{7-\delta}$ [1–3]. However, little is known about the synthesis of $RBa_2Cu_3O_{7-\delta}$ (R = lanthanides except Pr and Ce) using BaO_2. Previous results have shown that the phase diagrams of Nd–Ba–Cu–O and Gd–Ba–Cu–O are different from that of the Y–Ba–Cu–O system [4–6]. In this work, some properties and microstructural aspects of $NdBa_2Cu_3O_{7-\delta}$ obtained using the peroxide route are reported.

2. Materials and methods

Nd_2O_3, CuO (99.999% purity) and BaO_2 (99%) powders were sieved to − 32 μm, weighed and mixed under dry nitrogen to avoid the formation of $BaCO_3$ [7]. Green pellets were obtained by pressing the mixture at 200 MPa and afterwards heated up to the chosen reaction temperature at a rate of 4 °C min^{-1} and kept at that temperature for 24 h before cooling to 400 °C at a rate of 2 °C min^{-1}. Flowing oxygen was used during the heat treatments.

Resistivity measurements were obtained using the conventional four-point-probe method. The critical current measurements (J_c) were performed in boiling liquid nitrogen using 12 mm × 2 mm × 2 mm bars cut from sintered pellets. Four electrical contacts were made by sputter-depositing a gold layer on the pellet surface, forming four conducting pads on which copper wires were attached using an indium solder [8]. The J_c values were obtained when a difference of 1 μV appeared between the two voltage contacts.

A.c. susceptibility measurements were carried out on powdered samples. The powders were sieved through a 38 μm screen and about 0.3 g were placed in the susceptometer. The amplitude b_0 of the a.c. field was 33 μT and the frequency was 27 Hz. A constant field B up to 25 mT could be superimposed on the a.c. field. There was no shield around the susceptometer to reduce the Earth's field in the measurement volume.

X-ray diffraction analysis was performed using the Cu$K\alpha$ line. Energy-dispersive X-ray (EDX) analyses were obtained with a standardless software whose expected accuracy was of the order of a few per cent.

3. Results

$NdBa_2Cu_3O_{7-\delta}$ phase is obtained after a synthesis step at a temperature as low as 890 °C, confirming the high reactivity of BaO_2. However, at this temperature X-ray diffraction analysis reveals that Nd_2BaCuO_5 and $BaCuO_2$ are present as secondary phases (Fig. 1). The amount of Nd_2BaCuO_5 can be reduced by heating at a higher temperature. For treatments above 910 °C, only the $NdBa_2Cu_3O_{7-\delta}$ and $BaCuO_2$ phases are detected. In fact $BaCuO_2$ is a secondary phase found in all samples.

The effect of the synthesis temperature on the sample microstructure is shown in Fig. 2. A gradual density increase occurs when samples are heated from

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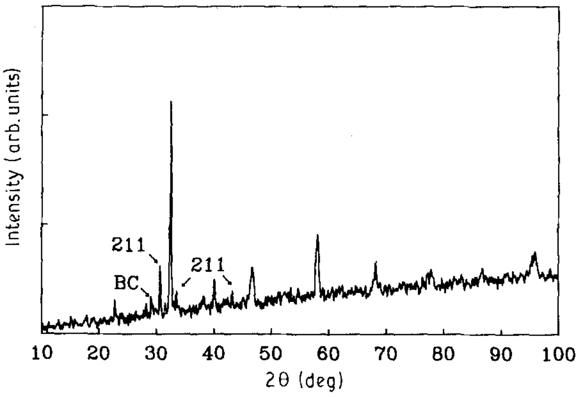

Figure 1 X-ray diffraction pattern of a mixture of Nd_2O_3, CuO and BaO_2 powders synthesized at 890 °C. BC and 211 correspond to $BaCuO_2$ and Nd_2BaCuO_5, respectively.

910 to 1070 °C. The $BaCuO_2$ distribution within samples varies with the heat treatment. Large islands of $BaCuO_2$, marked by an arrow on Fig. 2, are found in samples treated at 910 °C. The $BaCuO_2$ is found near the pores in samples treated at intermediary temperatures and between crystals in denser samples treated from 1030 to 1070 °C. Samples treated above 1070 °C are severely deformed and are unusable. The melting point of $NdBa_2Cu_3O_{7-\delta}$ is reported to be 1107 °C in oxygen [5].

$NdBa_2Cu_3O_{7-\delta}$ sample microstructures observed under polarized light (Fig. 3) reveal that the grain size distribution is only slightly affected by the heat-treatment temperature. Grains smaller than 10 µm compose samples treated below 1010 °C. Grains begin to grow at 1030 °C and biggest ones reach a maximum size of 15 µm at 1070 °C.

The sample superconducting transition temperature (T_c) determined by resistivity measurements is not strongly affected by the synthesis temperature (Table I). The T_c values are relatively low, but a similar decrease of T_c has been observed for $YBa_2Cu_3O_{7-\delta}$ obtained using BaO_2 [1–3]. On the other hand, the resistivity in the normal state varies significantly with the synthesis temperature (Fig. 4). The material resistivity decreases with the synthesis temperature from 890 to 1050 °C but increases at 1070 °C. Samples treated at 1030 and 1050 °C present the lowest value of resistivity, which is 360 µΩ cm at 100 K. This value is comparable to the value of 320 µΩ cm reported for $YBa_2Cu_3O_{7-\delta}$ synthesized using BaO_2 [7].

Magnetic susceptibility data are plotted in Fig. 5 as a function of temperature from 15 to 120 K. Results are normalized to $\chi' = -1$ for the value measured at 15 K with the sample synthetized at 950 °C. The superconducting transition onsets are not significantly affected by the synthesis temperature as observed for the resistivity measurements. However, the magnitude of the a.c. susceptibility signal increases rapidly with the synthesis temperature. This is illustrated in Fig. 6 where the magnitude of the susceptibility signal $|\chi'|$ at 77 K is drawn as a function of the synthesis temperature. The signal $|\chi'|$ increases rapidly and reaches about 0.7 as the treatment temperature increases from 890 to 950 °C. The signal magnitude is about constant for treatment temperatures ranging from 950 to

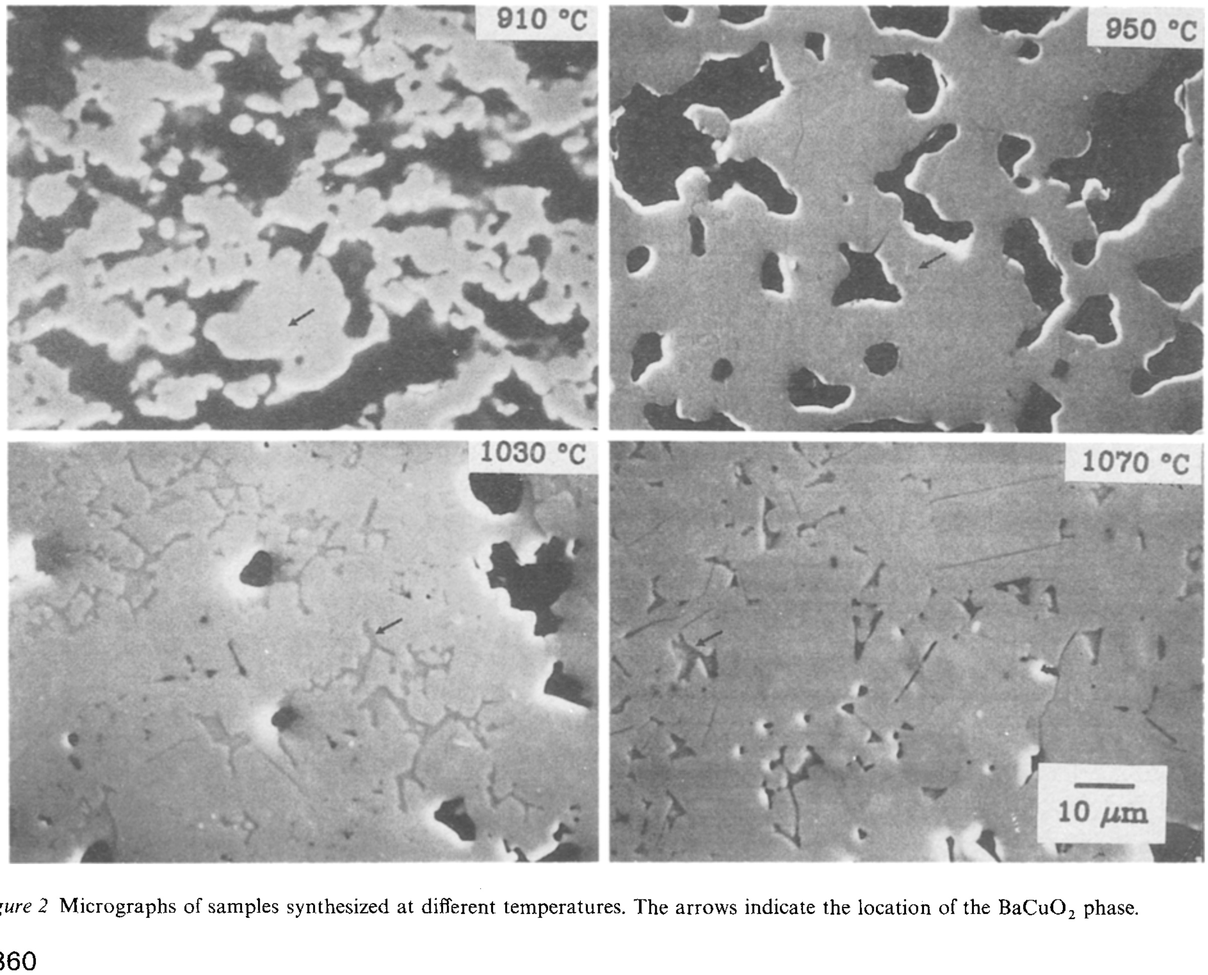

Figure 2 Micrographs of samples synthesized at different temperatures. The arrows indicate the location of the $BaCuO_2$ phase.

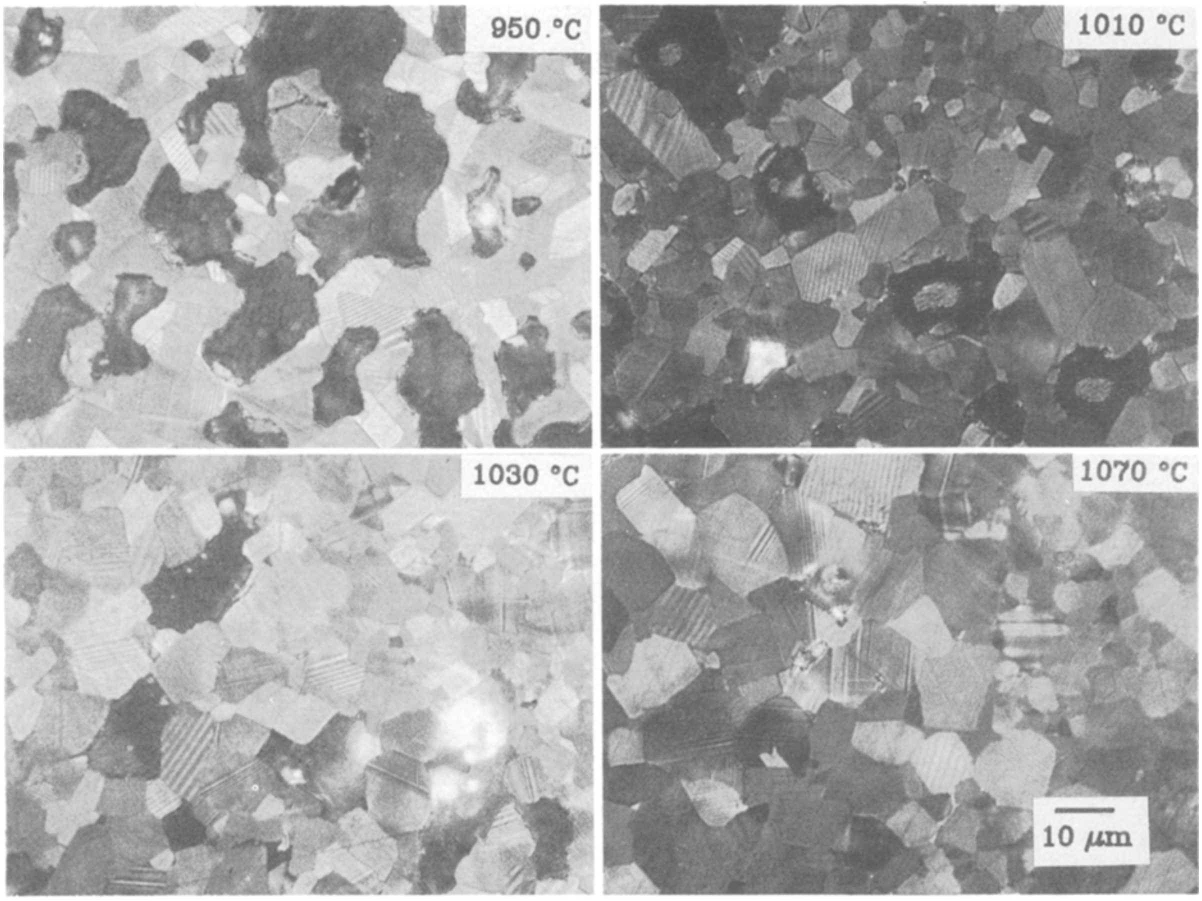

Figure 3 Micrographs under polarized light of samples synthesized at different temperatures.

TABLE I Characteristics of the superconducting transition in $NdBa_2Cu_3O_{7-\delta}$ from resistivity measurements

Heat treatment temperature (°C)	T_c ($R = 0$) (K)	ΔT (K)
890	88.4	3.0
910	88.8	3.0
930	91.8	1.0
960	91.8	1.0
970	91.0	1.1
990	90.4	1.1
1010	91.8	0.9
1030	91.4	0.9
1050	91.8	0.6
1070	90.0	1.5

1010 °C and then increases with temperature up to 1050 °C.

For all treatment temperatures, the signal magnitude is lowered when a d.c. field $B = 24$ mT is superimposed. In that case, the signal increases rapidly with temperature from 890 to 970 °C and then decreases gradually with the treatment temperature. The signal increase noted in a zero d.c. field, and absent when $B = 24$ mT for treatments at 1030 and 1050 °C, may be due to the higher density of these samples (Figs 2 and 3). Indeed, closed porosity tends to be maximum when the total porosity is relatively low (5 to 10%) [9] and screening intergrain currents flowing in the superconducting powders may shield closed pores when only a weak 33 μT a.c. field is applied, leading to a larger apparent susceptibility value. It is also worth noting that if intrinsic critical currents inside grains are large enough, the flux-penetration depth of the weak a.c. field ($b_0 = 33$ μT) is small compared with the

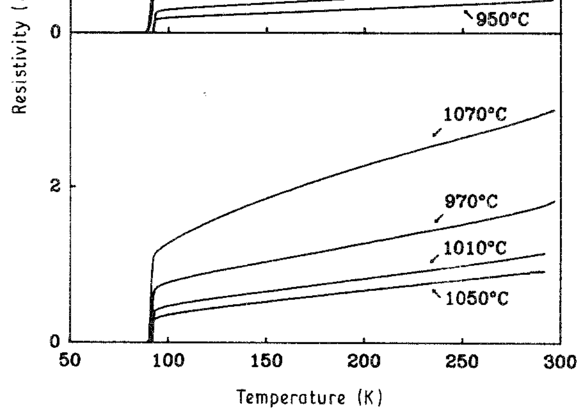

Figure 4 Resistivity–temperature curves of samples treated at different temperatures.

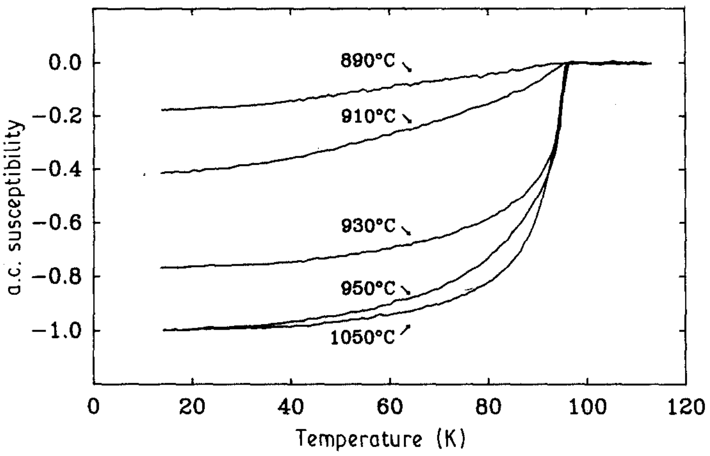

Figure 5 A.c. magnetic susceptibility as a function of temperature for samples synthesized at different temperatures.

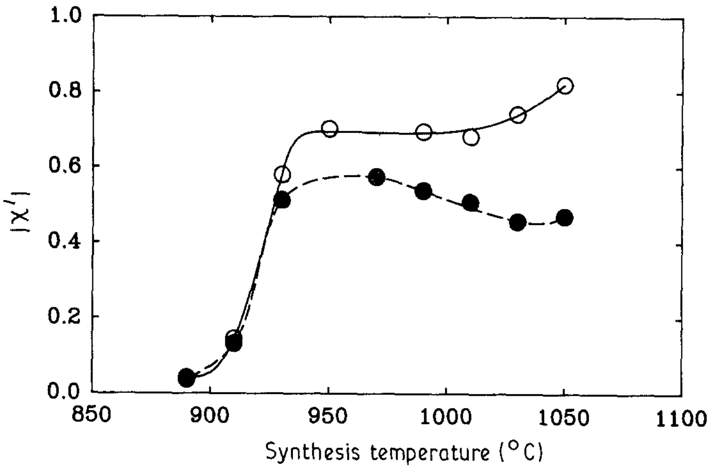

Figure 6 Magnitude of the a.c. susceptibility signal $|\chi'|$ at 77 K as a function of the synthesis temperature in a d.c. field of (○) 0 mT and (●) 24 mT.

sample grain size [10, 11] and the $|\chi'|$ signal is proportional to the superconducting volume in a pore-free powder [10].

Fig. 7 depicts the effect of the synthesis temperature on J_c. Roughly, J_c increases with the synthesis temperature from 930 to 1010 °C and then decreases at higher temperatures. In fact, J_c is related to the material resistivity as shown in Fig. 8, where the measured J_c values are plotted as a function of the resistivity values obtained at 100 K for all samples.

4. Discussion

The room-temperature sample resistivity decreases with the synthesis temperature up to 1050 °C. This is related to a magnitude increase of the a.c. susceptibility signal from 890 to 950 °C and to an important density increase for the whole temperature range investigated in the present study. The lowest measured resistivity is 920 μΩ cm, which is still about five times the expected value for a single crystal of $YBa_2Cu_3O_{7-\delta}$ [12]. However, the resistivity of an $NdBa_2Cu_3O_{7-\delta}$ single crystal may be higher because of the possible substitution of Nd^{3+} on the Ba^{2+} sites. It is reported that the resistivity in the normal state increases by a factor of three when 2.5% of the barium sites are occupied by Nd^{3+} ions [13].

Similarly to $YBa_2Cu_3O_{7-\delta}$, many factors can increase the resistivity of polycrystalline $NdBa_2Cu_3O_{7-\delta}$ samples. One of these factors is the random orientation of crystals for which the resistivity along the *ab* plane is different from that along the *c*-axis. This anisotropy has been estimated to double the resistivity of polycrystalline $YBa_2Cu_3O_{7-\delta}$ samples [12]. The presence of a non-conducting secondary phase at the grain boundary is another factor that can increase the sample resistivity. $BaCuO_2$ is one of these phases and has been found in all $NdBa_2Cu_3O_{7-\delta}$ samples. $BaCuO_2$ is a normal intermediary in the formation of $YBa_2Cu_3O_{7-\delta}$. It forms in a few minutes from reaction between CuO and BaO and then reacts rapidly with Y_2O_3, and CuO to produce the $YBa_2Cu_3O_{7-\delta}$ compound [14]. The behaviour is different in the Nd–Ba–Cu–O system. $BaCuO_2$ is formed as an intermediary of the reaction but is found in a relatively large amount in the final product. The presence of $BaCuO_2$ can be due to the low diffusion rate of the intermediaries or to a different equilibrium in the phase diagram of the Nd–Ba–Cu–O system. Other phases such as carbonate also increase the sample resistivity and have been found at the grain boundaries of polycrystalline $YBa_2Cu_3O_{7-\delta}$. Even though carbonate has not been used in the preparation process of our $NdBa_2Cu_3O_{7-\delta}$ samples, it is not excluded that it could have formed in small amounts during measurements which involved an exposure to atmospheric CO_2.

Factors that increase the resistivity of polycrystalline samples have a decreasing effect on J_c. It is expected that the magnitude of the effect of each factor on J_c could be different for the resistivity. For example, the presence of a thin layer of carbonate at the

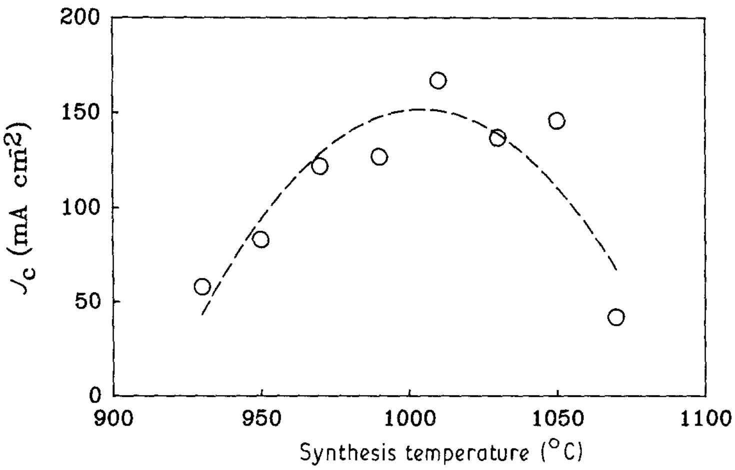

Figure 7 Relation between J_c and the sample synthesis temperature.

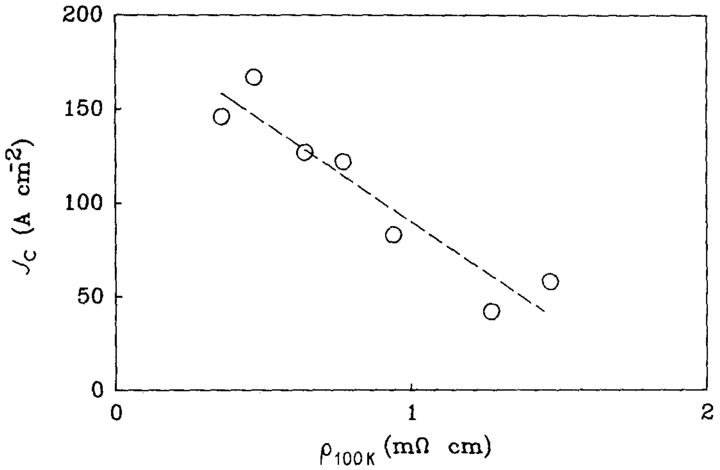

Figure 8 Relation between J_c and the sample resistivity at 100 K.

grain boundaries could hamper the tunnelling of electrons and reduce J_c by many orders of magnitude but affect the resistivity only by a geometrical factor. However, a relation exists between the resistivity and J_c in our samples (Fig. 5). This relation is approximately direct: the resistivity decreases by a factor of two when J_c doubles. Such a relation could be expected for variations of sample density without substantial modifications of grain size and the nature of the interface between grains. Thus, the observed variation of J_c with the synthesis temperature is likely to be mostly related to material densification, leading to an increase of the conduction cross-section.

It is worth noting that our J_c values remain low in comparison with the 1000 A cm^{-2} obtained for a random polycrystalline material produced by tape-casting of slurries of $YBa_2Cu_3O_7$ powder [15]. Different causes may explain these low J_c values. Among them the presence of a very thin carbon or carbonate film at the grain boundaries may not be rejected, even if BaO_2 is used as starting material instead of $BaCO_3$. Moreover, the secondary $BaCuO_2$ phase observed in all of our samples is possibly responsible to a large extent for the low J_c values. This phase was not detected in such a large amount in $YBa_2Cu_3O_7$ samples produced by the same method [7]. It is likely that the amount of $BaCuO_2$ can be reduced if a longer heat-treatment and intermediary grindings were carried out to permit a more complete reaction of the starting powders.

5. Conclusions

Superconducting $NdBa_2Cu_3O_{7-\delta}$ samples can be obtained by the peroxide route using a synthesis treatment between 890 and 1070 °C. However, all samples contain $BaCuO_2$ as a secondary phase. A direct relation exists between the resistivity in the normal state and the critical current in the superconducting state. This relation is attributed to the densification of the material which occurs during the heat treatment. The measured J_c values are relatively low, due in part to the presence of the $BaCuO_2$ as a secondary phase.

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