Growth, characterization and physical properties of high-quality large single crystals of Bi$_2$(Sr$_{2-x}$La$_x$)CuO$_6+\delta$
high-temperature superconductors

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Abstract

High-quality large Bi$_2$(Sr$_{2-x}$La$_x$)CuO$_6+\delta$ (La–Bi2201) single crystals have been successfully grown by the traveling solvent floating zone technique. The samples are characterized by compositional and structural analyses and their physical properties are investigated by magnetic susceptibility and resistivity measurements. Superconducting samples with sharp superconducting transitions are obtained, covering a wide range of doping from overdoped (x < 0.40), optimally doped (x ∼ 0.40), underdoped (0.40 < x < 0.84) to heavily underdoped without superconducting transition (x > 0.84). Crystals as large as ∼40 × 2.0 × 1 mm$^3$ are obtained for x = 0.73. A sharp superconducting transition with a width less than 2 K and a nearly perfect Meissner signal of superconductivity are achieved for x = 0.40. The availability of the La–Bi2201 single crystals will provide an ideal system to study the physical properties, electronic structure and mechanism of high-temperature superconductivity.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The physical properties of the copper-oxide (cuprate) superconductors are characterized by the unusually high critical temperature ($T_c$), the unusual superconducting state with predominantly d-wave pairing [1], and the exotic normal state, where a pseudogap is present in the underdoped and optimally doped regions [2]. Since the conventional Fermi liquid theory for metals [3] and the BCS theory for conventional superconductivity [4] cannot be directly applicable to the cuprate superconductors, new theories have to be developed. Nearly 20 years after its first discovery [5], the mechanism of high-temperature superconductivity in cuprates remains an outstanding issue in condensed matter physics [6, 7]. Critical experiments such as angle-resolved photoemission spectroscopy (ARPES) [8], neutron scattering [9], scanning tunneling microscopy/spectroscopy (STM/STS) [10] etc are necessary for stimulating, checking and developing new theories. High-quality single-crystal samples are crucial for carrying out these experiments. In some experiments, a large size and large quantity of single crystals are needed, as in neutron scattering measurements.

The Bi$_2$Sr$_2$CuO$_6$ (Bi2201) superconductor is an ideal system for investigating high-temperature superconductivity in cuprates [11]. First, it has a layered structure which can be easily cleaved to get a clean and smooth surface, which is necessary for experiments like ARPES and STM/STS. Second, it has a simple single-layered crystallographic structure with one CuO$_2$ plane within two adjacent block layers; this gives a single band and a single Fermi surface sheet, avoiding possible complications from two-layered or multi-layered compounds such as bilayer splitting in double-layered Bi$_2$Sr$_2$CaCu$_2$O$_8$ (Bi2212) [12]. Third, by partially replacing Sr$^{2+}$ with some rare-earth ions (R$^{3+}$) in
B_{2}(Sr_{2−x}R_{x})CuO_{x+y}, the critical temperature of Bi2201 can be increased from around 9 K for the pristine Bi2212 [13, 14] to nearly 38 K for R = La (lanthanum) [15–17]. The lower critical temperature, compared with that of Bi2212 and YBa_{2}Cu_{3}O_{y−δ} with a maximum T_{c} higher than 90 K, is beneficial in investigating normal state properties while suppressing possible thermal broadening caused by high temperatures. Fourth, by substituting Sr^{2+} with rare earth (R^{3+}), which introduces electrons, together with oxygen annealing, the doping level of the samples can be varied over a wide range. In the case of La-doped Bi2201, various doping levels from underdoped, optimally doped and overdoped samples, and even heavily underdoped non-superconducting samples, can be obtained [13, 14, 18–20]. This large doping range is very important for addressing many important issues such as metal–insulator transition, nonsuperconducting transition and a nearly perfect Meissner shield. Since the onset of Bi2201 can be increased from around 9 K for the pristine Bi2201 [13, 14], to optimally doped (x = 0.25), to optimally doped (x = 0.40), to underdoped (x larger than 0.40) all the way to heavily underdoped without superconducting transition (x = 0.84). The crystal size we have obtained is up to 3–4 cm long. The superconducting samples show a sharp superconducting transition and a nearly perfect Meissner shielding of superconductivity. The successful growth of these single crystals will be very helpful in carrying out some critical experiments to investigate high-temperature cuprate superconductors.

## 2. Experimental method

The B_{2}(Sr_{2−x}La_{x})CuO_{y+z} single crystals are grown by the traveling solvent floating zone method using an infrared radiation furnace (Crystal Systems Inc.) equipped with four 300 W halogen lamps. The high-temperature gradient required to stabilize the molten zone can be achieved by ellipsoidal mirrors that focus the image of the four lamps at a common position. The temperature of the molten zone can be controlled precisely by adjusting the output power. The crystal growth was carried out in an enclosed quartz tube, where the growth atmosphere can be controlled.

Feed rods and seed rods are first prepared by the conventional solid-state reaction method before growing single crystals. Starting materials of Bi_{2}O_{2}, SrCO_{3}, La_{2}O_{3} (pre-heated for 5 h at 860 °C to remove the adsorbed water and CO_{2}) and CuO with 99.99% purity were weighed according to the chemical formula B_{2}(Sr_{2−x}La_{x})CuO_{y+z} with different x and mixed in an agate mortar for about 8 h. The mixed powder was calcined at 780 °C for 24 h and the calcined product was reground into fine powders. This calcination and grinding procedure was repeated four times to ensure a complete reaction and homogeneity of the calcined powders. The calcined powder was pressed into a cylindrical rod of 7 mm in diameter and 120 mm in length under a hydrostatic pressure of ~70 MPa, followed by sintering in a vertical molišika furnace at 870 °C for 48 h in air. The sintered rod was then pre-melted in the floating zone furnace at a traveling velocity of 25–30 mm h^{-1} to obtain a dense feed rod ~6 mm in diameter and ~120 mm in length. The pre-melting is a crucial step in achieving a stable molten zone during the crystal growth because it may prevent the molten zone from penetrating into the feed rod. An ingot about 1.5 cm long cut from the pre-melted feed rod was used as a seed rod.

The crystal growth involves many trials to optimize growing conditions, including the powder used, growth rate, rotation rates of feed rod and seed rod, and growing atmosphere. These conditions vary for different compositions. Table 1 lists La–Bi2201 crystals with different compositions, their growth conditions, and the structural and superconducting properties. Some key parameters to obtain high-quality large La–Bi2201 single crystals are briefly described below:

1. The output power is in principle dictated by the melting point of the feed rod. In practice it can be estimated during the pre-melting process. An optimized output power can be achieved by fine-tuning within a narrow range which gives rise to an appropriate molten zone that can stay stable during the entire growth process.

2. The growth rate is determined by the atomic diffusion kinetics during the crystal growing process, which may vary significantly among different materials. The stability of the molten zone and the crystal size are other factors to take into account. For La–Bi2201, when a lower growth rate (<0.45 mm h^{-1}) was used, the molten zone tends to become unstable, causing frequent collapse of

| Nominal composition | Measured composition | Growth rate (mm h^{-1}) | Growth atmosphere | c (Å) | T_{c onset} (K) |
|---------------------|----------------------|-------------------------|-------------------|-------|-----------------|
| Bi_{2}Sr_{2−x}La_{x}CuO_{y+z} | Bi_{2}Sr_{2−x}La_{x}CuO_{y+z} | 0.5 | 100 cm^{3} min^{-1} air flow | 24.519 | 28 |
| Bi_{2}Sr_{2}La_{0.6}CuO_{y+z} | Bi_{2}Sr_{2}La_{0.6}CuO_{y+z} | 0.5 | 100 cm^{3} min^{-1} O_{2} flow | 24.445 | 30 |
| Bi_{2}Sr_{2}La_{0.8}CuO_{y+z} | Bi_{2}Sr_{2}La_{0.8}CuO_{y+z} | 0.5 | 100 cm^{3} min^{-1} O_{2} flow | 24.392 | 32 |
| Bi_{2}Sr_{2}La_{1}CuO_{y+z} | Bi_{2}Sr_{2}La_{1}CuO_{y+z} | 0.5 | 50 cm^{3} min^{-1} O_{2} flow | 24.222 | 24.5 |
| Bi_{2}Sr_{2}La_{1.2}CuO_{y+z} | Bi_{2}Sr_{2}La_{1.2}CuO_{y+z} | 0.5 | 20 cm^{3} min^{-1} O_{2} flow | 24.171 | 20 |
| Bi_{2}Sr_{2}La_{1.4}CuO_{y+z} | Bi_{2}Sr_{2}La_{1.4}CuO_{y+z} | 0.5 | 20 cm^{3} min^{-1} O_{2} flow | 24.148 | 18 |
| Bi_{2}Sr_{2}La_{1.6}CuO_{y+z} | Bi_{2}Sr_{2}La_{1.6}CuO_{y+z} | 0.5 | 20 cm^{3} min^{-1} O_{2} flow | 24.052 | ns |
the zone. When a higher growth rate (>0.8 mm h\(^{-1}\)) is used, although the molten zone gets more stable, the size of the single crystals gets smaller. As a compromise, a growth rate of 0.5 mm h\(^{-1}\) was used for growing La–Bi\(_{2201}\) single crystals.

(3) The feed rod and the seed rod rotate in opposite directions in order to ensure efficient mixing and uniform temperature distribution in the molten zone. A 30/20 rpm rate was used for the feed rod (upper shaft)/seed rod (lower shaft) in growing La–Bi\(_{2201}\). The upper shaft rotates faster to make the molten zone more homogeneous, while the lower shaft with a slower rate is to keep the molten zone stable. It is important to make sure that there is no deflection between the seed rod and feed rod during their rotations.

(4) The growth atmosphere has an important effect on the stability of the molten zone and the crystal quality. Depending on the composition, we used both air and oxygen atmosphere (table 1). We note that when oxygen pressure is used the pressure should be no higher than 2 bar, otherwise there would be bubbles appearing in the molten zone that cause it to be unstable. The gas flow rate is an important factor for affecting the crystal size; large La–Bi\(_{2201}\) crystals are obtained when 20–100 cm\(^3\) min\(^{-1}\) oxygen or air flow rate is used, as listed in table 1 for different compositions.

Figure 1 shows some typical La–Bi\(_{2201}\) single crystals with different La concentration that were cleaved from the top of the as-grown ingots. We note that for the initial part of the ingot (0–3 cm), because the growing conditions are not yet optimized and stable, the crystal size is usually small with lower quality. Large high-quality crystals are obtained in the final part of the ingot when the growth process is optimized and stable.

The as-grown single crystals were post-annealed in flowing oxygen at different temperatures (450–700 °C) for 2–12 days to adjust the carrier concentration and make the samples uniform. During the annealing process, the crystals were embedded in sintered powders with the same composition to avoid evaporation of some constituents. After annealing, the samples were quenched in liquid nitrogen. Compared with the as-grown crystals, such an annealing process has a weak effect on the \(T_c\) value for most of the compositions, except for \(x = 0.84\) which, when as grown, is not superconducting down to 2 K, but can become superconducting with a \(T_c\) up to 10 K after annealing in oxygen for sufficiently long time.

### 3. Results and discussion

As shown in figure 1, large La–Bi\(_{2201}\) single crystals with various compositions, \(x\), have been successfully grown. For the composition \(x = 0.73\), a single crystal as long as \(\sim 40\) mm has been obtained. It is found that the crystal size relies closely on the starting composition. The viscosity of La–Bi\(_{2201}\) increases with increasing La concentration, \(x\), which makes the molten zone more stable. This is probably why it is easier to get large single crystals at high La concentration (figure 1).

Figure 1. Photos of Bi\(_3\)(Sr\(_{2–x}\),La\(_x\))CuO\(_6\) single crystals cleaved from as-grown ingots with various nominal compositions: \(x = 0.25, 0.37, 0.40, 0.60, 0.70, 0.73\) and 0.84. Some crystals with large \(x\) can reach 3–4 cm in length.

After post-annealing, the single crystals were characterized in the composition and crystal structure. The superconducting properties were investigated by both resistivity and magnetic susceptibility measurements.

#### 3.1. Compositional analysis

The chemical composition of the La–Bi\(_{2201}\) crystals was determined by induction-coupled plasma atomic emission spectroscopy (ICP-AES). The results are given in table 1. The actual composition of the grown single crystals is very close to their nominal composition for \(x = 0.37–0.73\) while the deviation of the \(x = 0.25\) and 0.84 samples is slightly larger. Overall, this indicates that the sample homogeneity and composition are well controlled during the entire single-crystal growth process.

#### 3.2. Structure characterization

The structure and quality of the single crystals are characterized by x-ray diffraction (XRD) using a rotating anode x-ray diffractometer with Cu K\(\alpha\) radiation (\(\lambda = 1.5418\) Å). The experiments were carried out under \(\theta–2\theta\) scan mode with the incident ray along the \(c\)-axis of the single crystal, and the continuous scanning range of 20 is from 5° to 75°. Figure 2 shows XRD patterns for La–Bi\(_{2201}\) with various compositions \(x = 0.25, 0.37, 0.40, 0.60, 0.70, 0.73\) and 0.84. All the observed peaks can be indexed to the Bi\(_{2201}\) structure, indicating a pure single phase of the obtained single crystal. The peaks are sharp, as exemplified from the (008) peak in the inset of figure 2, which has a width of 0.08–0.09° (full width at half maximum), indicating high crystallinity and high orientation of the single crystals.

The \(c\)-axis lattice parameters of the single crystals undergoes a systematic change with the La content \(x\), as shown by the peak position shift in the inset of figure 2. The \(c\)-axis lattice constant is calculated from XRD data [26], as listed in table 1 and shown in figure 5(b). It decreases with increasing La content, which is consistent with the fact that La\(^{3+}\) has a smaller ionic radius than Sr\(^{2+}\). The \(c\)-axis lattice constant shows a linear relation with the nominal La
Figure 2. XRD patterns for cleaved single crystals with various La concentration ($x$), which can be approximated as $c$(nm) = 2.472–0.0795$x$. In figure 5(b), we also plot the data from other groups [19, 20, 23], which show a good agreement with each other.

3.3. Superconductivity

The superconducting transition temperature of the annealed La–Bi2201 crystals is determined by both magnetization (figure 3) and resistivity (figure 4) measurements. Figure 3 shows the temperature dependence of DC magnetization for La–Bi2201 single crystals with various La contents $x$, measured using a Quantum Design MPMS XL-1 system with a low magnetic field of 1 Oe. The crystals with $x = 0.25–0.75$...
Hole concentration, $T$ data. (c) As estimated from thermopower measurements by Ono et al [24] is plotted in figure 5(a). Data from other groups are also included [18–20, 27, 28]. The solid line is fitted to our measured data. (c) $T_c$ as a function of nominal La content (x). Data by Ono et al are also plotted [24].

show clear superconducting transition while the as-grown $x = 0.84$ sample is non-superconducting down to 2 K. The superconducting transition temperature ($T_c$), defined by the onset of a diamagnetic signal, increases with $x$ first, reaching a maximum $T_{c,\text{onset}} = 32$ K near $x = 0.4$, and decreases with further increase of $x$. Since the substitution of Sr$^{2+}$ with La$^{3+}$ is expected to introduce electrons into the samples and it is well known that Bi2201 is a hole doped system, increasing La concentration would result in a decrease of the hole concentration. Therefore, samples with $x$ less than 0.4 are expected to be overdoped, $x \sim 0.4$ is optimally doped while $x$ larger than 0.4 is underdoped.

It is also clear from figure 3 that the prepared single crystals show a sharp superconducting transition with a transition width $\Delta T_c = 1–3$ K (10–90% standard). In order to further investigate the quality of the superconducting samples, we choose a well annealed $x = 0.40$ sample for quantitative investigation. Its magnetic susceptibility has been carefully calculated by considering its volume and correcting the demagnetization factor by considering its shape. As shown in figure 3(g), this sample shows a sharp superconducting transition at 31.5 K with a width of $\sim 1$ K. Its 100% shielding (zero-field-cooled, ZFC) signal indicates that there exists little macroscopic inhomogeneity or weak links. Its extremely high Meissner signal ($\sim 95\%$, field-cooled, FC) implies that this sample is nearly free of pinning disorders. Nearly complete shielding and Meissner effects demonstrate the high quality of this crystal.

Figure 4 shows the temperature dependence of in-plane resistivity $\rho_{ab}$ for all the grown La–Bi2201 single crystals with various compositions. The in-plane resistivity was measured using the standard four-probe method. Gold lead wires were attached to the contact pads using silver epoxy and then were annealed at 400°C. Consistent with DC magnetic measurements (figure 3), the samples with $x = 0.25–0.75$ show a clear superconducting transition while the $x = 0.84$ sample shows an insulating behavior. The superconducting transition temperature increases with $x$ first, reaching a maximum of 31 K (zero resistance) at $x = 0.40$, and getting smaller with further increase of $x$. While there may be a relatively large uncertainty in the absolute value of resistivity, the overall trend is that the magnitude of $\rho_{ab}$ increases with increasing La content from $x = 0.25$ to 0.84, consistent with previous measurements [18, 27, 28].

Figure 5 summarizes the $c$-axis lattice constant (figure 5(b)) and superconducting transition temperature (figure 5(c)) of the La–Bi2201 single crystals as a function of La concentration $x$. Data from other groups [18–20, 23, 27, 28] are also included for comparison and completeness. Particularly, the hole concentration estimated from thermopower measurements by Ono and Ando [24] is plotted in figure 5(a). These results provide useful information in relating the carrier concentration, $c$-axis lattice constant and superconducting transition temperature in the La–Bi2201 system.

In summary, high-quality and large La–Bi2201 single crystals with a wide range of compositions have been successfully prepared by the traveling solvent floating zone method. This will provide an ideal candidate for investigating the electronic structure [29] and physical properties, and the superconductivity mechanism of high-temperature superconductors.

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