Growth and characterization of large crystals of $\text{GdBa}_2\text{Cu}_3\text{O}_7$ superconductor

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Abstract. We report here on the growth of large crystals of Gd-Ba-Cu-O superconductor by using the ' K_2CO_3 -method' adopted earlier for preparing oriented ceramics and large crystals of Y-Ba-Cu-O superconductors. The temperature favourable for the growth of GdBaCuO crystals is found to be higher than that required for YBaCuO crystals. Also, the crystal perfection is better for these crystals and as a result, the oxygenation of the sample becomes more difficult. Resistivity measurements on these samples show a sharp drop in resistivity at 90 K which then tails off at lower temperatures and attains zero resistance around 35 K. Such behaviour is normally due to an inhomogeneous oxygen content in the sample. Chemical analysis shows that the deviation from '123' composition in GdBaCuO -samples is much less as compared to YBaCuO -samples obtained by the same technique.

Keywords. $\text{GdBa}_2\text{Cu}_3\text{O}_7$; large crystals; K_2CO_3 method.

1. Introduction

The recently discovered high temperature superconductors show a distinct anisotropic behaviour with respect to their electrical and magnetic properties (Iye 1989 and references therein). There is a great need for anisotropic samples (either in the form of oriented ceramics or as large crystals) for anisotropy characterization as well as for power applications. Oriented ceramics can be obtained by manipulating the microstructure of the powder before forming (Omori *et al* 1987), by isostatic pressing (Lynds *et al* 1988; Mukherjee *et al* 1989), by magnetic aligning (Farrell *et al* 1987; Seuntjens *et al* 1989; Nakagawa *et al* 1989), by melt-texturing (Jin *et al* 1988; Hermann *et al* 1988; Alford *et al* 1988; Hojaji *et al* 1989), ultrasonic method (Bhalla *et al* 1988), hot extrusion and hot pressing (Chen *et al* 1987), shock compaction (Johnson *et al* 1988) as well as several other methods in these materials. Normal flux methods of crystal growth yields very small crystals (Sadowski and Scheel 1989 and references therein). Melt techniques cannot be applied to these materials due to incongruent melting and decomposition at the crystal growth temperatures. A considerable number of unconventional methods have been developed recently to grow large crystals of high T_c superconducting materials (Bosi *et al* 1989; Wan *et al* 1988; Konaka *et al* 1988). In our laboratory we have developed the K_2CO_3 -method in order to prepare oriented ceramics and extended the same procedure to prepare large crystals of $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Murugaraj *et al* 1988, 1989a,b, 1990). We have used this method to grow large crystals of the rare earth (Gd, Dy, Pr etc) derivatives of the YBaCuO -compound. We present here our results on the preparation and characterization of large crystals of the GdBaCuO -superconducting material. The rare earth derivatives have certain advantages over the YBaCuO -compound. The $\text{RBa}_2\text{Cu}_3\text{O}_x$ ($R = \text{Y}$ or lanthanides) compounds are stable over a wide temperature range and in spite of the fact that they undergo incongruent melting at the processing temperatures their decomposition rate

is slow. Furthermore, there is no degradation of the superconducting properties due to the rare earth substitution.

2. Experimental

2.1 Preparation of large crystals

The 'K₂CO₃- technique' (Murugaraj *et al* 1988, 1989b) developed for processing YBa₂Cu₃O_x has been adopted here for preparing large crystals of GdBa₂Cu₃O_x. A brief description of the method (as used for making YBaCuO- crystals) is as follows: Y₂O₃, BaCO₃, K₂CO₃ and CuO are mixed in the molar ratio (0.5):(1.8–2.0):(0.1–0.5):(3.0). The mixture is dried at 600 K for 10 h and heated to 1270 K at 10 K/hr in a recrystallized alumina crucible. The soaking time is about 40 h after which the charge is slow-cooled to room temperature (5–10 K/h). The lower part of the charge (up to 30% of the total charge) is a porous mixture of polycrystalline '123' compound contaminated with Al and K, the '211' phase, BaCuO₂ and CuO. The upper portion of the charge contains many crystals which have grown adjacent to each other. Each of these larger crystals is in turn made up of layers ($d = 20$ to $100\ \mu\text{m}$) of smaller single crystals of YBa₂Cu₃O₇ with their *c*-axes approximately aligned. This portion of the charge contains up to 5 wt.% of secondary phases, the major component being the '211' phase and the rest CuO and BaCuO₂. With this technique, since the charge merely shrinks in size and does not wet the walls of the container, there is no contamination from the crucible material. The adverse effect of the contamination of the crystals with the crucible materials is well documented in the literature (Kaiser *et al* 1987; Bykor *et al* 1988; Campa *et al* 1988).

The processing parameters have been slightly modified for the growth of GdBaCuO- crystals. The amount of K₂CO₃ needed in this case is slightly larger than for the YBaCuO-compound and the soaking temperature favouring crystal growth is higher than that needed for the YBaCuO-material. Gd₂O₃, BaCO₃, K₂CO₃ and CuO (99.99% pure) are mixed in the molar ratio (0.5):(1.8–1.0):(0.5–1.0)(3.0) respectively. The mixture is dried at 600 K and then slowly heated to 1330 K. After 40 h of soaking, the charge is cooled to room temperature at 5–10 K/h. The physical nature of the charge is similar to that obtained earlier for YBa₂Cu₃O₇. The hard mass obtained can then be cut into blocks for further investigations. Large crystals can be extracted from these blocks (up to size $5 \times 5 \times 3\ \text{mm}$). These samples contain minor amounts of the '211' phase ($\sim 3\ \text{mol.}\%$), about 5 mol.% of CuO, BaCuO₂ and possibly some traces of Gd₂CuO₄.

2.2 Characterization

The crystal quality and the phase purity were verified by X-ray investigations. Microstructural studies were carried out using optical and electron microscopy. Wet chemical analyses (inductively coupled plasma) and EDX analyses were performed in order to identify the elemental composition. For EDX analyses, finely polished crystals were used. Oxygen analysis was performed by the 'hot-extraction' method, photometric technique as well as by volumetric techniques (Maier *et al* 1988). In some cases Raman spectroscopy was used to assign the oxygen content of the crystal samples (Thomsen *et al* 1988).

Superconducting properties of the crystal samples were studied using electric and magnetic measurements. Resistivity was measured by four-probe technique on rod-shaped specimens consisting of three to four crystals. The a.c. magnetic susceptibility was measured on powdered samples and compared with the signal strength obtained from a Pb powder sample to gain information about the superconducting fraction in the crystals.

3. Results and discussion

In many respects, the growth kinetics of $\text{GdBa}_2\text{Cu}_3\text{O}_x$ crystals were found to be similar to that of $\text{YBa}_2\text{Cu}_3\text{O}_x$ crystals prepared by the same technique. Two types of crystals can be identified in the charge: (i) small crystals of sizes ranging from $1 \times 1 \times 0.1$ mm to $2 \times 2 \times 1$ mm (figures 1a and 1b) and (ii) large crystals typically of sizes $5 \times 5 \times 3$ mm (figure 2). The small crystals are made up of single crystal plates of thickness $\leq 3 \mu\text{m}$ (figure 1b). The surfaces of these crystals were found to be very clean. The morphology of the large crystals is similar to the $\text{YBa}_2\text{Cu}_3\text{O}_x$ crystals obtained by the same method (Murugaraj *et al* 1989b). The crystals are made up of platelets (typically of thickness 10–150 μm).

Microstructural studies on the sample materials removed during the intermediate stages of the growth process cast some light on the interesting growth patterns of these materials. In figure 3, a crystal region during the growth process is shown in which brick-like structures arranged in an ordered fashion are observed. A closer look at the bricks show that they are made up of smaller particles as was the case with the $\text{YBa}_2\text{Cu}_3\text{O}_x$ crystals.

The phase purity and the orientation of the crystals were verified using X-ray diffraction and Raman spectroscopy. As in $\text{YBa}_2\text{Cu}_3\text{O}_7$ crystals, the single crystal platelets have their larger dimensions along *a-b* directions. X-ray diffraction on the powdered samples show that as-grown crystals are tetragonal. The reflections due to the impurity phase $\text{Gd}_2\text{BaCuO}_5$ were observed in the diffractogram and in some crystal batches BaCuO_2 and CuO were also detected. EDX analysis shows some interesting features. The crystal regions have very little deviation from the '123' stoichiometry ($(\text{Gd}_x\text{Ba}_{1-x})_3\text{CuO}_x$; $x = 0.33$ to 0.37). This observation is in contrast to that of $\text{YBa}_2\text{Cu}_3\text{O}_x$ crystals where large deviations of the composition with respect to '123' stoichiometry are observed indicating large defect concentrations in those samples. Thus the $\text{GdBa}_2\text{Cu}_3\text{O}$ crystals have ideal '123' composition with distinctly less substitutional defects as compared to the Y derivative. The secondary phases observed in the X-ray powder diffractogram were identified from EDX analysis also. They were found to exist mainly at grain boundary regions.

Comparison of the chemical analysis (typical results: 24.35 wt.% of Gd, 33.95 wt.% of Ba and 24.95 wt.% of Cu) with phase analysis by powder X-ray diffraction ($\text{GdBa}_2\text{Cu}_3\text{O}_x$, Gd_2BaCu_5) suggests the presence of small amount of a Gd-rich phase (~ 1.5 wt.% of a Gd_2CuO_4) which is below the detection limit. In spite of the higher processing temperatures, compared to the Y homologue, the amount of secondary phases is relatively low. It is not yet clear to what extent this is due to kinetic or equilibrium effects.

TGA studies on the samples show that incorporation of oxygen is extremely slow in the crystal samples while the powdered samples showed the expected weight change

Figure 1. (a) SEM micrograph of the small crystals of GdBa₂Cu₃O_x superconductor. (b) Magnified view of the edges of two crystals.

behaviour as reported in the literature. The bulk samples were oxygenated at 550°C for 40–100 h. Magnetic susceptibility measurements suggest that the superconducting phase is only 10–15% of the bulk. Four-probe resistivity measurements show a sharp drop in the resistivity of the sample at 90 K and finally tailing off to zero resistance at 35 K (figure 4). This behaviour supports the fact that the bulk of the specimen remains

Figure 2. SEM micrograph of the fractured surface of the large crystal of $\text{GdBa}_2\text{Cu}_3\text{O}_x$. The c -axis of the crystal lies on the plane of the paper with its direction perpendicular to the parallel grain boundaries.

oxygen-deficient. The long equilibrium times required may not only be due to well-developed microstructure (lack of extended defects) but also may be ascribed to the low concentration of point defects in the bulk. As shown for YBaCuO (Maier *et al* 1989), R_{Ba} defects in the metal sublattice should be a decisive reason for an enhanced oxygen defect concentration and thus for an increased chemical diffusion coefficient. In addition, oxygen diffusion could also be hindered by the blocking type of secondary phases segregated at the grain boundaries.

There are a number of reports in literature regarding the resistivity anisotropy of these materials (Iye 1989 and references therein). A wide range of values (10 to 1000) for the ρ_{ab}/ρ_c are reported. There are earlier reports claiming that the temperature dependence of the resistivity along the c -axis should be of the semiconducting type as expected according to resonating-valence-bond theory (Tozer *et al* 1987; Anderson 1987; Anderson and Zou 1988), however, the recent experiments increasingly seem to support the view that the conductivity in all the directions is indeed metallic and earlier results are in fact due to sample quality (Weigang and Winzer 1989 and references therein; Maier *et al* 1989a). Owing to the improved microstructure in the Gd compounds it is worth repeating our anisotropy measurements with respect to electronic and ionic transport properties with this compound.

In summary, we have applied our ' K_2CO_3 -method' developed earlier for preparing oriented ceramics and large crystals of $\text{YBa}_2\text{Cu}_3\text{O}_x$ to $\text{GdBa}_2\text{Cu}_3\text{O}_x$ and have succeeded in optimising the conditions for growing large $\text{GdBa}_2\text{Cu}_3\text{O}_x$ crystals. The

Figure 3. (a) SEM micrograph of the $\text{GdBa}_2\text{Cu}_3\text{O}_x$ crystal during the intermediate stages of growth. Brick like frame work is clearly seen. (b) Magnified view of one such brick.

crystal perfection in Gd derivatives is much better as compared to the Y derivative but at the same time oxygenation of the crystals becomes more difficult. Further work is needed in order to improve the superconducting property of these crystals.

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Figure 4. Resistivity vs temperature for a rod-type sample of $\text{GdBa}_2\text{Cu}_3\text{O}_x$ containing three crystals.

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