A method for preparing superconducting single crystals of $Ba_2GdCu_3O_{7-y}$

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(Received 24 March 1988; accepted for publication 13 June 1988)

A method has been developed for growing single crystals of $Ba_2GdCu_3O_{7-y}$ of much larger size ($\sim 2\times3\times6$ mm^3). The crystals as grown were semiconductors and became superconductors with a zero resistance temperature of 92 K after they were annealed in flowing oxygen. Good x-ray diffraction and Laue patterns were obtained from a superconducting crystal ($\sim 2\times3\times4$ mm^3) that was cleaved in (001) plane, and lattice constants were determined to be $a = 3.8401$ Å, $b = 3.9007$ Å, and $c = 11.7104$ Å.

A single crystal of $Ba_2YCu_3O_{7-y}$ with a size of about $1\times1\times0.3$ mm^3 was grown from nonstoichiometric melts.[1] Some small single crystals ($\sim 0.035\times0.02\times0.07$ mm^3) were picked from sintered pellets.[2] The limited crystal size prevented the thorough measurement of the physical properties of this interesting material. Thus, it is necessary to obtain single crystals with a much larger size for further understanding of the novel superconductivity as well as for its practical uses. In this communication we described a method for preparing single crystals of $Ba_2GdCu_3O_{7-y}$ of a much larger size ($\sim 2\times3\times6$ mm^3). Good x-ray diffraction and Laue patterns were obtained from a superconducting crystal ($\sim 2\times3\times4$ mm^3) with a cleaved plane (001) along which resistance was measured showing metallic behavior in the normal state and superconductivity at 92 K.

Powders of $BaCO_3$ (99.99%), Gd_2O_3 (99.99%), and CuO (99%) in a ratio of Ba:Gd:Cu = 2:1:3 were thoroughly ground, reacted in air at 930 °C for 24 h, and then cooled to room temperature within about 10 h. The powders were reground and pressed into pellets with a diameter of 20 mm and a thickness of 2–3 mm. The following procedures for preparing single crystals can be described as

$$1005\,^\circ\mathrm{C}(2\,\mathrm{h}) \xrightarrow{2\,^\circ\mathrm{C/h}} 980\,^\circ\mathrm{C}(48\,\mathrm{h}) \xrightarrow{2\,^\circ\mathrm{C/h}} 940\,^\circ\mathrm{C}(8\,\mathrm{h})$$

$$\xrightarrow{2\,^\circ\mathrm{C/h}} 900\,^\circ\mathrm{C}(8\,\mathrm{h}) \xrightarrow{5\,^\circ\mathrm{C/h}} 850\,^\circ\mathrm{C}(8\,\mathrm{h})$$

$$\xrightarrow{5\,^\circ\mathrm{C/h}} 750\,^\circ\mathrm{C}(24\,\mathrm{h}) \xrightarrow{50\,^\circ\mathrm{C/h}} 550\,^\circ\mathrm{C}(24\,\mathrm{h})$$

$$\xrightarrow{3\,^\circ\mathrm{C/h}} 400\,^\circ\mathrm{C} \xrightarrow{\text{oven cooled}} \text{room temperature.}$$

After these procedures, about 10 pieces of single crystals were grown in a pellet and the largest one had a size of about $2\times3\times6$ mm^3. They all exhibited semiconducting behavior and had no superconductivity. To obtain superconductivity in these crystals, we annealed them at 550 °C in flowing oxygen for 72 h.

X-ray diffraction analysis was conducted on an oxygen-annealed single crystal of $2\times3\times4$ mm^3 size. The direction of the Cu$K\alpha$ radiation is perpendicular to a cleaved plane of the crystal. The diffraction pattern obtained is shown in Fig. 1. The pattern reveals all the 14 grades of diffraction peaks of the (001) cleaved plane. They can be indexed as (001), (002), ... (0014). The split of the peaks as shown in the pattern can be attributed to the slightly different radiations of the $K\alpha_1$ and $K\alpha_2$ which correspond to different intensities with a ratio of about 2:1. The lattice constant along the c axis can be determined as c = 11.7104 Å by least-square fitting.

In Fig. 2 we show another x-ray diffraction pattern which was obtained from another plane of the crystal. The larger split of these peaks gives some evidence of twinning in the crystal with an orthorhombic structure. By least-square fitting to the (200), (300), (400), (020), (030), and (040) peaks, we obtained the lattice constants as a = 3.8401 Å and b = 3.9007 Å, some larger than those in $Ba_2YCu_3O_{7-y}$.[3]

To confirm that the sample is a single crystal as a whole, we obtained the Laue patterns at three sites which translated 1 mm from each other along the direction parallel to the larger edge. The radiation is also perpendicular to the (001) plane. The interesting result is that these patterns are completely identical, meaning that the sample is a crystal as a whole. The typical Laue pattern is shown in Fig. 3. The pattern has C_4 symmetry and does not give noticeable orthorhombic features, possibly due to smaller orthorhombic distortion or to a twin structure. On the basis of the lattice constants as determined above, the pattern can be indexed as A(413), B(111), C(423), D(343), E(356), F(132), K(223), P(403), Q(101), where A, B, C,...,Q correspond to the dots in the Laue pattern.

To characterize the electrical quality of the annealed crystal, we measured its resistance with a standard four-probe technique. The four electrodes were easily attached on

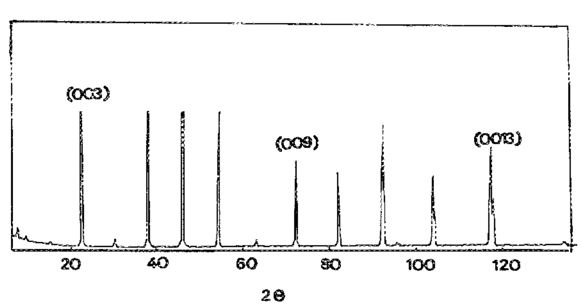

FIG. 1. X-ray diffraction pattern for a single crystal with a size of $2\times3\times4$ mm^3. The radiation is perpendicular to the cleaved plane (001).

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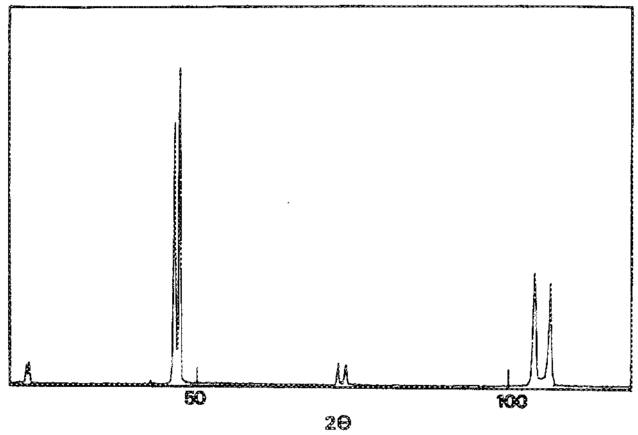

FIG. 2. X-ray diffraction pattern which was obtained from a plane normal to the (001) plane.

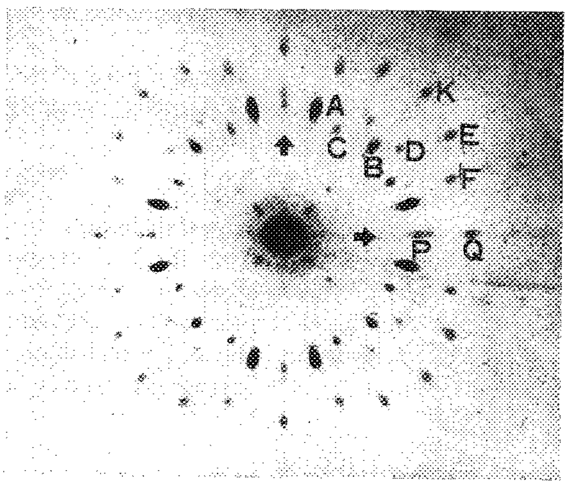

FIG. 3. Laue pattern for the oxygen-annealed single crystal.

the (001) plane of the crystal with Ag paint due to its larger size. Figure 4 shows temperature dependence of the resistance for the oxygen-annealed crystal. It has much larger room-temperature resistivity than the superconducting polycrystal[4] and exhibits good superconductivity with T_c

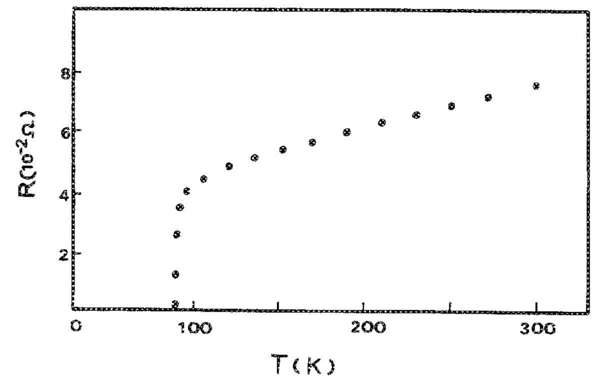

FIG. 4. Temperature dependence of the resistance of the single crystal. The four electrodes were attached on the (001) plane.

(onset) = 96.0 K, T_c(mid) = 94.0 K, $T_c(\rho = 0) = 92.0$ K, and $\Delta T_c = 1.0$ K. The larger resistivity in the single crystal may be due to smaller fraction of superconducting volume. Duan *et al.* have shown that the superconductivity may occur only in the thin shell of single crystals of $Ba_2YCu_3O_{7-y}$, possibly due to insufficient oxygen contents in the interior. However, the unambiguous split of the diffraction peaks in Fig. 2 indicates that a large fraction of the crystal has the orthorhombic structure and thus a large fraction of the crystal should have high T_c superconductivity. Thus, it is possible that resistive boundaries are responsible for the unexpectedly large resistivity because the crystals grew by the solid-state reaction.

In summary, we have developed a method for growing single crystals of $Ba_2GdCu_3O_{7-y}$ of a larger size. The method is different from the conventional methods such as the nonstoichiometric melt method. The isothermal temperature and time and cooling rate may be key factors in affecting the size and quality of single crystals.

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