A Reproducible Approach of Preparing High-Quality Overdoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ Single Crystals by Oxygen Annealing and Quenching Method *

Yu-Xiao Zhang(张玉晓)[1], Lin Zhao(赵林)[1**], Gen-Da Gu(顾根大)[2], Xing-Jiang Zhou(周兴江)[1,3**]

[1]*National Lab for Superconductivity, Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100190*

[2]*Condensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, USA*

[3]*Collaborative Innovation Center of Quantum Matter, Beijing 100871*

(Received 3 May 2016)

We report a reproducible approach in preparing high-quality overdoped $Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) single crystals by annealing Bi2212 crystals in high oxygen pressure followed by a fast quenching. In this way, high-quality overdoped and heavily overdoped Bi2212 single crystals are obtained by controlling the annealing oxygen pressure. We find that, beyond a limit of oxygen pressure that can achieve most heavily overdoped Bi2212 with a T_c ~63 K, the annealed Bi2212 begins to decompose. This accounts for the existence of the hole-doping limit and thus the T_c limit in the heavily overdoped region of Bi2212 by the oxygen annealing process. These results provide a reliable way in preparing high-quality overdoped and heavily overdoped Bi2212 crystals that are important for studies of the physical properties, electronic structure and superconductivity mechanism of the cuprate superconductors.

PACS: 74.72.−h, 74.72.Gh, 81.40.−z, 81.40.Ef DOI: 10.1088/0256-307X/33/6/067403

The discovery of high-temperature cuprate superconductors[1] has posed a large challenge to the conventional Fermi liquid theory and BCS theory of superconductivity in condensed matter physics.[2−5] From the generic electronic phase diagram, starting from the parent compound where the doping level is zero, it is generally believed that superconductivity arises from doping the Mott insulator.[6] In the process of evolving from an antiferromagnetic state to a superconducting state with increasing doping, there are a number of phases that are identified in the underdoped region, including spin glass,[7] spin density wave or charge density wave,[8−12] and so on, in this enigmatic pseudogap region.[13] These new electronic phases coexist, compete or cooperate with superconductivity in the underdoped region, giving rise to rich physics, and at the same time producing complications in disentangling the origin of the high-temperature superconductivity. On the other hand, in the overdoped region, these states tend to become weak and may even vanish. It is assumed that in the heavily overdoped region where superconductivity disappears, the conventional Fermi liquid state is recovered. Judging from the electronic phase diagram, it is clear that there are two ways to approach the superconductivity region, either from left with increasing doping starting from the parent compound, or from right with decreasing doping from the heavily overdoped Fermi liquid state. However so far, most of the studies have been focused on the underdoped region, with much fewer studies in the overdoped region. Quantum critical point (QCP) or crossover is proposed to exist in the overdoped region.[14,15] Assuming plausibly that the same single superconductivity mechanism is at operation under the superconductivity dome, it seems to be more advantageous to study the superconductivity mechanism from the overdoped side due to the fact that it starts from the conventional Fermi liquid state and involves much fewer complications in the evolution to the superconducting state upon reducing the doping level.

$Bi_2Sr_2CaCu_2O_{8+\delta}$ (Bi2212) is a prototypical high-temperature superconductor that has been extensively studied. It has relatively high superconducting transition temperature (T_c over 90 K),[16] highly two-dimensional crystal structure and electronic structure, and is easy to become a smooth and shiny surface. It has therefore become a workhorse for some powerful experimental techniques like angle-resolved photoemission spectroscopy (ARPES)[17−19] and scanning tunneling microscopy/spectroscopy (STM/STS).[20] Many significant insights have been obtained through ARPES and STM/STS studies of Bi2212, including the observation of strongly anisotropic superconducting gap,[21,22] the revelation of pseudogap,[23,24] and the many-body effects due to electron interactions with other entities.[25−30] However, extensive studies on Bi2212 have been hindered due to the fact

*Supported by the National Natural Science Foundation of China under Grant Nos 11190022, 11334010 and 11534007, the National Basic Research Program of China under Grant No 2015CB921000, and the Strategic Priority Research Program (B) of Chinese Academy of Sciences under Grant No XDB07020300.

**Corresponding author. Email: lzhao@iphy.ac.cn; XJZhou@aphy.iphy.ac.cn

© 2016 Chinese Physical Society and IOP Publishing Ltd

that the accessible hole doping level is mostly limited around the optimal doping. In $Bi_2Sr_2CaCu_2O_{8+\delta}$, different doping levels are realized mainly by annealing the sample to change its oxygen content, δ. Different methods have been employed in preparing overdoped Bi2212 samples. The most common way is to insert extra oxygen in $Bi_2Sr_2CaCu_2O_{8+\delta}$ by high oxygen annealing.[31,32] In this case, high oxygen pressure of up to ∼30 MPa is used to achieve overdoped Bi2212 with a T_c of ∼65 K.[32] Another way is to dope lead (Pb) into Bi2212 to introduce extra holes,[33,34] which inevitably introduces disorder into the sample at the same time. Researchers have proven that it is difficult to obtain overdoped Bi2212 samples with a T_c lower than ∼60 K,[35,36] and the origin is not well understood. It is therefore important to develop a reliable and reproducible way to prepare heavily overdoped Bi2212 samples to tackle superconductivity issues from the overdoped side.

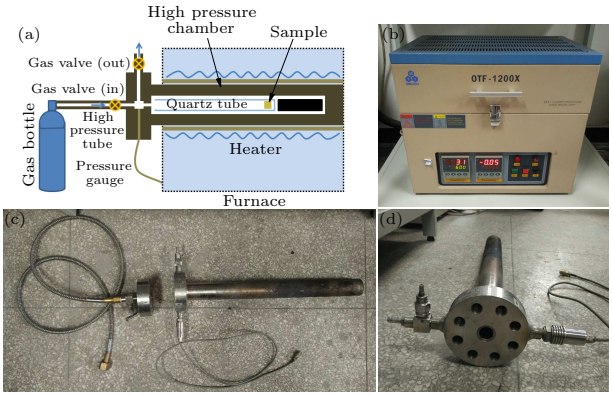

Fig. 1. Experimental apparatus for high-pressure oxygen annealing. (a) Schematic diagram of the high-pressure oxygen annealing apparatus. (b) A photo of the heating furnace. (c) A photo of the high pressure chamber. (d) Another view of the high-pressure chamber from different angles.

In this Letter, we report an effective way to reproducibly obtain high-quality overdoped Bi2212 single crystals. This is accomplished by combining high oxygen pressure annealing with fast sample quenching. By testing different conditions including the annealing temperature, oxygen pressure and the various cooling methods, we have found a reliable way to prepare overdoped Bi2212 samples with different T_c by controlling the oxygen pressure. The oxygen atmosphere we used (∼7 MPa) to obtain overdoped Bi2212 samples with a comparable T_c is much lower than that used before (∼30 MPa).[32] The fast cooling after annealing is critical for obtaining high quality overdoped Bi2212 samples and we have developed an effective way to quench the annealed samples. We find that, beyond a limit of oxygen pressure that can achieve most heavily-overdoped Bi2212 with a T_c ∼63 K, the annealed Bi2212 begins to decompose. This explains the existence of the hole-doping limit and thus the T_c limit in the heavily overdoped region of Bi2212 by the oxygen annealing process. Our results provide a reliable way of preparing high-quality overdoped and heavily overdoped Bi2212 crystals that are important for studying cuprate superconductors.

Figure 1 shows the high-oxygen-pressure annealing apparatus we developed for preparing overdoped Bi2212 samples. Figure 1(a) shows the schematic diagram of the operation principle. The main component is the high-pressure chamber that is made of special alloy to withstand high pressure (see the right side of Figs. 1(c) and 1(d)). This high-pressure chamber is connected and sealed through a conventional CF flange (the left side of Fig. 1(c)) to an oxygen gas bottle which can supply high-purity oxygen gas (99.99%) with the pressure varying between 0.1 MPa to 15 MPa. The oxygen pressure inside the high-pressure chamber is controlled by the two gas valves and measured by the pressure gauge. The Bi2212 single crystals are wrapped in a gold foil and put near the bottom of a quartz tube to avoid sample contamination. Then the sample together with the quartz tube is inserted into the high-pressure chamber. The high-pressure chamber is put into the heating furnace (Fig. 1(b)). The sample is close to the furnace center to obtain a uniform temperature heating and an accurate temperature controlling. This apparatus makes it possible to control the annealing temperature and the oxygen pressure rather accurately, and in particular, to have different ways of cooling down the sample after the annealing process.

The Bi2212 single crystals we annealed were grown by using an infrared radiation furnace (Crystal Systems Inc.).[37–39] Magnetic measurements show a critical temperature of ∼91 K and a transition width of ∼2 K (blue curves in Fig. 2). The as-grown Bi2212 crystals have a large size, which are cut into many small pieces for annealing to make sure that all the annealings have similar starting samples. We first tried different annealing temperatures between 400°C to 600°C. It is found that T_c of the annealed Bi2212 samples is not sensitive to the annealing temperature. We therefore fix our annealing temperature at 500°C for all the annealings in the following. To have a sufficient oxygen exchange, the annealing time is kept at five days. The starting oxygen pressure is varied between 0.1 MPa and 8.1 MPa. For completeness and comparison, we also anneal the Bi2212 crystals under an oxygen pressure of 0.01 MPa. This was realized in a slightly different way by sealing the Bi2212 crystals in a quartz tube. The quartz tube with Bi2212 crystals was first filled with 0.1 MPa oxygen, and was then pumped to 0.01 MPa oxygen pressure before it was sealed. The Bi2212 crystals in the sealed quartz tube was annealed at 500°C for five days and was then quenched into liquid nitrogen.

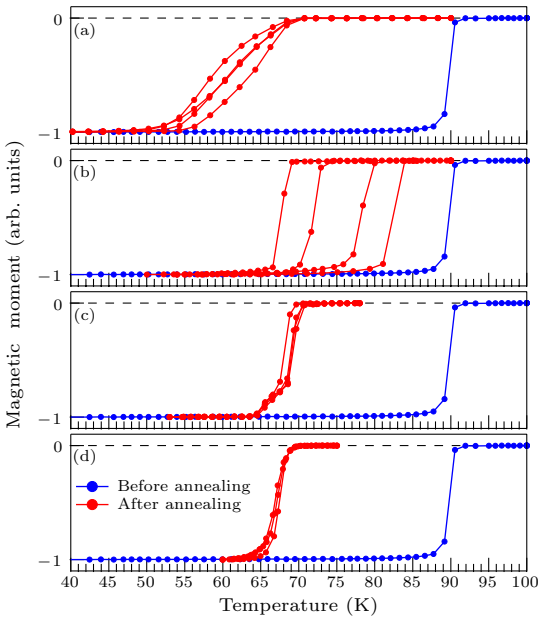

Fig. 2. Magnetic measurements on the superconducting transition of Bi2212 single crystals annealed and cooled under different conditions. The magnetic measurement of the as-grown Bi2212 before annealing is shown by the blue curve, while the measurements for annealed Bi2212 are shown by the red curves. (a) Bi2212 crystals are naturally cooled down to room temperature in the high-pressure oxygen chamber. (b) Bi2212 crystals are dumped out of the quartz tube into liquid nitrogen after annealing and releasing the high-pressure oxygen. (c) Bi2212 crystals are naturally cooled down to ∼400℃ firstly, then the high-pressure chamber is dropped into water to cool down to room temperature. (d) The high-pressure chamber is dropped into water right after annealing at 500℃ and quickly cooled down to room temperature. The oxygen pressure used here is 6 MPa.

We find that the quenching process is critical for obtaining high-quality overdoped Bi2212 samples after annealing. Figure 2 shows the testing results of the Bi2212 samples by using different cooling methods after annealing. (1) If we turn off the power of the furnace after annealing and let the Bi2212 samples cool down naturally to room temperature, the superconducting transition is rather broad (Fig. 2(a)), that is, more than 10 K. Different trials are quite repeatable while it is impossible to obtain high-quality Bi2212 samples with sharp superconducting transition using this cooling method. (2) We then tried the first kind of fast quenching method. After the annealing process, we first released the high-pressure oxygen to ambient pressure while keeping the heating temperature unchanged. Then we opened the seal part from the high-pressure chamber and dumped the Bi2212 samples wrapped in the gold foil from the quartz tube into liquid nitrogen as fast as possible. This method is repeated four times and the results of the obtained Bi2212 samples are shown in Fig. 2(b). All four samples show very sharp superconducting transition with a transition width of 2∼3 K. This demonstrates the necessity and importance of fast quenching in obtaining high-quality overdoped Bi2212 samples. However, although these four tests were carried out in a similar way, the obtained T_c's are rather scattered. This indicates that this quenching process is hard to reproduce due to some uncontrollable factors involved in the fast operation process. (3) We then tried the second quenching method by pulling the high-pressure chamber out of the furnace and threw it into water. For safety reason, we did not throw it into liquid nitrogen. Even for water quenching, to be safe, we first shut down the power of the furnace to let the high-pressure chamber cool down naturally from 500℃ to 400℃, then pulled out the high-pressure chamber and put it into water. The results are shown in Fig. 3(c). The obtained T_c for four times are reproducible and sharp while containing two transitions that correspond to two different cooling processes. This again demonstrates the importance and necessity of the single quenching process. (4) We then directly pull the high-pressure chamber out of the furnace right after the annealing and put it into water rapidly. The results of three times give very reproducible results on T_c and the superconducting transition is sharp (∼2 K). This is a controllable way to obtain high-quality overdoped Bi2212 samples that are good enough for high-standard ARPES and STM measurements.

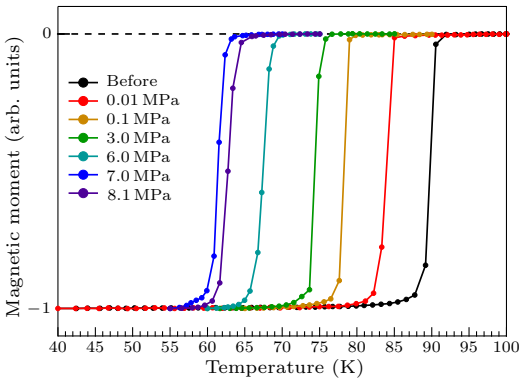

Fig. 3. Preparation of overdoped Bi2212 single crystals by annealing under different oxygen pressures and cooled down by dumping the high-pressure chamber into water right after the annealing. Different superconducting transitions with sharp transition can be obtained for Bi2212 by using this reliable and reproducible approach.

After establishing a reproducible method to obtain high-quality overdoped Bi2212 samples, we moved on to obtain Bi2212 samples with different T_c's by tuning the oxygen pressure that is known to be a sensitive knob in dictating T_c.[7,31,40] Figure 3 shows the superconducting transitions of the Bi2212 samples we obtained by the above fast quenching method under different oxygen pressures. With the increase of the oxygen pressure, T_c of the obtained overdoped Bi2212 samples can vary from the initial 91 K, to overdoped T_c ∼79 K at 0.1 MPa, to heavily overdoped T_c ∼63 K at 7 MPa. The values of T_c show a mono-

tonic and systematic change with the oxygen pressure, and the superconducting transitions are all very sharp. These results demonstrate the effectiveness of our post-annealing process in producing high-quality overdoped Bi2212 samples with different T_c's. We note that the pressure we used here (7 MPa) is considerably lower than that used previously (~30 MPa)[32] in obtaining the Bi2212 samples with comparable T_c. We also note that there appears to be a limit of the lowest T_c (and hence the hole doping level) achieved by increasing the oxygen pressure. When the oxygen pressure reaches 8.1 MPa, the corresponding T_c does not become lower, instead becomes higher (Fig. 3).

We carried out the x-ray diffraction analysis on the above-mentioned annealed Bi2212 samples under different oxygen pressures to sort out the relation between the structure and superconductivity. Figure 4(a) shows the x-ray diffraction patterns of the Bi2212 crystals annealed and quenched in water (the same samples in Fig. 3). The (00$\underline{10}$) peaks are expanded in Fig. 4(b) to illustrate the peak position shift with the oxygen pressure. The corresponding lattice constant c can be calculated from Figs. 4(a) and 4(b) and is shown in Fig. 4(c). It is clear that, when the oxygen pressure increases to 7 MPa, the annealed Bi2212 crystals keep in the single phase (Fig. 4(a)), and their lattice constant c decreases with increasing the oxygen pressure. It is interesting to find that the lattice constant c shrinks with the insertion of extra oxygen into the lattice. It is also interesting to find that the lattice constant c (Fig. 4(c)) and the corresponding T_c (Fig. 4(d)) of these annealed Bi2212 samples show a good correspondence. In particular, when the oxygen pressure reaches 8.1 MPa, there are additional peaks that appear in the XRD pattern (Fig. 4(a)). This indicates that the Bi2212 sample starts to decompose when annealed under such a high pressure. Due to this, the corresponding lattice constant c does not decrease further, instead becomes larger (Fig. 4(c)), corresponding to an increase of T_c. This observation explains why there is a limit on the hole-doping level, thus the corresponding lowest T_c is achieved in the heavily overdoped region due to the fact that there is a limit of oxygen insertion. Beyond the limit, the extra oxygen may decompose the annealed Bi2212 samples. Such an understanding is helpful in realizing the limitation of the high oxygen annealing procedure in obtaining overdoped Bi2212 samples and trying to find other ways in overcoming this hole-doping barrier.

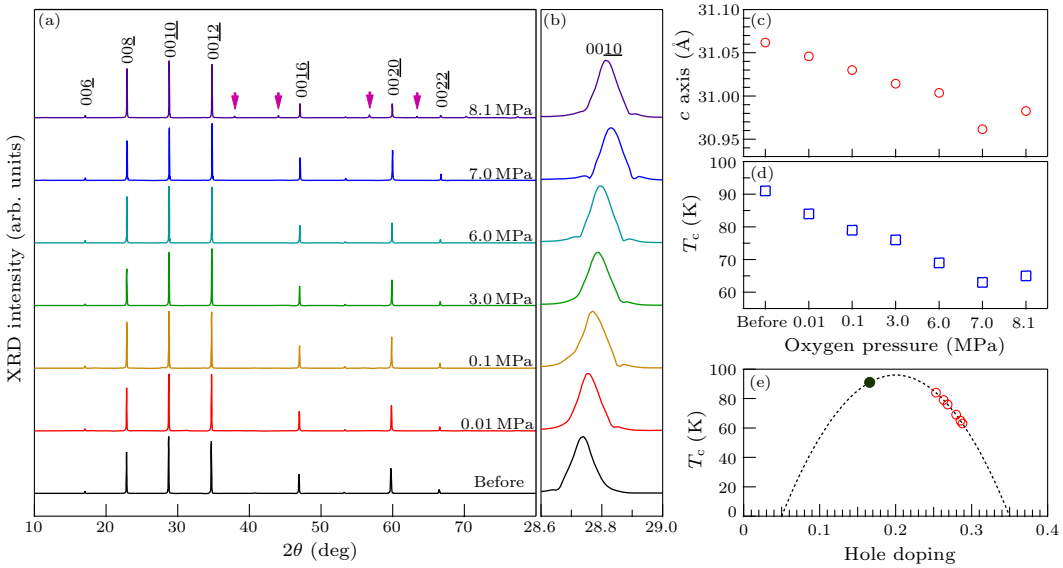

Fig. 4. Relationship between the annealing condition and the resultant crystal structure and superconducting transition for Bi2212 single crystals. (a) X-ray diffraction patterns of the Bi2212 single crystals annealed under different oxygen pressures. The data are taken by using a rotating anode x-ray diffraction machine under θ-2θ scan mode with Cu K_α radiation ($\lambda = 1.5418$). (b) The expanded (00$\underline{10}$) peaks to highlight the peak position shift under different annealing oxygen pressures. (c) Lattice constant c of Bi2212 crystals under different annealing oxygen pressures. The corresponding superconducting transition temperature (T_c) is shown in (d). (e) Schematic phase diagram of Bi2212 with the obtained overdoped samples marked (red circles).

In summary, we have developed an effective method in preparing high-quality overdoped Bi2212 single crystals with different critical temperatures. This is realized by a controllable fast-quenching procedure after the annealing. Overdoped and heavily overdoped Bi2212 samples with different T_c's have been obtained by this quenching procedure and tuning the oxygen pressure during the annealing process. Such a method can be extended to other superconducting cuprate systems. This high oxygen pressure annealing method has a limit on the hole-doping level, and thus on the lowest T_c that can be achieved. This is due to

the fact that beyond this oxygen pressure limit, the annealed Bi2212 may start to decompose. New ideas have to be developed to break the doping and T_c barriers in the overdoped region. A combination of the present annealing and quenching approach with the Pb-substitution in Bi2212 could be a reasonable way that can be further explored.

References

[1] Bednorz J G and Müller K A 1986 *Z. Phys.* B **64** 189
[2] Orenstein J and Millis A J 2000 *Science* **288** 468
[3] Bonn D A 2006 *Nat. Phys.* **2** 159
[4] Zaanen J et al 2006 *Nat. Phys.* **2** 138
[5] Keimer B et al 2015 *Nature* **518** 179
[6] Lee P A, Nagaosa N and Wen X G 2006 *Rev. Mod. Phys.* **78** 17
[7] Wantanabe T, Fujii T and Matsuda A 1997 *Phys. Rev. Lett.* **79** 2113
[8] Ghiringhelli G et al 2012 *Science* **337** 821
[9] Achkar A J et al 2012 *Phys. Rev. Lett.* **109** 167001
[10] Chang J et al 2012 *Nat. Phys.* **8** 871
[11] Blackburn E et al 2013 *Phys. Rev. Lett.* **110** 137004
[12] Neto S et al 2014 *Science* **343** 393
[13] Timusk T and Statt B 1999 *Rep. Prog. Phys.* **62** 61
[14] Tallon J L and Loram J W 2001 *Physica* C **349** 53
[15] Castellani C, Castro C D and Grilli 1995 *Phys. Rev. Lett.* **75** 4650
[16] Eisaki H et al 2004 *Phys. Rev.* B **69** 064512
[17] Damascelli A, Hussain Z and Shen Z X 2003 *Rev. Mod. Phys.* **75** 473
[18] Campuzano J C, Norman M R and Randeria M 2004 *Phys. Superconductors* (Berlin: Springer) vol 2 p 167
[19] Zhou X J et al 2007 *Handbook of High-Temperature Superconductivity* (New York: Springer) chap 3 p 87
[20] Fischer O et al 2007 *Rev. Mod. Phys.* **79** 353
[21] Shen Z X et al 1993 *Phys. Rev. Lett.* **70** 1553
[22] Ding H et al 1996 *Phys. Rev.* B **54** R9678
[23] Loeser A G et al 1996 *Science* **273** 325
[24] Ding H et al 1996 *Nature* **382** 51
[25] Bogdanov P V et al 2000 *Phys. Rev. Lett.* **85** 2581
[26] Johnson P D et al 2001 *Phys. Rev. Lett.* **87** 177007
[27] Kaminski A et al 2001 *Phys. Rev. Lett.* **86** 1070
[28] Lanzara A et al 2001 *Nature* **412** 510
[29] Zhang W T et al 2008 *Phys. Rev. Lett.* **100** 107002
[30] Bok J M et al 2016 *Sci. Adv.* **2** e1501329
[31] Morris D E et al 1989 *Phys. Rev.* B **39** 6612
[32] Feng D L et al 2001 *Phys. Rev. Lett.* **86** 5550
[33] Bogdanov P V et al 2001 *Phys. Rev.* B **64** 180505
[34] Kordyuk A A et al 2002 *Phys. Rev.* B **66** 014502
[35] Chatterjee U et al 2011 *Proc. Natl. Acad. Sci. USA* **108** 9346
[36] Vishik I M et al 2012 *Proc. Natl. Acad. Sci. USA* **109** 18332
[37] Liang B and Lin C T 2002 *J. Cryst. Growth* **237** 756
[38] Wen J S et al 2008 *J. Cryst. Growth* **310** 1401
[39] Liu S Y et al 2012 *Chin. Phys. Lett.* **29** 087401
[40] Wang N L et al 1996 *Phys. Rev.* B **54** 7445