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Superconductivities of *n*-type $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ prepared under high pressure

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In this work we provide the report on the preparation of a bulk *n*-type NdCeCuO superconductor using a high-pressure high-temperature sintering procedure. The superconductor was obtained by sintering as-prepared material at 4.0 GPa at 530 °C for 20 min and required no additional reducing treating. The sample shows a higher onset temperature T_{con} (32 K), a higher zero resistance temperature T_{c0} (22 K), and a much lower resistivity than a standard bulk sample. Indeed the room-temperature resistivity and the quasimetallic resistivity in the normal state for our polycrystalline sample are similar to those of single crystals. This high-pressure sintering procedure reduces weak link effects and opens the possibility of preparing high-quality bulk *n*-type superconductors.

Since the discovery of the copper-based oxide superconductors, much effort has been made to increase the density and to improve the weak link character of ceramic superconductors using high-pressure sintering, hot pressing, and hot isostatic pressing. Unfortunately, in *p*-type systems, such as LaSrCuO, YBaCuO, BiSrCaCuO, and TlBaCaCuO,[1–5] almost all pressure treatments in air have degraded the superconducting properties. One reason is that the high-pressure and high-temperature reaction reduces these materials and leads to an oxygen deficiency that is deleterious to the *p*-type superconducting phase.

In early 1989, a new kind of copper-based oxide superconductor, $Nd_{2-x}Ce_xCuO_{4-y}$, was reported.[6] Unlike *p*-type superconductors showing hole-like carriers, $Nd_{2-x}Ce_xCuO_{4-y}$ showed electron-type conduction. In order to form the superconducting phase with a T' structure, the new system had to be annealed in a reducing environment. In general, it has been found to be very difficult to fabricate *n*-type superconductors of similar quality to *p* type. Since high pressure provides an appropriate reducing environment that is favorable to the formation of the *n*-type superconducting phase, we decided to investigate whether a high-pressure, high-temperature treatment is a useful process for improving the quality of this kind of high T_c materials. In this letter we report the fabrication of high-density, high-quality bulk material of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ by directly treating the as-prepared sample under 4.0 GPa at 530 °C for a short time. Possible reasons for the high-pressure, high-temperature procedure's improved superconductivity in this *n*-type material are suggested.

With a nominal composition of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$, very pure powders of Nd_2O_3, CeO_2, and CuO were homogeneously mixed, and sintered in a muffle furnace at 1100–1150 °C for 50 h in air. The sample was ground and sintered at 1100 °C for 40 h, and finally cooled down to room temperature. The resultant material was pressed into the pellets, and sintered again at 1050 °C for 20 h. These as-prepared pellets were not superconducting. The pellets were directly treated under 4.0 GPa at 530 °C for 20 min, then quenched from high temperature by turning off the electric power and finally released from the high-pressure cell. The high pressure was generated using a 3500 ton press, which drives synchronously the six tungsten carbide anvils and produced a uniform pressure on the six faces of the sample cell. The sample was heated by a graphite tube, which was mounted in a cubic pyrophilite. The sample was wrapped by silver foil to prevent contamination by the pressure transfer medium. The temperature was measured by a NiCr-NiAl thermocouple mounted near the sample. The resistance was measured by the standard four-probe method. Since the sample is very hard, we found it very difficult to make electrical contact. As such, we cut the silver foil that covered the pressed sample to provide electrodes.

Figure 1 illustrates the results of resistance measurements for the high-pressure sintered sample of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (curve a). For comparison, Fig. 1 also gives a typical result for conventional bulk material (produced by annealing the as-prepared $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ pellet in flowing N_2 at about 890 °C for several hours) (curve b) and the result of the single crystal reported by Tarascon *et al.*[6] (curve c). From Fig. 1 it is clear that the high-pressure sintered polycrystalline sample shows a re-

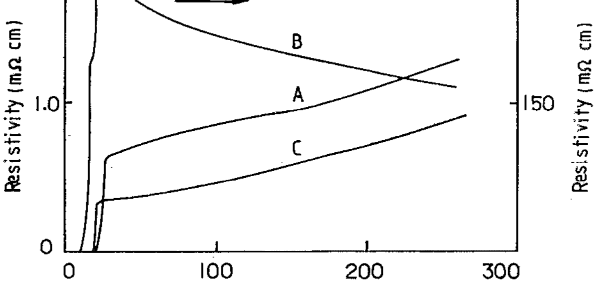

FIG. 1. Resistance dependence on temperature: (a) high-pressure sintered bulk, (b) conventional bulk, (c) the single crystal.

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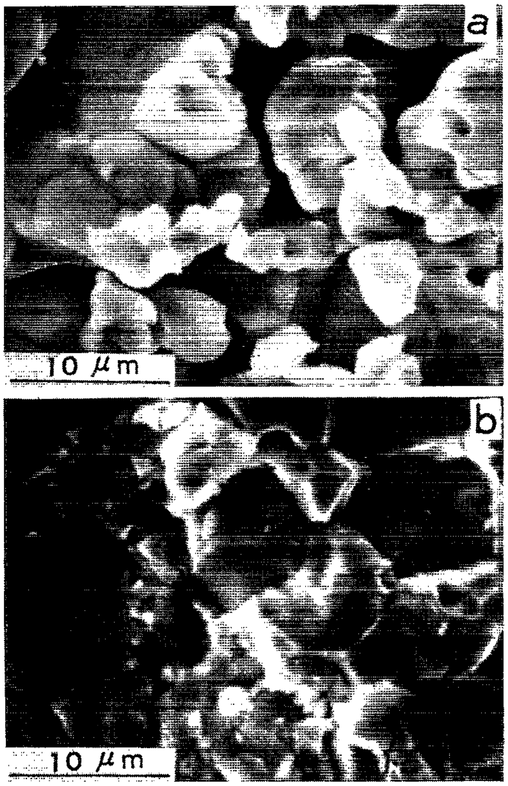

FIG. 2. Scanning electron microscopy photograph of a fracture section for (a) the conventional and (b) high-pressure sintered sample.

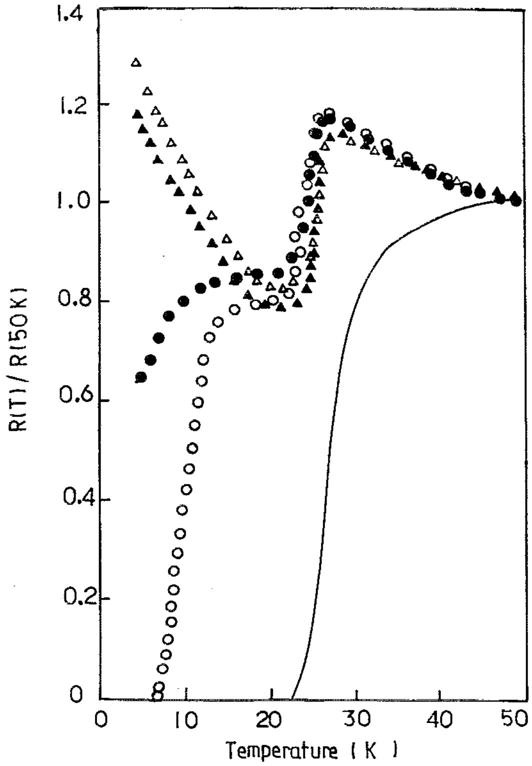

FIG. 3. Resistance dependence on temperature for a typical conventional bulk at different measuring currents: 10 μA (○), 100 μA (●), 1 mA (▲), 10 mA (△), and the high-pressure sintered sample (solid line).

sistance behavior similar to that of the single crystal and in marked contrast to that of the conventional polycrystalline material. The most important feature of the high-pressure sintered sample is the quasimetallic resistivity in the normal state, like the single crystal, in stark contrast to the strong semiconducting-like behavior in the conventional bulk material.[7–9]

Furthermore, the high-pressure sintered sample shows a small resistivity at normal state. It is of the same order of magnitude as the single crystal and is about two orders of magnitude lower than that of the conventional bulk material. In addition, its resistivity exhibits a sharp drop at the transition temperature, just like the single crystal. Finally, the pressure sintered sample also shows a marginally higher critical temperature, with an onset temperature T_{con} of 32 K and a zero resistance temperature T_{c0} of 22 K, compared to the T_{con} and the T_{c0} reported for the conventional bulk and the single-crystal values which are usually lower than 30 K and 20 K, respectively.

It is generally accepted now that the superconducting properties of the ceramic oxide superconductors are very dependent on microstructure. Hence, we conclude that the poor superconducting properties in conventional *n*-type bulk materials, as compared to single crystals, are due to the poor grain boundaries. That the pressure sintered sample shows electronic characteristics similar to single crystals implies high-pressure processing improves their intergranular properties. In fact, cold pressing does not improve coupling between grains; moreover, it degrades the superconductivity.[10,11] But high-pressure sintering not only increases the density, but also promotes the intergranular coupling by thermal diffusion, like diffusion welding. An investigation of the microstructure of both conventional and high-pressure sintered samples of $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ carried out using scanning electron microscopy is consistent with this interpretation. Figure 2 shows scanning electron microscopy photographs of a fracture section. From Fig. 2 it is clear that the conventional sample is porous, while the high sintered sample is dense. The density of the high-pressure sintered sample is 94% of the theoretical value (7.3 g/cm^3).

It has been well documented that the grain boundaries in the high T_c superconductors can act as Josephson-type weak links, which are strongly influenced by magnetic field or measuring current.[11,12] Figure 3 gives the resistance measurements of a typical conventional sample at various measuring currents: 10 μA (○), 100 μA (●), 1 mA (▲), and 10 mA(△), and the high-pressure sintered sample at 100 mA (the highest current we could apply to the sample). Figure 3 demonstrates that with increasing measuring current, the transition process for the conventional sample undergoes a remarkable change: from the double structured drop in resistance (low measuring current) to a quasireentrant form (high measuring current), similar to the result of the *n*-type $Sm_{1.85}Ce_{0.15}CuO_{4-y}$ reported by Gerber *et al.*,[12] and also to those of the *p*-type Bi(Pb)SrCaCuO.[10,11] The first drop at T_c (onset) caused by the intragranular part does not change its profile very much for all the measuring currents. While the second drop at T_{cj} (Josephson temperature) caused by the grain boundary (which is a function of the Josephson-type coupling) changes considerably from the dropping at low current to increasing at high current. In contrast, the sharp resistance drop of the high-pressure sintered sample does not change much even at the highest measuring current of 100 mA. These results demonstrate that well-coupled grains have been fabricated in the high-pressure sintered sample with improved weak links. A possible explanation for the influence of high-pressure sintering on the superconductivity of *n*-type $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ is as following. Uniform cerium concentration[13] and oxygen content in the grain boundary play an important role in the superconductivity of this kind of material. The strong Ce—O bond, which suppresses cerium diffusion during annealing, may be easily broken under high pressure. As such, high pressure promotes the diffusion and homogeneous distribution of cerium. Moreover, under high pressure no oxygen accumulates in the grain boundaries, therefore during cooling no extra oxygen will return to lattice. As a result, the high-pressure sintered sample has narrow and clean grain boundaries.

In summary, high-quality $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ bulk material can be directly obtained by sintering the as-prepared material under high pressure. This is a successful example of using high-pressure sintering in air to improve the superconductivity of the copper-based oxide superconductors although Lopez-Morales *et al.*[13] prepared an *n*-type superconductor using two steps under ambient atmosphere. High pressure greatly improves the properties of the weak links between the grains, accelerates diffusion and lowers the sintering temperature. We conclude that high-pressure sintering is an excellent method for preparing *n*-type superconductors.

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