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Large Bi-2212 single crystal growth by the floating-zone technique

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Abstract

Effects of growth velocity on the crystal-growth behavior of $Bi_2Sr_2Ca_1Cu_2O_x$ (Bi-2212) have been studied by the floating-zone technique. The results show that a necessary condition for obtaining large single crystals along the *c*-axis is that the solid–liquid interface of a growing rod maintains a stable planar growth front. The planar liquid–solid growth interface tends to break down into a cellular interface when the growth velocity is higher than 0.25 mm/h. Single crystals of up to $50 \times 7.2 \times 7\,mm^3$ along the *a*-, *b*- and *c*-axes, respectively, have been cut from a 7.2 mm diameter rod obtained with optimum growth conditions. T_c^{onset} is 91 K as determined from magnetization measurements on as-grown crystals. Optical polarization microscopy and neutron diffraction show that the quality of the large single crystals is good.
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It is not a great challenge for crystal growers to obtain thin plate-like crystals of $Bi_2Sr_2Ca_1Cu_2O_x$ (Bi-2212), with a thickness of up to 0.1 mm along the *c*-axis, by the flux method and the Bridgman method [1–6]. One can also use the traveling-solvent floating-zone (TSFZ) technique to grow Bi-2212 single crystals [7–10]. The latter work has shown that Bi-2212 single crystals with a thickness of less than 0.2 mm along the *c*-axis are easily obtained under various growth conditions and initial compositions. Gu et al. have succeeded in using the TSFZ technique to grow relatively large Bi-2212 single crystals and showed that the optimal starting composition was $Bi_{2.1}Sr_{1.9}Ca_{1.0}Cu_{2.0}O_x$ [11,12]. They reported that while deviating from the optimal starting composition, the planar interface broke into cellular interface. However, it is still very difficult to grow Bi-2212 single crystals with size large enough for neutron scattering measurements. In this paper, we report the effect of the growth velocity on Bi-2212 crystal-growth behaviors. The optimum growing conditions for preparing large single crystals with a thickness of up to 7 mm along the *c*-axis are presented.

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An infrared radiation furnace equipped with two ellipsoidal mirrors and two 500 W halogen lamps placed in the focus of the mirrors was used for the crystal growth. Powders of Bi_2O_3, $SrCO_3$, $CaCO_3$ and CuO (99.99%) in their metal ratios were mixed, ground in an agate mortar and calcined for 48 h at 810 °C. The calcined powders were then reground and calcined for a second time. The reground powders were placed in a rubber tube and hydrostatically pressed under 6000 kg/cm^2. The pressed rods were sintered for 72 h at 860 °C for use as feed rods and at 840 °C for solvent materials. The sintered rods were then pre-melted at a velocity of 0.25 mm/h; this is necessary for obtaining a stable molten zone during the crystal-growth cycle. The experimental conditions are summarized in Table 1. All experiments were performed in air, and the temperature gradient at the solid–liquid interface of the seed rods was not measured. In order to reveal the morphology of the growth front, the molten zone between the feed rod and the seed rod was quenched.

The microstructure of the polished sections was examined by an optical polarization microscope under which differently oriented crystals appear with different colors. Single crystals were identified and extracted based on the images taken with the microscope. The quality of the single

crystals was analyzed by neutron scattering measurements and the static magnetic susceptibility of the as-grown crystal was measured with the magnetic properties measurement system (MPMS).

Fig. 1 shows the crystals grown with the starting composition $Bi_{2.1}Sr_{1.9}Ca_{1.0}Cu_{2.0}O_x$. Fig. 1(a) is an entire as-grown crystal rod, with *a*-axis along the growth direction. For the initial part of the rod (0–6 cm, at left in Fig. 1(a)), the growing conditions are not optimized and the growth is not stable. Therefore, the size of the crystals is not large and the composition may not be right (being affected by the solvent composition). At a certain point, the growth becomes stable and the size of individual crystals optimizes. Fig. 1(b) shows single crystals cut from the as-grown rods. They are 50 mm along *a*-axis and 7.2 mm along *b*-axis. The largest crystal has a thickness of 7 mm along *c*-axis. For the neutron scattering experiments, we have co-aligned the crystals using the Laue X-ray back reflection technique and the resulting ensemble of crystals are shown in Fig. 1(c).

Table 1
Growth conditions for Bi-2212 crystals

Feed rod diameter	8 mm
Feed rod rotation	30 rpm
Feed rod velocity	0.25 mm/h
Feed rod composition	$Bi_{2.1}Sr_{1.9}Ca_{1.0}Cu_{2.0}O_x$
Seed rod diameter	7.2 mm
Seed rod rotation	30 rpm
Seed rod velocity	0.25 mm/h
Solvent composition	$Bi_{2.5}Sr_{1.9}Ca_{1.0}Cu_{2.6}O_x$

Polarization photographs of the longitudinal and cross-sections of the as-grown rods at the velocity of 0.5 and 0.25 mm/h are shown in Fig. 2.

With a high growth velocity such as 0.5 mm/h, the solid–liquid interface is cellular as shown in Fig. 2(a) which is the longitudinal section of a quenched rod. The cross-section of the as-grown rod (Fig. 2(b)) exhibits many small crystals. When using a lower velocity of 0.25 mm/h, the planar interface can be maintained, as shown in Fig. 2(c), and large single crystals can be obtained (Fig. 2(d)). The growth front morphology is very sensitive to the growth velocity, which is critical for obtaining large single crystals along the *c*-axis. Apparently, a low velocity is very useful in maintaining a smooth growth front of a rod.

The magnetization was measured under zero field cooling (ZFC) with a field of 2 Oe along the *c*-axis and the result is shown in Fig. 3. It shows that the sample is homogeneous with ΔT_c (10–90%) = 2 K. Based on the T_c

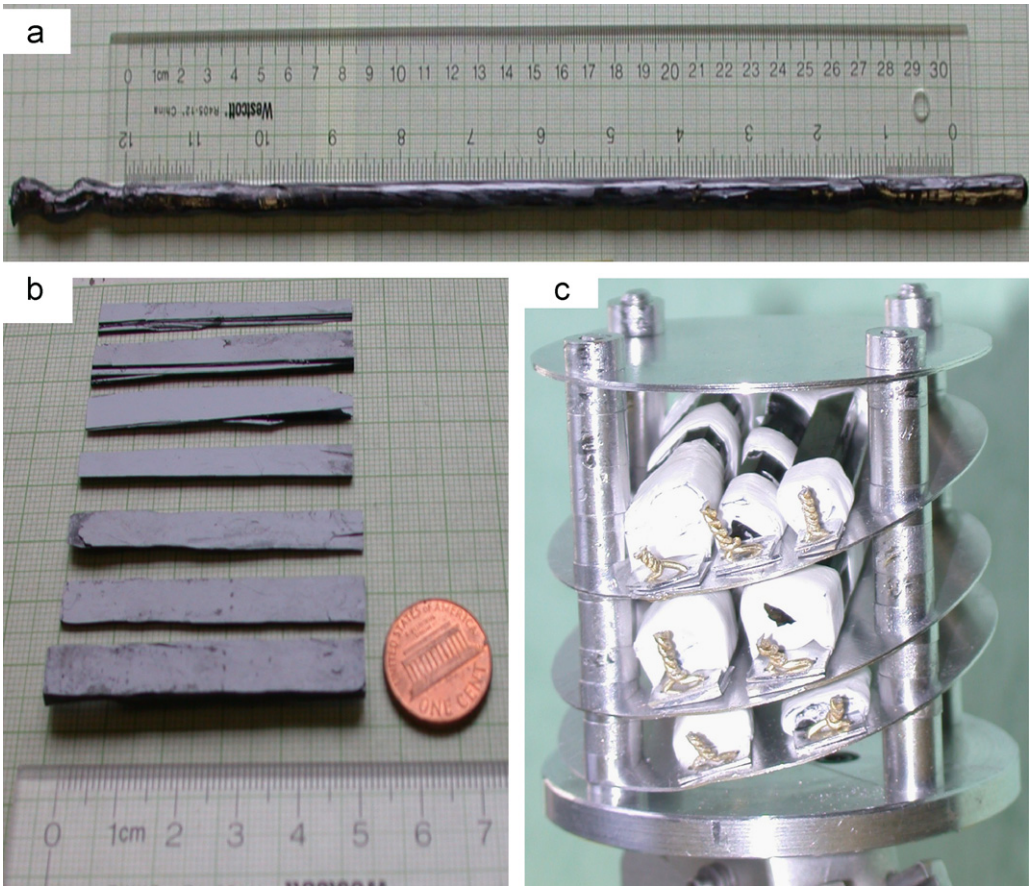

Fig. 1. (a) As-grown crystal rod, 32 cm long. (b) Single crystals cut from the as-grown rods. (c) Co-aligned single crystals for neutron scattering measurements.