Growth and post-annealing studies of Bi$_{2}$Sr$_{2-\delta}$La$_{\delta}$CuO$_{6+\delta}$ ($0 \leq x \leq 1.00$) single crystals

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Abstract

Bi$_{2}$Sr$_{2-\delta}$La$_{\delta}$CuO$_{6+\delta}$ ($0 \leq x \leq 1.00$) single crystals with high quality have been grown successfully using the traveling-solvent floating-zone technique. The patterns of x-ray diffraction suggest high crystalline quality of the samples. After post-annealing in flowing oxygen at 600$^\circ$C, the crystals show sharp superconducting transitions revealed by AC susceptibility. The hole concentration $p$ is deduced from the superconducting transition temperature ($T_c$), which exhibits a linear relation with La doping level $x$. It ranges from the heavily overdoped regime ($p \approx 0.2$) to the extremely underdoped side ($p \approx 0.08$) where the superconductivity is absent. Comparing with the superconducting dome in the Bi$_{2}$Sr$_{2}$CuO$_{6+\delta}$ system, the effects from out-of-plane disorders show up in our samples. Besides the La doping level $x$, the superconductivity is also sensitive to the content of oxygen which could be tuned by the post-annealing method over the whole doping range. The post-annealing effects on $T_c$ and $p$ for each La doping level are studied and give some insights on the differences in nature between the overdoped and underdoped regimes.

1. Introduction

The high temperature superconductivity (HTSC) in copper oxides is one of the most important issues in condensed matter physics. In hole doped cuprates, the antiferromagnetic Mott insulator at half filling will be gradually replaced by a novel metallic state when the hole concentration $p$ increases [1]. The hole doping dependence of superconducting transition temperature ($T_c$), which forms a superconducting dome in the phase diagram [2], which is one of the central challenges to explain the mechanism of HTSC.

The single-layered cuprate Bi$_{2}$Sr$_{2}$CuO$_{6+\delta}$ (Bi2201) is one of the well studied materials for the mechanism of HTSC due to its advantage of relative lower $T_c$ ranging from 30 to 10 K at the optimal doping level in each system [4]. The Bi$_{2}$Sr$_{2}$La$_{\delta}$CuO$_{6+\delta}$ (La-Bi2201) system has the weakest influence of disorders and the highest $T_c$ in this family, while the Bi$_{2}$Sr$_{2}$CuO$_{6+\delta}$ system represents the opposite extreme. The relationship between the disorders and $T_c$ gives more opportunities to access the central problems in the mechanism of HTSC [5, 6], and single crystals with high quality are highly desired for such investigations.

It was reported that the Bi2201 single crystals could be grown by the self-flux and KCl-solution-melt method [7–10]. However, as far as we know, sizeable crystals with high homogeneity and less contamination could be obtained only through the optical traveling-solvent floating-zone (TSFZ) method [11–13]. We have successfully grown high quality Bi$_{2}$Sr$_{2}$CuO$_{6+\delta}$ single crystals with highly dense doping levels in the underdoped regime. The characterizations show that our crystals have high crystalline quality and sharp...
superconducting transitions. The quick contraction of the c-axis accompanied by the suppression of superconductivity suggests that more disorders are introduced by doping Bi\(^{3+}\) into the Sr–O plane \([14]\).

Besides the ionic substitution out-of-plane, it is known that the hole concentration of cuprates is also controlled by the oxygen content which could be tuned by post-annealing method. When a sample is annealed at a certain temperature and atmosphere, the activated oxygen atoms redistribute inside the sample. The holes on O sites in the Cu–O plane will be redistributed. For the overdoped samples with 0.40 < x < 0.45, the oxygen content which could be tuned by post-annealing plays a significant role in the superconductivity. The holes on O sites in the Cu–O plane will redistribute. The quick contraction of the c-axis accompanied by the suppression of superconductivity suggests that more disorders are introduced by doping Bi\(^{3+}\) into the Sr–O plane \([14]\).

In this paper, we report on the successful growth of Bi\(_2\)Sr\(_2\)-\(_x\)La\(_2\)CuO\(_{6+x}\) single crystals with high quality by the TSFZ method. The nominal composition of the La doping level x varies from 0 to 1.0, and the hole concentration of our crystals ranges from the heavily overdoped regime to the extreme underdoped regime where the superconductivity is absent. Post-annealing experiments have been extensively carried out on the samples at each La doping level at different temperatures in flowing oxygen. The post-annealing effects on p and T\(_c\) are studied, which give insights into the differences between the underdoped and overdoped regimes.

2. Experiments

The Bi\(_2\)Sr\(_2\)-\(_x\)La\(_2\)CuO\(_{6+x}\) (0 \(\leq\) x \(\leq\) 1.00) single crystals were grown by the TSFZ technique. The starting materials were prepared by a standard solid state reaction method before the crystal growth. In order to eliminate the moisture, the powders of SrCO\(_3\) (99.99%) were baked at 200 °C for more than 5 h. The powders of La\(_2\)O\(_3\) (99.99%) were calcined at 1000 °C for 10 h to make sure that La(OH)\(_3\) had decomposed completely. After the pre-processes, they were mixed with Bi\(_2\)O\(_3\) (99.99%) and CuO (99.5%) in the stoichiometric proportion (2 - x):x/2:1:1. The mixed powders were ground by hand in a dry agate mortar for about 4 h, and then they were calcined in a crucible at 800°C for 24 h inside a muffle furnace. As soon as the product was cooled down to room temperature, it was crushed into powder then ground and calcined again. This procedure was repeated four times to ensure the homogeneity of the starting material. Finally, the homogeneous polycrystalline powder was pressed into a cylindrical rod of \(\varnothing\)7 mm \(\times\) 90 mm under hydrostatic pressure at ~70 MPa, then it was sintered in a vertical furnace at 850°C for 36 h in air. In order to get a feed rod with higher density and sufficient oxygen content, the premelting process was performed under oxygen pressure P(O\(_2\)) = 2 atm, and the moving speed of the mirror stage was 30 mm h\(^{-1}\). After premelting, a homogeneous feed rod with \(\varnothing\)6-7 mm in diameter and 60–80 mm in length was obtained.

Single crystal growth by the TSFZ method was performed with an optical floating-zone furnace which was produced by Crystal Systems Corporation. A steep temperature gradient was obtained by using four 300 W halogen lamps as the heating sources. The crystal growth was done under an oxygen pressure with 2.0–3.5 atm in an enclosed quartz tube, and the flow rate of O\(_2\) was about 20–40 cm\(^3\) min\(^{-1}\). The typical growth rate is about 0.50 mm h\(^{-1}\), and the rotation rate is 25.0 rpm for the upper shaft and 15.0 rpm for the lower shaft in opposite directions. The post-annealing was carried out under 1 atm flowing oxygen at a finite temperature for more than 150 h at each step. At the end of treatment, the samples were quenched to room temperature in air.

The crystals cleaved from the as-grown ingots were selected carefully under a polarization microscope, and then characterized by various techniques. The x-ray diffraction (XRD) measurements of the crystals were carried out by a Mac-Science MXP18A-HF equipment with \(\theta–2\theta\) scan to examine the crystalline quality of the samples. The K\(_z\) radiation of a Cu target was used, and the continuous scanning range of 2\(\theta\) is from 5° to 80°. The composition of crystal was examined by the energy dispersive x-ray (EDX, Oxford-6566) analysis. The superconductivity of the crystals was characterized by AC susceptibility based on an Oxford cryogenic system Maglab-EXA-12 and a Quantum Design magnetic property measurement system (MPMS). An alternating magnetic field with H = 0.1 Oe was applied perpendicular to the ab-plane with a frequency f = 333 Hz during the AC susceptibility measurement. The transition temperature of the samples was derived from the AC susceptibility curve from the point where the real part of the susceptibility deviates from the flattened normal state part.

3. Results and discussion

3.1. Crystal growth and characterization

The crystal growth was performed under oxygen atmosphere enclosed by a quartz tube. In order to obtain high quality single crystals, the shape of melting zone must be rather stable during the growth. Thus the power of lamp, growth rate, rotation rate of shafts, pressure and flowing rate of oxygen should be carefully tuned. According to our experiences, the melting point of the feed rod increases when more and more La\(_2\)O\(_3\) is mixed into the starting material, and it is also related to the oxygen pressure. Two levels of pressure were applied: P(O\(_2\)) = 2.2 atm for underdoped samples with 0.40 < x < 1.00 and P(O\(_2\)) = 3.4 atm for overdoped samples with 0 < x < 0.30, respectively. The other parameters are almost the same for each nominal composition during the growth. Large plate-like single crystals could be obtained easily for x \(\geq\) 0.70. When x is reduced to 0.40–0.60, the cleaved as-grown crystals are lamellar. For the overdoped samples with x < 0.40, the growth of crystals is much more difficult. Since the viscosity of the melted compound is low during the growth, only needle-like crystals could be obtained for the compositions with x = 0 and 0.05. One of the as-grown ingots with x = 0.85 (below) and the cleaved ingot with x = 0.40 (above) are shown in figure 1. The crystals cleaved from them are sizeable and flat over a large area.

The crystal structure was examined by XRD measurement with the incident ray along the c-axis of the single crystal.
Some typical diffraction patterns are shown in Fig. 2. All peaks are along (00l) with a narrow full-width-at-half-maximum (FWHM) around 0.1°, which demonstrates the high crystalline quality and c-axis orientation in our samples. The c lattice parameters deduced from these patterns are about 24.61 Å, 24.24 Å and 24.03 Å for x = 0.20, 0.60 and 0.90, respectively. The small variation of the c-axis for different La doping levels reveals the ionic substitution effects out-of-plane.

3.2. Hole concentration and superconductivity

The superconductivity of the crystals was characterized by the measurements of AC susceptibility. The La-Bi2201 system is so sensitive to a low magnetic field that the superconducting transition could be suppressed by a tiny DC field as low as 1 G. Figure 3(b) shows that the superconductivity is suppressed quickly under low external DC fields. In order to obtain the exact magnitude of Tc under zero external DC field, the residual field in the external superconducting coils should be eliminated completely before the measurements. In our experiments, the external persistent DC field is lower than 0.5 G, and the results are more reliable and repeatable. Because of the high anisotropy and inhomogeneity in Bi2201 systems and segregation during the growth, the superconducting transition is broad for the as-grown crystals. The Tc also has a broad distribution among different crystals cleaved from the same ingot. However, after post-annealing in flowing oxygen for more than 150 h, the superconducting transition gets much sharper, and the Tc among the samples with the same nominal composition is almost the same. Figure 3(a) shows the typical AC susceptibility data for the samples annealed at 600 °C with x = 0.05, 0.10, 0.20, 0.40, 0.60 and 0.80. The Tc was defined as the point where the real part deviates from the flattened normal state part. The narrow transition width is about 1–2 K for the annealed samples from the overdoped regime to the underdoped regime, which also indicates the high quality of our samples over the whole superconducting dome.

According to previous works, the superconducting dome in the phase diagram of Bi2201 is narrower than the ‘universal bell shape’ shown as Tc/Tc,max = 1 – 82.6(p – 0.16)² [2]. Thus we deduced the hole concentration by using the corrected formula in Bi2201, which was proposed by Ando et al. in the form of Tc/Tc,max = 1 – 255(p – 0.16)² [17]. It should be noticed that the hole concentration p decreases as the La doping level x increases, thus the substitution of Sr²⁺ with La³⁺ enhances the electron doping and reduces the hole concentration [16]. It is found that the hole concentration p for the samples annealed at 600 °C had a linear relation...
with La doping level \(x\) (circles in figure 4(a)), which is consistent with the previous work [17]. The hole concentration locates on the superconducting dome, ranging from the heavily overdoped regime to the extremely underdoped side where the superconductivity is absent (circles in figure 4(b)). In addition, the hole concentration shown in figure 4 for our Bi-Bi2201 samples is deduced from ARPES measurements by integrating the whole Fermi surface area after a tight-binding fitting to the raw data [18]. The data in the heavily overdoped regime could not be given for the unavailable samples. For the overdoped sample above \(p = 0.18\), the nominal content of Bi for Bi-Bi2201 is less than Sr, which means Bi: Sr < 1 (or \(x < 0\)). For our experiments, those samples with \(x = 0\) are very tiny as needles, and ARPES measurements could not be made on them. Moreover, it seems impossible to grow sizeable crystals with Bio: Sr < 1 by the floating-zone method [11, 12, 14, 15]. Anyway, just like our expectations, the curve of \(p\) versus \(x\) for Bi-Bi2201 exhibits almost a straight line correlation (squares in figure 4(a)). However, the slopes of the two lines are different. Because the strength of A-site disorders is weakest in the La-Bi2201 system and strongest in the Bi-Bi2201 system among the Bi2201 family, the \(T_c\) is suppressed more quickly by further substitutions on Sr sites. The real doping level of La is deduced from the linear formula in figure 4(a). It can be seen that the ‘bell shape’ is distorted in Bi-Bi2201.

It should be noted that we use the nominal doping content of La (the value of \(x\)) in the starting material to represent the composition of our crystals throughout this paper. Actually, segregation always happens for the crystals grown from melt, particularly in Bi-2201 systems. We thus became aware that the content of La in the single crystals may be quite different from the initial doped concentration in the polycrystalline powder. So we carried out the EDX measurements on each crystal with a different doping of La, and obtained the relative percentage for each element approximately. Based on the assumption that the proportion of Sr:La in the crystals equates to \((2 - x')x'\), the real doping level of La \(x'\) is deduced and shown in the inset of figure 4(a). It can be found that the real content of La \(x'\) is slightly larger than the nominal content \(x\) with the relation \(x' = 1.05x\). Thus the crystal composition is very close to the starting material, where the segregation coefficient \(K = C_v/C_i\) is only about 1.05, slightly above 1 (b). The superconducting dome for Bi and La doped Bi2201, where the hole concentration is deduced from the linear formulas in figure 4(a). It can be seen that the ‘bell shape’ is distorted in Bi-Bi2201.

### 3.3. Post-annealing effects on superconductivity

In order to investigate the connection between the superconductivity and oxygen content, post-annealing experiments were carried out on our single crystals. For each nominal composition with different La doping level \(x\), a typical as-grown single crystal was selected and then annealed at different temperatures. All treatments were made under 1 atm oxygen pressure with a flow rate of 30–50 cm\(^3\) min\(^{-1}\) for more than 150 h. It was found that the oxygen distribution in the crystal with moderate size reached the equilibrium state after annealing for more than 100 h, because the superconducting transition and \(T_c\) could not be changed any more by further annealing at the same temperature. We conclude that 150 h for each step of post-annealing is enough. At the end of the treatment, the samples were quenched to room temperature in air, and then their AC susceptibility was measured. Several post-annealing temperatures were chosen, varying from 600 to 800°C at 50°C per step. As a final check of reversibility, all samples were annealed at 600°C again as the final step. We used the same sample for each nominal doping level of La throughout the whole procedure.

Figure 5 shows the post-annealing effects on the samples with \(x = 0.10\) and 0.80. Apparently, the superconductivity could be tuned by post-annealing. For the sample with \(x = 0.10\), the \(T_c\) increases as the post-annealing temperature increases. In the final step of post-annealing at 600°C, the superconducting transition could not return to the same shape as that in the first step. There is a long tail above the sharp peak of the imaginary part of AC susceptibility, which indicates that the crystal becomes very inhomogeneous in its oxygen distribution. The as-grown crystals with \(x = 0.80\) exhibit no superconductivity above 1.6 K. However, after post-annealing at 600°C for the first step, superconductivity with \(T_c = 11.9\) K emerges, and it can be promoted by post-annealing at higher temperatures 650–750°C. The superconducting transition width and the magnitude of the diamagnetic signal only change a little during these steps. Unfortunately, after post-annealing at 800°C, \(T_c\) drops down by several Kelvins and
the superconducting transition gets much broader. Although the sample was annealed again at 600 °C at the last step, the transition and \( T_c \) cannot be improved much more. This is similar to the Bi doped Bi2201 system. It seems that it is not easy to tune the \( T_c \) of Bi-Bi2201 by post-annealing [19–21]. According to our previous work, the Bi-Bi2201 system has no significant post-annealing effects at any temperatures less than 600 °C, while annealing at higher temperatures makes the crystals melt down [14].

The post-annealing effects on \( T_c \) are summarized in figure 6(a) for each doping in La-Bi2201 system. Obviously, the magnitude of \( T_c \) varies as the post-annealing temperature changes, and the detailed behaviors also vary for different La doping levels. For the optimal doping samples with \( x = 0.40 \), \( T_c \) is very robust under most post-annealing cases. However, in the heavily underdoped regime with \( x \geq 0.70 \), \( T_c \) is easily affected by post-annealing. The \( T_c \) reaches its maximum magnitude after post-annealing at 750 °C in the underdoped regime. While in the overdoped regime, the highest \( T_c \) could be obtained by post-annealing at 800 °C. Unfortunately, the result of post-annealing at 800 °C is anomalous for all underdoped samples, which gives a much lower \( T_c \) and a broader transition. The ‘bell shape’ is distorted in the case of post-annealing at 800 °C. Moreover, after post-annealing at 600 °C again at the final step, the \( T_c \) cannot return to its value at the first step. This suggests that the crystal structure may distort at such high temperatures being close to its melting point. It is more serious in the overdoped regime, since the melting points for these samples are lower than those in the underdoped region. The \( T_c \) after post-annealing at 600 °C for the final step drops to a much lower level, and the long-tail feature in the AC susceptibility is also very clear. Furthermore, if we plot the hole concentration \( p \) for each \( T_c \) in the same La doping level, it could be found that the hole concentration related to the oxygen content also varies with different post-annealing temperatures (figure 6(b)), where \( p \) is determined by the formula from Ando et al. [17] using \( T_{\text{cm}} = 29.2 \) K. For the first step of post-annealing at 600 °C, the relation between \( p \) and \( x \) is almost linear. It is deviates seriously in the case of post-annealing at 800 °C. After the second step of post-annealing at 600 °C, the hole concentration \( p \) could not return to the same level as the first step of post-annealing at 600 °C. It increases in the overdoped regime, while the opposite happens for the underdoped regime. These different effects of post-annealing suggest that the nature of the superconducting mechanism in the overdoped regime may not be the same as the underdoped regime [1]. One typical example is that phase separation may exist in the overdoped regime [22], where it is absent in the underdoped regime [23, 24].

4. Summary

In summary, we have successfully grown high quality Bi\(_2\)Sr\(_{2-x}\)La\(_x\)CuO\(_{6+\delta}\) (0 \( \leq x \leq 1.00 \)) single crystals by the TSFZ method. The sharp peaks in the patterns of XRD
indicate the high crystalline quality of our samples. After post-annealing in flowing oxygen at 600 °C, the results of AC
susceptibility show sharp superconducting transitions. The hole concentration \( p \) exhibits a linear relation with La doping
level \( x \). It ranges from the heavily overdoped regime (\( p \approx 0.2 \)) to the extremely underdoped region (\( p \approx 0.08 \)) where the
superconductivity is absent. Comparing the La-Bi2201 and Bi-Bi2201 system, the superconducting dome has a narrower
shape in the latter due to the stronger effects from A-site disorders. The hole concentration could also be tuned by
post-annealing at different temperatures in flowing oxygen. The effects of post-annealing on \( T_c \) and \( p \) are summarized
over the whole superconducting regime of the phase diagram, which indicate that the nature of the superconductivity in
the overdoped regime may be different from that in the underdoped regime.

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