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Growth of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ single crystals at different oxygen ambient pressures

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Bi-2212 superconducting single crystals were grown by the travelling solvent floating zone method at different oxygen ambient pressures. Electron probe micro-analysis showed a systematic increase of the Sr/Ca ratio in the as-grown crystals with increasing oxygen ambient pressure and a maximal superconducting transition temperature of $T_{\text{c-onset}} = 95$ K, and $\Delta T_{\text{c}} = 1.5$ K was obtained for crystals grown at an oxygen ambient pressure of 200 kPa. Thermogravimetric and post-annealing experiments in air at 500 and 800°C have shown that the oxygen content and the $T_{\text{c-onset}}$ values in the crystal do not depend only on the annealing temperature, but also on its chemical composition. The in-field current density J_{c} measured at 5 K on crystals grown at 200 kPa oxygen ambient pressure was considerably smaller than that of crystals grown in air.

1. Introduction

The availability of bulk single crystals is indispensable for the systematic study of the intrinsic physical properties of the high- T_{c} superconducting compounds. The travelling solvent floating zone (TSFZ) method has proved to be most successful for growing large, contamination-free and high-quality single crystals of some of the high- T_{c} superconductors, especially those of the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$ [1–4], $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ [5] and $\text{Nd}_{2-x}\text{Ce}_x\text{CuO}_4$ [5] compounds. In our previous work we reported on the growth of the pure and Ni-substituted Bi-2212 superconducting phase [1].

For some physical measurements probing the local field distribution of the vortex lattice phase, there is an increasing need for high-quality and large-size single crystals of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+x}$. Therefore we have grown several large boules of the Bi-2212 85 K superconducting phase in air by the TSFZ method.

It is well known that the oxygen content plays a crucial role in determining the physical properties of the high- T_{c} ceramic superconductors, such as transition temperature, anisotropy and flux-pinning phenomena, also those of the Bi-2212 compounds. Many studies on this aspect have been published [6–12]. To our knowledge, however, most of them were carried out on the basis of cation substitution and annealing experiments at different temperatures and in different oxygen ambient pressures. In this paper we report for the first time on the growth of the Bi-2212 single crystals by the TSFZ method at different oxygen ambient pressures up to 300 kPa.

2. Experimental procedure

A “wet” preparation route from nitrates was used in order to achieve homogeneous starting materials. Powders of Bi_2O_3 , SrCO_3 , CaCO_3 and CuO were weighted in the ratios of Bi:Sr:Ca:Cu = 2.1:1.9:1.0:2.0 and Bi:Sr:Ca:Cu = 2.6:1.9:1.0:2.6 for the feed rods and the solvent respectively; all starting compounds were 99.9%

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purity or better. The mixtures were then dissolved in HNO_3 . After the drying procedure, the mixtures were calcined at 710–820°C with several intermediate grindings. The calcined powders were pressed into rods of 6 to 7 mm in diameter and 80 to 100 mm in length under a hydrostatic pressure of 3.5 kbar. These rods were then sintered in a vertically hanging furnace at 840°C for 48 h in air. Prior to the crystal growth procedure, feed rods were first densified in air by passing through a molten zone at a velocity of 60 to 80 mm/h. A $\text{Bi}_{2.16}\text{Sr}_{1.91}\text{Ca}_{1.03}\text{Cu}_2\text{O}_{8+x}$ crystalline boule from a previous experiment was used as the seed. The growth experiments were performed by the TSFZ method in the NEC SC-N35HD image furnace with double ellipsoidal reflectors and two 1.5 kW halogen lamps as the heat source. This furnace was specially adapted in our laboratory for application at high oxygen ambient pressures up to 600 kPa. During the growth process the feed and seed shafts were counter rotated at a rate of 30 rpm. The growth rate was approximately 0.26 mm/h in the static ambient atmosphere of air, 200 and 300 kPa oxygen pressure.

The as-grown crystals were checked on composition, homogeneity and single-crystallinity by electron probe micro-analysis (EPMA), and X-ray Laue diffraction techniques, respectively. The lattice parameters were determined on selected small single crystals by X-ray powder diffraction.

EPMA and X-ray powder diffraction were performed by JEOL JXA-8621 and Philips PW-1710 equipments, respectively. Post-annealing experiments were carried out at 500 and 800°C on two single crystals which were grown in air and at 200 kPa oxygen ambient pressure. After annealing, the samples were directly quenched in liquid nitrogen. Thermogravimetric analysis was done in a SETARAM TAG-24 thermoanalyzer with a resolution of $\pm 2.5 \mu\text{g}$. The superconducting transition temperature of the as-grown and as-annealed samples was determined from AC susceptibility measurements in an AC magnetic field of 1.2 G and a frequency of 90 Hz, the critical temperature $T_{\text{c-onset}}$ is defined as the onset temperature of diamagnetism and the width of the transition has been taken as the temperature difference between 10% and 90% of the full AC field expulsion. The magnetic-field dependence of the magnetization was measured at 5 K with a vibrating-sample magnetometer [13].

3. Results and discussion

From all growth experiments, single-crystalline boules of typically 6 mm in diameter and 60 to 80 mm in length were obtained. Single-crystalline samples were prepared by first cutting and then cleaving the boules. For the growth in air, a

Fig. 1. Bi-2212 single crystal pieces cleaved from a boule grown at 200 kPa oxygen ambient pressure.

“large-volume” and a “large-surface” sample were made for neutron scattering and muon-spin rotation experiments, respectively. The “large-volume” sample was a big crystal of approximately $12 \times 5 \times 1.5 \text{ mm}^3$ which weighted 690 mg. Neutron diffraction results showed that this sample actually consisted of one large aid one small single crystal which were closely aligned with their c -axis coinciding within 2° and with respective rocking curve widths of 0.4° and 0.6° [14]. The “large-surface” sample for muon-spin rotation experiments was composed from 5 thin single-crystalline pieces of typical size of $5 \times 5 \times 0.5 \text{ mm}^3$ with well-defined a - and b -directions, and the c -direction perpendicular to the surface [15,16].

Compared to the growth experiments in air, the lamp power necessary to melt the solvent increased and some copper had precipitated on the surface of the crystal boules in the growth experiments at 200 and 300 kPa oxygen ambient pressure. Large plate-like single crystals with sizes up to $16 \times 4 \times 0.5 \text{ mm}^3$ were separated from the boules, as shown in fig. 1.

The results of the EPMA, X-ray diffraction and AC susceptibility measurements on the as-grown single crystals are presented in table 1.

The sample homogeneity was examined by comparing the EPMA-observed compositions at different points on each crystal for a few different crystals which were cleaved from the same as-grown boule. To determine the composition of

Fig. 2. The Sr/Ca ratio and c -axis parameter of Bi-2212 single crystals grown in air, and 200 and 300 kPa oxygen ambient pressure.

the crystals, EPMA data were typically taken at five different points on each sample. The final composition was calculated by averaging these data and normalizing them to $\text{Cu} = 2$. As can be seen in table 1, the Sr/Ca ratio increases linearly with increasing oxygen ambient pressure. From the phase equilibria in the system Bi_2O_3 – SrO – CaO – CuO [17–19], one can see that the Bi-2212 phase exhibits an extended single-phase region with variable Sr/Ca ratios and Bi contents (all normalized to $\text{Cu} = 2$), and with increasing temperature, this single-phase region extends to Sr-rich composition. According to our observations, the growth temperature (referred to solvent-melting temperature, indirectly indicated by the power applied to the lamp) increased with increasing oxygen ambient pressure. This may be the possible reason for the increased Sr/Ca ratio in the crystals which were grown at higher oxygen ambient pressures.

X-ray powder diffraction was performed on selected small single crystals. Within the experimental resolution we can ascribe all subcells with the tetragonal symmetry. No change in the a -axis parameter is observed. However, there is a very distinct difference in the c -axis parameters of the crystals grown at different oxygen ambient pressures. The correlation between the Sr/Ca ratio, the c -axis parameter and the oxygen ambient pressure is demonstrated in fig. 2. As it can be seen, the c -axis parameter seems to pass through a maximum at about 200 kPa. A probable expla-

Table 1
Characterization of the Bi-2212 single crystal grown in different oxygen pressures

EPMA (at%)	Oxygen pressure		
	Air	200 kPa	300 kPa
Bi	2.16	2.17	2.18
Sr	1.91	2.03	2.06
Ca	1.03	1.00	0.98
Cu	2.00	2.00	2.00
Sr/Ca	1.85	2.03	2.10
Lattice parameters			
a (nm)	0.382	0.383	0.382
c (nm)	3.078	3.088	3.081
$T_{c\text{-onset}}$ (K)	88	95	91
ΔT_c (K)	2.2	1.5	2.0

Fig. 3. Magnetic AC susceptibility of the as-grown single crystal samples grown at different oxygen ambient pressures. The AC field (1.2 G, 90 Hz) was applied parallel to the c -axis.

nation for this comes from different ionic radii of Bi^{3+} , Sr^{2+} and Ca^{2+} ($\text{Bi}^{3+} = 0.117$ nm, $\text{Sr}^{2+} = 0.118$ nm and $\text{Ca}^{2+} = 0.100$ nm). Therefore, the length of the c -axis is expected to correlate with the Sr/Ca ratio and the Bi content. However, with increasing oxygen ambient pressure, it is also possible that more additional oxygen ions are incorporated into the BiO layers [21]. This induces a contraction of the BiO layers and causes an increase in the covalency of the Bi–O bonds [22], this effect results in a significant decrease of the length of the c -axis [8]. The combination of both effects may give rise to the maximum in the c -axis parameter.

Results of the AC susceptibility measurements on the as-grown crystals are shown in fig. 3. It is

obvious that the superconducting onset temperature depends strongly on the growth conditions, namely the oxygen ambient pressure. T_c is enhanced for crystals grown at the higher oxygen ambient pressures, resulting in a sharpest transition width of $\Delta T_c = 1.5$ K and a highest transition onset temperature of $T_{c\text{-onset}} = 95$ K at 200 kPa oxygen pressure. From the literature [8–12,15–20], we have known that the superconducting transition temperature T_c of the Bi-2212 compound depends strongly on the cation concentration and the oxygen content. It can vary between 50 and 95 K. The T_c values for our as-grown crystals can be influenced by these two effects. If we keep the same cation concentration of the Bi-2212 phase, the superconducting transition temperature can also be controlled by the change in oxygen content at various post-annealing temperature. This is shown in figs. 4a and 4b. One can clearly see that T_c is enhanced when the samples are annealed at higher temperature, and this enhancement is much more pronounced in the crystal grown at 200 kPa oxygen ambient pressure than in the crystal grown in air. These changes in T_c can be attributed to the different oxygen content in the samples as a function of the annealing temperature. However, it should be mentioned that there is no unambiguous relationship between T_c and the post-annealing temperature or oxygen ambient pressure. This is because the oxygen content is not only a function of post-annealing temperature and oxygen ambient

Fig. 4. Magnetic AC susceptibility of Bi-2212 single crystals grown (a) in air and (b) at 200 kPa oxygen ambient pressure, which were subsequently annealed in air at different temperatures (500 and 800 °C), and then quenched in liquid nitrogen. The AC field (1.2 G, 90 Hz) was applied parallel to the c -axis.

Fig. 5. Field dependence of the critical current density at 5 K for Bi-2212 single crystals grown in air and at 200 kPa oxygen ambient pressure. The field was applied parallel to the c -axis.

pressure, but also depends on the cation concentration of the Bi-2212 phase. From thermogravimetric analysis, we have also deduced that heating the samples of figs. 4a and 4b in air from 500 to 800°C, the weight loss was respectively 0.038% and 0.056% and the related change in oxygen stoichiometry, $\Delta x = x_{500} - x_{800}$ (assuming O_{8+x}) was 0.022 ± 0.002 and 0.033 ± 0.002 , respectively. So, compared with fig. 4a, a larger change of T_c is expected in fig. 4b.

The magnetic hysteresis loop for the samples grown in air and at 200 kPa oxygen ambient pressure was measured at 5 K. The critical current density was estimated using the Bean model and is shown in fig. 5. It is obvious that the critical current density J_c obtained for the crystal grown at 200 kPa oxygen pressure was nearly ten times smaller than that for the crystal grown in air.

4. Conclusions

We have successfully grown Bi-2212 single crystals by the travelling solvent floating zone method, applying different oxygen ambient pressures up to 300 kPa. Large and high-quality Bi-2212 single crystals were obtained, from which two kinds of samples were prepared for neutron scattering and muon-spin rotation experiments. In the growth experiments at higher oxygen ambient pressures, the temperature necessary to melt

the solvent was increased and an almost linear correlation between Sr/Ca ratio and oxygen ambient pressure was observed. The c -axis lattice parameter and superconducting onset temperature depend strongly on the cation concentration and oxygen content of the 2212 phase. The latter is not only a function of post-annealing temperature and oxygen ambient pressure, but also depends on the cation concentration of the Bi-2212 phase. The critical current density J_c is found to be much lower in the crystals grown at higher oxygen ambient pressure. Further investigations of the flux-pinning phenomena in crystals grown at different oxygen ambient pressures are currently underway [23].

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