Enhancement of the superconducting critical temperature of $Sr_2CuO_{3+\delta}$ up to 95 K by ordering dopant atoms

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We address the question of whether the superconducting transition temperature (T_c) of high-T_c cuprates is enhanced when randomly distributed dopant atoms form an ordered array in the charge reservoir layers. This study is possible for the $Sr_2CuO_{3+\delta}$ superconductor with K_2NiF_4-type structure in which oxygen atoms only partially occupy the apical sites next to the CuO_2 planes and act as hole dopants. We show that remarkable T_c enhancement up to 95 K in this mono CuO_2 layered high-temperature cuprate superconductor (HTS) is associated with the apical oxygen ordering, not to the hole concentration change. The result points a route toward further enhancement of T_c in cuprate superconductors.

One of the central concerns of high-temperature cuprate superconductor (HTS) is how to raise the superconducting transition temperature T_c. The doping level and the number of CuO_2 planes (n) in a unit cell have been considered to be most feasible parameters controlling T_c. For each member of cuprates, T_c becomes maximum T_c^{max} at optimal doping concentration, which is usually in the range between 0.15 and 0.20/Cu site,[1] and T_c is highest when $n=3$ for multilayer cuprates (or homologous series).[2] HTS is an alternating array of charge reservoir blocks and the CuO_2 conducting planes. The charge reservoir blocks supply holes or electrons into the CuO_2 planes, and in most cases are disordered since dopant atoms reside in the blocks and are randomly distributed.

Tuning the oxygen content in the charge reservoir blocks is one of the most fundamental chemical doping mechanisms of HTS. As a typical example, by breathing in or out oxygen and forming the Cu-O chain layer, $YBa_2Cu_3O_{6+\delta}$ can be either a 90 K superconductor or a nonsuperconducting insulator. In this case oxygen doping and its ordering is in the second-nearest neighbor charge reservoir blocks, and it has been believed that disorder in these blocks has minimal effect on the electronic state in the CuO_2 planes as the relative long separation. On the other hand, the oxygen atoms at the apical sites of a CuO_5 pyramid or a CuO_6 octahedron called "apical oxygen" form the nearest-neighbor charge reservoir block.[2–4] Disorder in this block is expected to have an appreciable effect on the adjacent CuO_2 plane since they have direct chemical bonding in terms of electron exchange interaction.[5] *However, for almost all HTSs, apical oxygen sites are fully occupied,*[6] *leading to the apical oxygen amount is unchangeable, not less to modulate the order state.* Study of a compound with partially occupied apical oxygen sites is thus of fundamental physical interest for a deeper understanding of the yet unresolved doping/order effect on high-T_c superconductivity.

The $Sr_2CuO_{3+\delta}$ superconductor synthesized under high pressure is quite a unique cuprate, which crystallizes into an oxygen-deficient La_2CuO_4 (i.e., K_2NiF_4) structure with partially occupied apical sites (Fig. 1), and the apical oxygen

acts as hole dopant.[6–10] We have investigated the effect of low-temperature annealing on superconductivity in single phase $Sr_2CuO_{3+\delta}$, and found that a remarkable enhancement of T_c in this superconductor is associated with the ordering of the apical oxygen atoms, not with a change of doped hole density.

At ambient pressure, the stoichiometric Sr_2CuO_3 forms an orthorhombic structure with Cu-O chains along the a axis.[14,15] Introducing extra O and applying high pressures leads to the formation of a K_2NiF_4-type tetragonal structure containing a CuO_2 plane as shown in Fig. 1. Although high-pressure synthesis is a very powerful tool to search for unique HTS materials,[6–13] preparation of a single-phase sample is generally difficult, and sometimes it is hard to
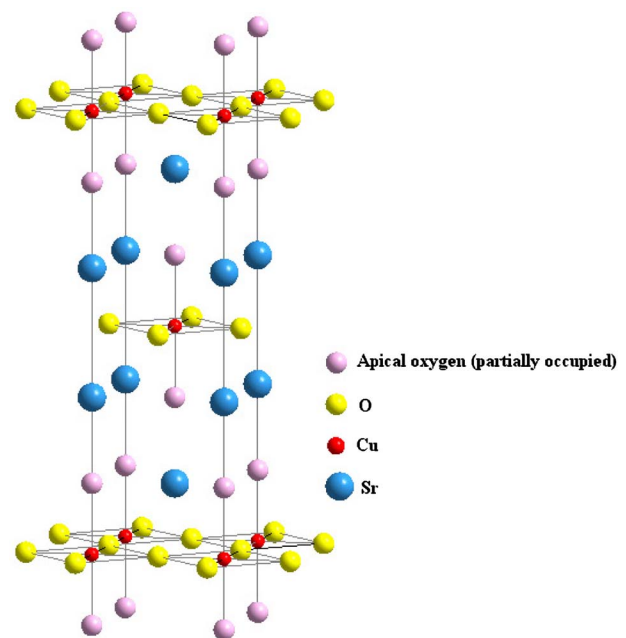

FIG. 1. (Color online) Schematic view of the crystal structure of $Sr_2CuO_{3+\delta}$ with K_2NiF_4 type tetragonal structure containing the CuO_2 plane, but the apical oxygen sites are partially occupied.
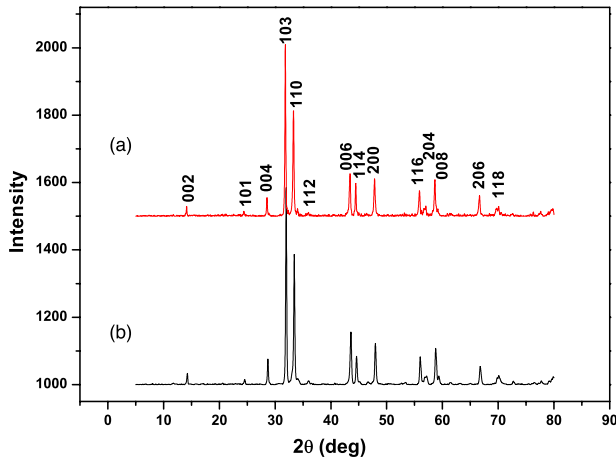
FIG. 2. (Color online) X-ray powder diffraction pattern for the sample $Sr_2CuO_{3+\delta}$ with nominal $\delta=0.4$: (a) the high pressure as-prepared sample, (b) the sample after post heat treatment at 300 °C in N_2 at ambient pressure.

FIG. 3. (Color online) Temperature dependence of the dc magnetic susceptibility in the field-cooling mode for as-prepared $Sr_2CuO_{3+\delta}$ and those after annealed at various temperatures in the N_2 atmosphere.

identify the superconducting phase in the sample.[16,17] Using $KClO_4$ as an oxidizer, Hiroi *et al.*[8] succeeded in fabricating tetragonal $Sr_2CuO_{3+\delta}$ showing superconductivity at T_c =70 K. They suggested that the main phase in this material is a highly apical oxygen-deficient K_2NiF_4-type tetragonal structure. After this discovery $Sr_2CuO_{3+\delta}$ superconductors were synthesized by several groups using the high-pressure technique as well as thin-film growth,[18] and T_c was enhanced above 90 K by post annealing.[9,10]

In the previous studies, two types of modulated structures were reported. Hiroi *et al.*[8] and Laffez *et al.*[9] found $4\sqrt{2}a_p \times 4\sqrt{2}a_p \times c_p$ and $5\sqrt{2}/2a_p \times 5\sqrt{2}/2a_p \times c_p$ modulated structures in their as-prepared samples, and suggested that the superconductivity might be occurring in the latter tetragonal phase. This was also supported by Wang *et al.*[19] and Zhang *et al.*[20] However, these superconducting samples were multiphase mixtures and superconducting volume fraction was very small, so it was difficult to determine the detailed structure and to identify the superconducting phase definitely.

To make the phase as pure as possible, we synthesized the $Sr_2CuO_{3+\delta}$ sample under pressures using SrO_2 as an oxidizer. The high-pressure synthesis (6 GPa and 1100 °C for 1 h) was performed using a cubic-anvil-type apparatus. Sr_2CuO_3, SrO_2, and CuO were mixed to yield the nominal composition $Sr_2CuO_{3+\delta}$ at various molar ratios in a dry box. The role of SrO_2 peroxide is to create an oxygen atmosphere during the high-pressure synthesis as we previously used in the related Sr-Ca-Cu-O-Cl system.[11] The oxygen pressure was controlled by the amount of SrO_2 in the starting materials. The main reason for using SrO_2 oxidizer instead of $KClO_4$ is to avoid the formation of the superconducting phase containing Cl as found in Ref. 17 or other unwanted pollution from the third element, which will make the identification of the real superconducting phase easier. The single phase $Sr_2CuO_{3+\delta}$ in terms of powder x-ray diffraction provides us with the solid ground to make clear the origin of the mysterious high T_c in this monolayered La_2CuO_4 type superconductor. The crystal structure was analyzed by means of powder x-ray diffraction (XRD) using Cu Kα radiation. The dc magnetic susceptibil-
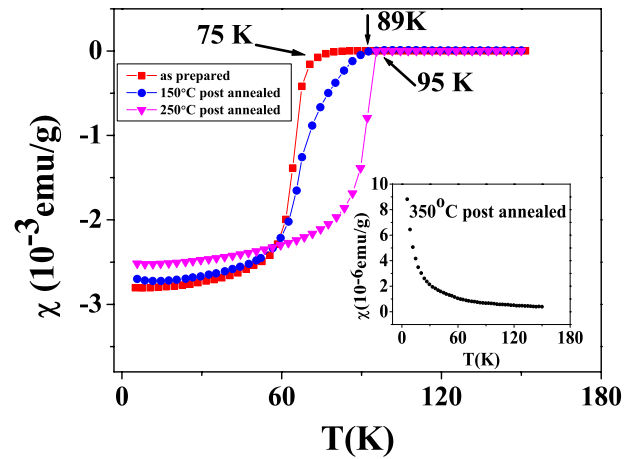
ity was measured with a SQUID magnetometer in an external magnetic field of 20 Oe. A Tecnai F20 electron microscope with a field emission gun was used for electron diffraction experiments.

A series of $Sr_2CuO_{3+\delta}$ samples were prepared under high-pressures by changing the initial amount of SrO_2. The superconducting phase was found in the range 0.1–0.6 and a maximum $T_c \approx 75$ K occurs at $\delta=0.4$. The x-ray diffraction pattern of $Sr_2CuO_{3+\delta}$ $\delta(=0.4)$ shows tetragonal structure with space group $I4/mmm$, indicating an apparently single-phase pattern with lattice parameters $a=3.795(3)$ Å, $c=12.507(1)$ Å. In order to further "optimize" T_c, the sample was then annealed in the temperature range of between 150 and 350 °C for 12 h under 1 atm N_2 atmosphere in a tube furnace. The XRD pattern shows that the sample maintains the same tetragonal single phase as that of as-prepared up to 300 °C, and then becomes a mixture of the tetragonal and the orthorhombic chain phases when heat treated at 350 °C. Figure 2 presents the x ray diffraction patterns of $Sr_2CuO_{3+\delta}$ $\delta(=0.4)$superconductor for both as-prepared and post annealed at 300 °C. There is no obvious phase difference detected from XRD between the post annealed below 300 °C and the as-prepared materials. However, different modulation phases were found from TEM observation in the materials.

Figure 3 and the inset of Fig. 3 show the magnetic susceptibility measured for as-prepared and annealed sample in the Meissner (field cooling) mode, which reflects the superconducting volume fraction. It is found that with raising the annealing temperature to 200–250 °C, T_c increases to 95 K, which is one of the highest among the known single-layer cuprate superconductors, much higher than that of 39 K T_c in the isostructure compound $Sr_2CuO_{2+\delta}Cl_{2-x}$ superconductor.[21] The annealing at temperatures above 300 °C destroyed superconductivity as illustrated in the inset of Fig. 3. We highlight that the post annealing temperatures (150–250 °C) are too low to cause a change of oxygen content (which usually happens at temperatures above 300 °C) as discussed in the following text. At such low temperatures metal ions cannot

migrate, either, so the effect of post annealing is most likely to rearrange the apical oxygen atoms and make them to order. To confirm this, we performed a transmission-electron-microscope (TEM) study.

Electron diffraction (ED) and high-resolution TEM investigations show that almost all grains in the superconducting samples exhibit modulated structures in the basal a-b plane. In the as-prepared sample, two types of modulated structures were found. Figure 4(a) shows the ED patterns of the two modulated phases taken along $[001]_p$ zone axis. One is the previously reported face-centered orthorhombic modulated structure (space group $Fmmm$) of about $5\sqrt{2}a_p \times 5\sqrt{2}a_p \times c_p$ periodicity.[9] The other is a new base-centered monoclinic modulated structure (space group $C2/m$) with the unit-cell parameters $a=5\sqrt{2}a_p$, $b=c_p$, $c=\sqrt{26}\sqrt{2}/2a_p$, and $\beta=101.3°$. We investigated 50 grains to estimate the relative fraction of the two phases. Statistically about 80% of the grains have the $Fmmm$ structure, and the rest are the $C2/m$ phase.

After heat treatment at 150 °C, 15% of the $C2/m$ modulated phase was found to convert to another new modulated phase (space group $Cmmm$) with the unit-cell parameters $a=c_p$, $b=5\sqrt{2}a_p$, and $c=5\sqrt{2}a_p$, while the $Fmmm$ modulated structure is unchanged, keeping almost the same volume fraction. Figure 4(b) shows the ED pattern along $[001]_p$ of the new modulated phase ($Cmmm$). The phase transformation from $C2/m$ to $Cmmm$ can also be seen in the HRTEM images. The HRTEM image [Fig. 4(b)] shows coexistence of the two modulated phases. The domain A and B correspond to the $C2/m$ and the $Cmmm$ modulated phases, respectively.

When the annealing temperature was increased to 250 °C, all the $C2/m$ and $Cmmm$ modulated phases were converted to a single modulated phase (space group $Pmmm$) with the unit-cell parameters $a\approx b=4\sqrt{2}a_p$ and $c=c_p$, which was previously reported by Hiroi et $al.$ [8]. Figure 4(c) displays the ED pattern along $[001]_p$ of the $Pmmm$ modulated phase. Again, the $Fmmm$ modulated phase remains in the sample and continues to occupy 80% volume of the sample.

The results of our experiments strongly suggest that the observed superconductivity is related to those modulated phases. The as-prepared sample with $T_c=75$ K contains two types of modulated phases with space groups $Fmmm$ and $C2/m$, so either $Fmmm$ or $C2/m$ modulated phase is superconducting. We see that the $Fmmm$ modulated phase always exists as a major phase in both as-prepared and annealed superconducting samples. This means that, if the $Fmmm$ modulated phase were superconducting, nearly the same T_c ($\sim$75 K) could have been observed for the annealed samples. Therefore, the $Fmmm$ modulated phase is not superconducting, and the $C2/m$ modulated phase is a superconductor with $T_c=75$ K. These observations indicate that the superconductivity or T_c of $Sr_2CuO_{3+\delta}$ evolves with change of modulated structure: Starting from $T_c=75$ K of the $C2/m$ modulation structure in an as-prepared sample, T_c goes up to 89 K in the $Cmmm$ modulation structure after the 150 °C annealing, and finally $T_c=95$ K is attained in the $Pmmm$ modulation structure of the 250 °C post-annealed sample. The $Pmmm$ modulated phase is, in this respect, the *optimally* modulated phase. This resolves the mystery/controversy associated with this material.[6–10,16–18]
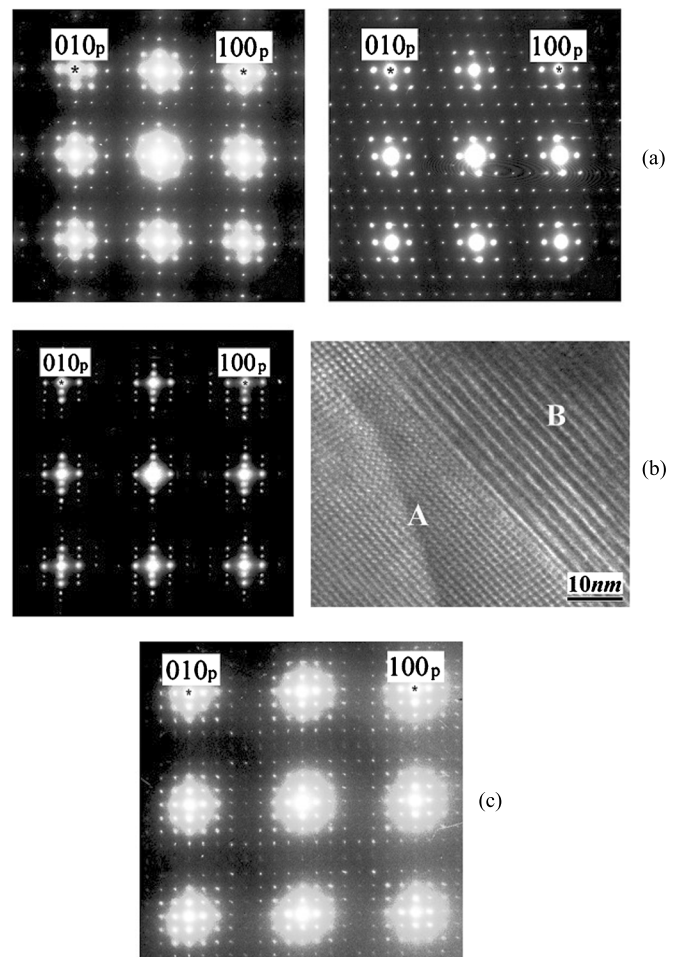

FIG. 4. (a) ED patterns taken along the $[001]_p$ zone axes of the $Fmmm$ modulated phase (left) and the $C2/m$ modulated phase (right). The latter is superconductor with $T_c=75$ K. (b) (Left) ED pattern taken along the $[001]_p$ zone axis of the $Cmmm$ modulated phase observed in the sample of T_c 89 K. (Right):HRTEM image along the $[001]_p$ direction showing the coexistence of the $C2/m$ (domain A) and the $Cmmm$ modulated phase (domain B), which is superconducting with $T_c=89$ K. (c) ED pattern taken along the $[001]_p$ zone axis of the $Pmmm$ modulated phase in the sample (heat treated at 250 °C), showing superconducting transition at 95 K.

As regards the relationship between oxygen vacancies and the observed modulation structures, the thermogravimetry (TG) analysis on the $Sr_2CuO_{3+\delta}$ superconductor found little weight change below 300 °C as shown in Fig. 5, indicating a negligible change of oxygen content and hence the doping level after annealing. Since the modulation is along the a-b plane directions, its location is most likely on the rock salt type SrO charge reservoir block, and the modulation would be induced by the apical oxygen rearrangement/ordering.[22,23] It is consequently inferable that the apical oxygen ordering has a substantial effect on the superconducting transition temperature. The oxygen ordering has been well established in $YBa_2Cu_3O_{6+\delta}$ even at room temperature[24] but it takes place at the chain layer, i.e., the second nearest neighbor in charge reservoir block. Here the ordering in $Sr_2CuO_{3+\delta}$ superconductor is at the apical oxygen layer, which locates at the first nearest layer of charge reservoir.
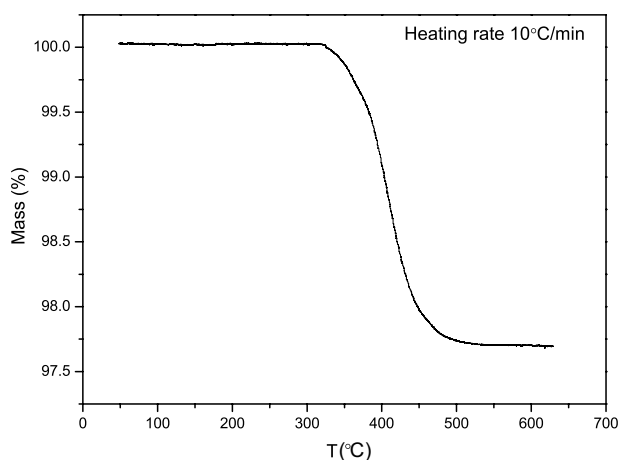
FIG. 5. The thermogravimetry (TG) analysis on the $Sr_2CuO_{3+\delta}$ superconductor, showing no weight loss below 300 °C.

Then the question that arises is why the apical oxygen ordering has such a significant effect on T_c. The LDA band calculation illustrates that the distance d_a of apical oxygen with respect to the CuO_2 plane has a substantial effect on the second-nearest neighbor hopping integral t' between nearest Cu-Cu atoms in the CuO_2 plane[5] and t' has a correlation with the maximum T_c of each cuprate material. The LDA band calculation[5] and also the evaluation of the Madelung potential difference between apical and planar O sites[25] find a general trend that T_c becomes higher as $|t'|$ becomes larger or as the apical oxygen distance d_a becomes longer. In this respect, the CuO_2 plane without apical oxygen atoms such as that in T'-Nd_2CuO_4 would sustain highest T_c if it could be doped with *holes*. Normally, it is hard to dope holes into such CuO_2 planes due to relatively electropositive circumstances around the CuO_2 plane, but an exceptional situation is realized in the multilayered cuprates with the consecutive CuO_2 plane number n larger than 3 (inclusive). In the multilayer systems, the inner CuO_2 planes have no apical oxygen and thus fewer hole density compared with the two outer layers.[26] It might be that the outer layers supply a sufficient density of holes, while the inner layers provide a place for strong pairing correlation, both working cooperatively to enhance T_c. In analogy with this we suppose that a similar situation may be realized in $Sr_2CuO_{3+\delta}$ in which the CuO_4 plaquettes with apical oxygen and those without apical oxygen form some ordered structure within the same CuO_2 plane. Further, the ordering of apical oxygen atoms would minimize the disorder effect, and probably enhance T_c in this monolayer cuprate.

The high-pressure synthesis and the subsequent quenching to ambient pressure would leave some residual strains in the lattice. The annealing at low temperatures at ambient condition is expected to reduce or relax these strains by the apical oxygen relocation. The release of strain was suggested by Attfield *et al.* to account for the disorder effects on T_c in the cation-substituted La_2CuO_4 type superconductor.[27]

Normally, the chemical doping introduces disorder into the charge reservoir blocks owing to random distribution of dopant atoms. It has been suggested that the disorder might be responsible for the observed electronic inhomogeneity on the nanometer scale in the CuO_2 plane.[28–30] It has also been demonstrated that in Bi2212 and Bi2201, intentionally introduced cation disorder in the nearest neighbor (SrO) block containing apical oxygen sites gives rise to an appreciable decrease in T_c.[28–30] The present system is a positive example in which the ordering of dopant atoms enhances T_c. Application of this method to other cuprates will lead to further enhancement of T_c of cuprate superconductors.

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