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Floating-zone growth and property characterizations of high-quality $La_{2-x}Sr_xCuO_4$ superconductor crystals*

Shen Xiao-Li(慎晓丽), Li Zheng-Cai(李正才), Shen Cai-Xia(申彩霞), Lu Wei(陆 伟), Dong Xiao-Li(董晓莉), Zhou Fang(周 放)†, and Zhao Zhong-Xian(赵忠贤)

National Laboratory for Superconductivity, Institute of Physics and Beijing National Laboratory for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100190, *China*

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We have grown underdoped ($x = 0.11$, 0.12) and optimally doped ($x = 0.16$) $La_{2-x}Sr_xCuO_4$ single crystals by the traveling-solvent floating-zone technique. In order to prepare good quality cuprate crystals, we have made much effort to optimize the preparation procedures. For example, we haveadopted the sol–gel route to prepare a highly fine and homogeneous $La_{2-x}Sr_xCuO_4$ precursor powder for fabricating a very dense ceramic feed rod used for the floating-zone growth, and we have also used quite a slow growth rate. The high quality of the grown crystals has been verified by double-crystal x-ray rocking curves, with the full-width-at-half-maximum being only 113–150 arcseconds, which are the best data reported so far for $La_{2-x}Sr_xCuO_4$ crystals. The superconducting critical temperatures of the grown crystals are 30, 31 and 38.5 K for $x = 0.11$, 0.12 and 0.16 samples, respectively, according to magnetic measurements.

Keywords: floating-zone crystal growth, sol–gel chemistry, x-ray rocking curves, superconductivity
PACC: 6150C, 7430C, 7470

1. Introduction

Among the cuprate superconductor family members, the $La_{2-x}Sr_xCuO_4$(LSCO) system is known to be one of fewer components and of a simpler layered structure of K_2NiF_4 type with a single CuO_2 plane. Its overall density of doped charge (holes) can be continuously tuned by substituting Sr^{2+} cations for La^{3+} ones, and its superconductivity, which evolves from the insulating antiferromagnetic region with strontium doping, occurs in a wide doping range, i. e. $x = 0.06 - 0.26$.[1] Because of these advantages, LSCO has been considered to be a good candidate for studying the origin of high-T_C superconductivity in strongly correlated electron systems since the discovery of the cuprate superconductor. Moreover, some interesting results have recently been reported for the LSCO system. For example, a composite charge model where only a small fraction of the doped holes take part in the free charge transport while the others form a 2D electronic lattice, has been proposed based on far-IR experiments.[2] It has also been found that there exist only two distinct intrinsic superconducting phases with the critical temperatures (T_C's) being either 15 K or 30 K at so-called 'magic' doping levels of $x = 1/16$ (0.0625) or 1/9 (∼0.11), respectively, in the underdoping regime of LSCO.[3−5] And these two intrinsic T_C's are found to be quite field-independent up to 5 T.[5] These facts imply that LSCO may serve as an important prototype for revealing the mechanism of high-T_C superconductivity.

Single crystal samples of high quality can exhibit truly intrinsic property and anisotropy of the cuprate system, they are therefore in high demand for the investigation of superconducting mechanisms. The application of the traveling-solvent floating-zone (TSFZ) method to the growth of LSCO crystals dates back to the early days of the discovery of cuprate superconductors,[6,7] and it has been accepted as a unique technique to grow such incongruent melting cuprate crystals. One key factor for preparing high-quality and homogeneously doped LSCO crystals is to maintain a stable and long-standing molten zone. We report in this paper on the advances we have made in studying the TSFZ growth of LSCO crystals and characterizing their properties. In order to grow high-quality LSCO crystals, we have taken various measures to optimize the whole preparation process. They

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†Corresponding author. E-mail: fzhou@ssc.iphy.ac.cn

include: (1) The Sol–gel technique, instead of the commonly used solid–state reaction, is adopted to synthesize very fine and homogeneous LSCO precursor powder with its final heating temperature no higher than 850 °C. This lower synthesis temperature results in a high sintering activity of LSCO powder. Therefore, by using this sol–gel precursor powder, the LSCO ceramic feed rod can be sintered very densely, and this is of great benefit to a perfect solid–liquid interface and a stable molten zone during TSFZ growth. (2) A slow growth rate of 0.6 mm/h is achieved in this work and the whole growth process is manipulated very carefully. (3) The grown crystals are checked by various measurements to ensure the improvement in crystal quality. For example, the full-width-at-half-maximum (FWHM) of the x-ray rocking curve is as good as 113–150 arcseconds for LSCO crystals grown in this work, which is the best data reported so far for LSCO crystals.[3,8]

2. Experiment

High-purity (better than 99.99%) oxides La_2O_3, CuO and carbonate $SrCO_3$ were used as raw materials based on the chemical formula of $La_{2-x}Sr_xCuO_4$, but with CuO being in excess of ∼2 mol% to compensate for its evaporation loss during the growth process. The La_2O_3 oxide was heated at 900–1000 °C for 6–10 h and $CuO/SrCO_3$ was heated at 125 °C overnight just before weighing. In this work, a sol–gel method was adopted to prepare very fine and homogeneous LSCO precursor powder through following steps:

(i) An appropriate amount of distilled water was first to put into a 1000 ml beaker containing the mixture of raw materials (totally 110–125 g for each batch), then nitric acid (concentration 65%) was added slowly into the beaker with stirring. This step should be done with caution to avoid spattering of the solution due to decomposition of $SrCO_3$. The quantity of the nitric acid used was calculated according to the mole numbers and valences of all the metal elements, usually with an excess of about 10 ml. The solution was heated at 80 °C for about 10 h until all the chemicals were dissolved completely. A blue, transparent nitrate solution was obtained.

(ii) Citric acid (chelating agent) and ethylenediamine were used to form metal-citrate complex sol. An appropriate amount of citric acid was weighed based on the mole numbers of the metals. The powder of citric acid was first dissolved in distilled water, then this citric acid solution was added into the nitrate solution obtained in step (i) with stirring. When ethylenediamine was dropped into the solution when stirring by machine, the blue, transparent solution first became light blue in colour and full of floccules, it then gradually changed into a purple and uniform sol solution without any floccules. Thus the obtained sol was checked by a pH meter and found to be slightly alkaline (pH∼7.6) and was ∼700 ml in volume.

(iii) A thick polymerized complex gel was obtained after the sol had been heated at 60–80 °C for about 10 h in a big alumina crucible when stirred by machine. After being heated again at 140 °C for 3 h in a muffle furnace to further remove the water, the gel changed into dried porous blocks. Then the blocks were crushed into small pieces and heated up to 350 °C in a ventilated muffle furnace to remove most organic species. This heating procedure took about 120 h, including temperature increasing and dwelling (final dwelling being at 350 °C for 15 h); the temperature should be increased very slowly to prevent the material from burning. This step is important for controlling the content of carbon residue in the material to a level less than 1/1000, as checked by a high-frequency combustion/infrared measurement. A light brown fine powder was obtained after ball milling of 2 h.

(iv) The light brown powder was then heated at temperatures of 600 °C and 850 °C for 15 h each. Again the temperature should be raised slowly. After each heating, the powder was ground with a laboratory planetary ball mill for 6–8 h. Then a black precursor powder of pure LSCO phase was synthesized as checked by XRD analysis.

The LSCO precursor powder was put into a silicone tube and pressed with a home-made hydrostatical press under a pressure > 600 MPa to form a very compact cylindrical rod. The rod had a dimension of about 8.5 mm in diameter and 135 mm in length. Then it was suspended with nickel wire in a specially designed vertical furnace (Crystal System Corp., VF-1800/EF-6000) and was sintered at 1240–1280 °C for 2 h depending on different compositions. During sintering the rod was kept rotating and moving up and down to attain an identical thermal history for the whole rod. Thus the prepared LSCO ceramic rod was very dense and uniform, mainly due to the use of the sol–gel precursor powder which was very fine and homogeneous and had a high sintering activity since it was synthesized at temperatures no higher than 850 °C. This synthesis temperature for the LSCO

powder is much lower than that of the standard solid–state reaction procedure, usually over 1000 °C.

The solvent was prepared by the solid state reaction method. The composition was 80–84 mol% CuO as a self-flux. We took into account the previously reported result of distribution coefficients of Sr doped into La_2CuO_4.[9] The mixture of chemical powders was heated twice at 980 ° for 15–20 h each followed by grounding before being pressed into small pellets. The pellets were then sintered at 1000–1020 °C for 15–20 h depending on each composition. In order to reduce bubbles that may emerge during the growth process, the solvent pellets should be sintered at a high enough temperature at which we can be sure that they are not molten.

An infrared-heating floating-zone furnace with a quartet ellipsoidal mirror (Crystal systems Corp., Model FZ-T-10000-H) was used to grow the LSCO crystal by the TSFZ method. LSCO crystals oriented along tetragonal [100] or [110] directions were used as seed crystals. The crystal growth was carried out under an oxygen pressure of 0.2–0.3 MPa to reduce the evaporation of Cu and at quite a slow zone travelling rate of 0.6 mm/h.

Powder x-ray diffraction (XRD) analysis was made on an MXP18A-HF diffractometer using Cu Kα radiation and 2θ ranging from 10° to 80° in 2θ scanning steps of 0.01°. The crystal compositions were checked by the inductively coupled plasma atomic emission spectroscopy (ICP-AES). The experiments of double-crystal x-ray rocking curves were performed on a diffractometer (Bede, model D1) with Cu Kα1 radiation reflected from Si (220) monochromator. The magnetic susceptibility measurements were carried out on a Quantum Design MPMS XL-1 system.

3. Results and discussion

Figure 1(a) is an image taken during the TSFZ growth of the LSCO crystal, showing a very stable molten zone with perfect solid–liquid interfaces as well as little penetration of liquid into the ceramic feed rod. This condition can be kept in the whole growth process (usually it lasts for 6–7 d for each experiment). Such a favourable growth status, as a consequence of the highly dense and uniform ceramic feed rod and careful operations, is very helpful for growing high-quality crystals. First, a long-standing perfect melting interface (upper solid–liquid interface in Fig.1(a)) indicates that the LSCO feed rod can be smoothly and uniformly melted into the molten zone. This helps to establish a constant mass transportation in the molten zone and eventually leads to a perfect growth interface (lower solid–liquid interface in Fig.1(a)) and a uniform Sr doping along the grown ingot. Second, the stable molten zone with perfect solid–liquid interfaces also makes it possible to achieve a slow growth rate (0.6 mm/h in this work), this is also important for improving the crystalline perfection. It needs to be pointed out that bad solid–liquid interfaces usually occur when the ceramic feed rod is not good (dense and uniform) enough. In such a case, a severe liquid permeation into the feed rod may occur and the melting interface may be shaped like jigsaw. When this occurs, the crystal growth is no longer uniform and stable, and the crystal must be grown faster otherwise the molten zone will break down. The size of grown crystal ingots is typically about 6.6 mm in diameter and 100 mm in length as shown in Fig.1(b).

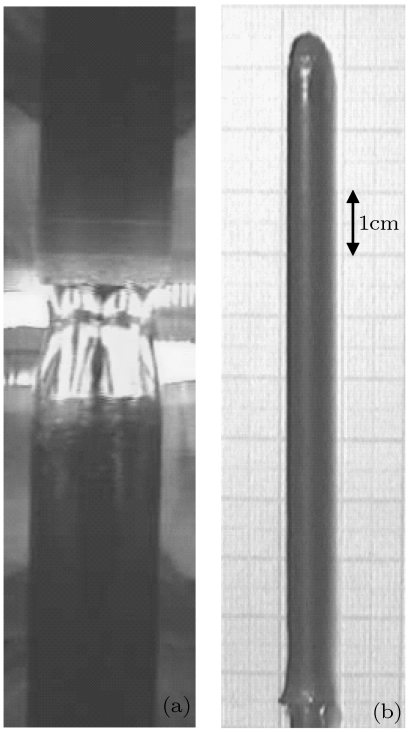


Fig.1. (a) An image taken during the TSFZ growth of the LSCO crystal with $x = 0.12$, showing the molten zone (mid part), the grown ingot (lower part), and the ceramic feed rod (upper part). (b) As-grown ingot of the $x = 0.11$ crystal. At the lower end is the seed crystal.

Figure 2 shows an example of back-scattering x-ray (tungsten target) Laue patterns used for crystal orientation, which is a result obtained on s (001) plane (ab plane) of LSCO $x = 0.11$ crystal and shows very

sharp and uniform diffraction spots with the 4-fold axis symmetry.

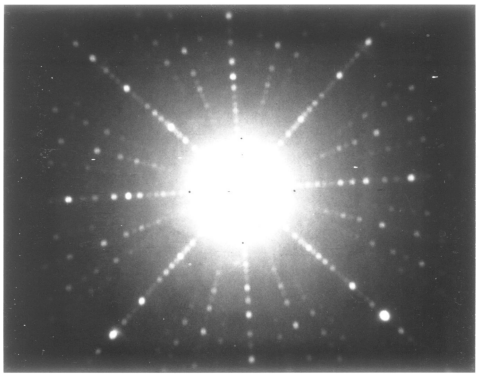


Fig.2. The x-ray (W target) Laue pattern of the (001) plane (the *ab*-plane) for the $x = 0.11$ LSCO crystal. Four small black dots near the middle are used for locating the centre of the Laue camera.

The crystalline perfection of the LSCO crystals (with doping $x = 0.11$, 0.12, 0.16) grown in this work was checked by double-crystal x-ray rocking curves of (008) Bragg reflection, as plotted in Fig.3. The FWHM was as small as 113″–150″ (or 0.03°–0.04°), indicating that the LSCO crystals are of high crystalline quality. As far as we know, this is the best FWHM data reported for LSCO crystals.

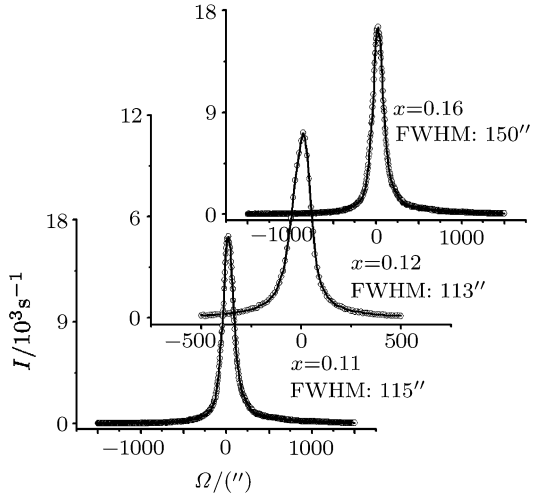


Fig.3. Double-crystal x-ray rocking curves of (008) Bragg reflection for all the three LSCO crystals ($x = 0.11$, 0.12 and 0.16), with FWHM being only 113″–150″ (0.03°–0.04°).

In order to check the phase purity and strontium doping uniformity along the whole grown ingots, we made careful XRD analysis and composition measurement by ICP-AES as follows. On each of the grown ingots with doping $x = 0.11$, 0.12 and 0.16, sectioned from different positions were two slices of a thin disc-shaped crystal of 1 mm thickness, which were designated as sample A and sample B. Sample A was located near the back end of the ingot where the crystal growth had been finished, and sample B was 6–8 cm from sample A. Samples A and B were ground into fine powders before they were measured by XRD and then by ICP-AES. The XRD patterns for the three pairs of samples with $x = 0.11$, 0.12 and 0.16 are shown in figure 4. All the samples are of pure LSCO phase, and each diffraction pattern can be indexed with an appropriate tetragonal unit cell and no impurity phase is detected within the experimental resolution. Listed in Table 1 are the ICP-AES measurements where the compositions in the grown crystals are the same as those in the ceramic feed rods as expected and no variation in Sr doping is observed for each pair of sample A and sample B. These results show that the grown ingots are uniform in composition and phase purity.

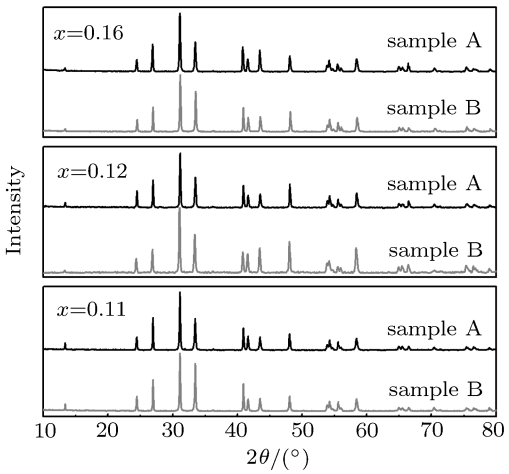


Fig.4. Powder x-ray diffraction patterns for three pairs of sample A and sample B (see text) of the LSCO crystals with $x = 0.11$, 0.12, and 0.16. All the patterns of samples A and B can be indexed on appropriate tetregonal unit cells: $a \sim 3.780$ Å and $c \sim 13.21$ Å for $x = 0.11$; $a \sim 3.777$ Å and $c \sim 13.21$ Å for $x = 0.12$; $a \sim 3.774$ Å and $c \sim 13.22$ Å for $x = 0.16$.

Table 1. A comparison among the compositions determined by ICP-AES for three pairs of sample A and sample B (see text) of LSCO crystals with $x = 0.11$, 0.12, 0.16.

	doping level		
molar ratio	$x = 0.11$	$x = 0.12$	$x = 0.16$
Cu:Sr (sample A)	1:0.11	1:0.12	1:0.16
Cu:Sr (sample B)	1:0.11	1:0.12	1:0.16

The Meissner (field-cooled) and the shielding (zero-field-cooled) signals of the crystals are shown

in Fig.5. The data were corrected for demagnetizing factors.[10] All the samples were processed into a regular dimension of 2 mm×1 mm×0.3 mm and were measured with the c axis along the field. The shielding volume fractions of all the samples are close to 100%, indicating that there is no macroscopic inhomogeneity and/or weak link. The onset superconducting transition temperatures (T_C's) were determined from the differential curves of the Meissner signals (in the same way as that described in Ref.[5]), with the T_C's being 30, 31 and 38.5 K for $x = 0.11$, 0.12 and 0.16 crystals, respectively, and they are consistent with the data reported previously. Moreover, both sample A and sample B of the $x = 0.11$ crystal were checked by the magnetic measurements. The two sets of results gave the same T_C values as expected, again indicating that both the crystalline and property are uniform along the ingot.

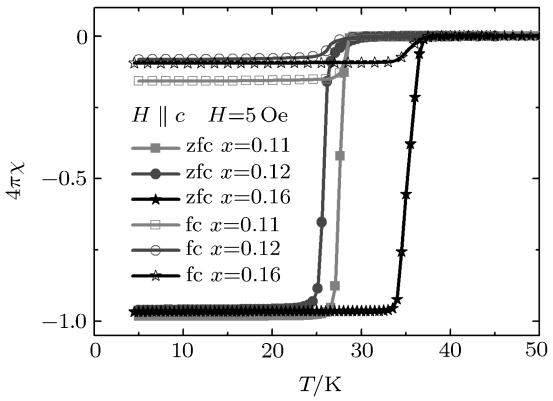


Fig.5. The Meissner curves (open symbol lines) and shielding curves (solid symbol lines) measured under a field of 5×10^{-4} T for LSCO crystals with different doping levels. Here 1 Oe=79.5775 A/m.

4. Conclusion

High quality and sizable $La_{2-x}Sr_xCuO_4$ crystals with $x = 0.11$, 0.12 and 0.16 are grown by the TSFZ technique. The crystal quality and properties of the grown ingots are characterized by several methods such as x-ray diffractions (powder diffractions, Laue patterns, rocking curves), composition analysis and magnetic measurements. The high crystal quality is evidenced by the double-crystal x-ray rocking curves with the FWHM being only 113″–150″ (0.03°–0.04°), which are the best data reported so far for $La_{2-x}Sr_xCuO_4$ crystals. The grown crystal ingots are uniform both in composition and in phase purity. The onset superconducting transition temperatures are 30, 31 and 38.5 K for $x = 0.11$, 0.12 and 0.16 crystals, respectively.

The use of highly fine and homogeneous $La_{2-x}Sr_xCuO_4$ precursor powders synthesized by the sol–gel route as well as other optimized preparation conditions is quite effective in producing very dense and uniform ceramic feed rods and high-quality crystals. A dense and uniform ceramic feed rod is crucial for maintaining perfect solid–liquid interfaces (e.g. little penetration of liquid into the feed rod) and a stable molten zone during the floating-zone growth. That also makes it possible to use a slow growth rate. All these factors are important for growing high-quality crystals by the TSFZ method.

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