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TEM and EELS studies of $Sr_2CuO_{3+\delta}$ (nominal $\delta = 0.1$–0.4): Effect of apical oxygen ordering on T_C of cuprate superconductors

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Abstract

In this paper, transmission electron microscopy (TEM) and electron energy-loss spectroscopy (EELS) techniques are utilized to study the as prepared superconducting samples of $Sr_2CuO_{3+\delta}$ with different nominal δ to reveal the origin of superconductivity. The 60, 68 and 75 K superconductivities observed in these samples are revealed to arise, respectively, from the *Pmmm* ($a = 5\sqrt{2}a_p$, $b = \sqrt{2}a_p$ and $c = c_p$), *Cmmm* ($a = c_p$, $b = 3\sqrt{2}a_p$ and $c = 4\sqrt{2}a_p$) and *C2/m* ($a = 5\sqrt{2}a_p$, $b = c_p$, $c = \sqrt{26}\sqrt{2}/2a_p$ and $\beta = 101.3°$) modulated phases. These superconducting modulated phases are suggested to be formed by the ordering of apical oxygen, and each of them is associated with a distinct type of the ordering. Oxygen K absorption edge measured by EELS indicates that these modulated phases have a similar hole doping level. Our experimental results suggest that the superconductivity differences in the $Sr_2CuO_{3+\delta}$ system are mainly caused by the reordering of apical oxygen.

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Keywords: High-T_C superconductor; Apical oxygen; TEM; Modulation structure

1. Introduction

Crystallographically hole doped high-T_C cuprate superconductor (HTS) is built up from alternating stackings of charge reservoir blocks and the CuO_2 conducting planes. Chemical substitution and tuning the oxygen content in the charge reservoir blocks are the fundamental chemical doping mechanics of HTS. In most cases, chemical disorder is created in the charge reservoir blocks as doping is made. Besides the doping level [1] and the number of CuO_2 planes (n) in a unit-cell [2], the disorder induced by doping has been shown to be another important parameter influencing the superconducting transition temperature of HTS [3]. On the other hand, the oxygen atoms above or below the CuO_2 plane(s), usually called "apical oxygen", form the nearest-neighbor charge reservoir block [2,4,5], and the apical oxygen serves as the connection between the charge reservoir blocks and the CuO_2 conducting planes in terms of electron exchange interaction [6]. Therefore, the apical oxygen doping (i.e., tuning the oxygen content in the nearest-neighbor charge reservoir block) and its ordering is expected to have an appreciable effect on the electronic structures of the CuO_2 planes and hence on high-T_C superconductivity. The $Sr_2CuO_{3+\delta}$ superconducting system crystallizing into a highly apical oxygen-deficient K_2NiF_4-type tetragonal structure supplies us a good example to study the effect of apical oxygen ordering on the high-T_C superconductivity. Recently, by studying the $Sr_2CuO_{3+\delta}$ (nominal $\delta = 0.4$) superconductor post-annealed at different temperatures, we found that the reordering of apical oxygen has dramatic effects on T_C [7,8].

At ambient-pressure, the Sr_2CuO_3 composition forms as an orthorhombic structure with Cu–O chains along the

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a-axis [9–11]. Introducing extra O leads to the formation of a K_2NiF_4-type tetragonal structure of $Sr_2CuO_{3+\delta}$, and at the same time holes are doped in this cuprate due to the introduction of extra O; however, superconductivity is displayed only in the samples synthesized using high-pressure techniques [12–18]. Although high-pressure technique is a very effective method in searching for new HTS materials [19–23], preparation of a single-phase sample is generally difficult, and sometimes it is hard to identify the superconducting phase in the sample. Using $KClO_4$ as an oxidizer, Hiroi et al. [12] first succeeded in fabricating the 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 and the superconductivity results from this tetragonal phase. Later, several groups also repeatedly synthesized the $Sr_2CuO_{3+\delta}$ superconductors using high-pressure technique [13–15], and T_C was enhanced up to 94 K by post annealing [15]. In all these high-pressure samples both as prepared and post-annealed, however, modulated structures that have the K_2NiF_4-type tetragonal structure of $Sr_2CuO_{3+\delta}$ as their basic sub-structure were observed. For example, Hiroi et al. [12] and Laffez et al. [13] observed, separately, a $4\sqrt{2}a_p \times 4\sqrt{2}a_p \times c_p$ and a $5\sqrt{2}a_p \times 5\sqrt{2}a_p \times c_p$ modulated structure in their as prepared samples, and the latter one was also found by Wang and Zhang et al. [24,25] in their as prepared and annealed samples. Contrary to the idea suggested in Refs. [12,13,15] that the non-modulated tetragonal form of $Sr_2CuO_{3+\delta}$ is the superconducting phase, Wang and Zhang et al. [24,25] suggested that the $5\sqrt{2}a_p \times 5\sqrt{2}a_p \times c_p$ modulated phase is actually responsible for the superconductivity. However, no convincing experimental results were given in all their works since those superconducting samples were multiphase mixtures and superconducting volume fraction was very small. In addition, the tetragonal form of $Sr_2CuO_{3+\delta}$ synthesized at ambient pressure has been shown to be isostructural with that obtained at high pressure on the basis of powder X-ray diffraction (XRD) analysis, but no superconductivity was observed in the ambient-pressure samples [16,17]. The above works seem not to support the predication that the tetragonal form of $Sr_2CuO_{3+\delta}$ is responsible for the superconductivity. At the same time, Shimakawa et al. [14] studied the compounds of $Sr_2CuO_{3+\delta}$ synthesized at high-pressure and ambient-pressure separately by means of neutron diffraction, and suggested that the compounds prepared at different pressures both have an oxygen-deficient K_2NiF_4-type tetragonal structure with oxygen vacancies located in the Cu–O planes instead of in the Sr–O layers, which indicates that the main phase in the samples is possibly non-superconducting in terms of our current understanding of superconductivity in the cuprates, which relies on oxygen vacancy-free in the Cu–O plane. Furthermore, Kawashima et al. [26] reported that the superconducting phase with $T_C = 70$ K prepared from the nominal starting powders of Sr_2CuO_3 with $KClO_4$ oxidizer was not of the 0201-type but of 0212-type Sr–Cu–O compound.

Up to now, despite extensive studies on the $Sr_2CuO_{3+\delta}$ system, it is still not clear what phase in the high-pressure material of this system can lead to the superconductivity. In order to find the answer, preparation of high-quality samples and the characterization of their detailed structures by means of transmission electron microscopy (TEM) are needed. To make the phase as pure as possible, recently we synthesized the $Sr_2CuO_{3+\delta}$ samples under high pressure using SrO_2 as an oxidizer. A series of superconducting samples of $Sr_2CuO_{3+\delta}$ for various values of δ, commonly displaying different values of T_C, were prepared by changing the initial amount of SrO_2, and a single-phase one detected to be a K_2NiF_4-type tetragonal structure from XRD data was formed when nominal $\delta = 0.4$. We annealed the tetragonal single-phase sample in N_2 atmosphere, and found that with increasing the annealing temperature the value of T_C increased from 75 K (as prepared), in turn, to 89 K (heat treatment at 150 °C), 95 K (heat treatment at 250 °C), and then disappeared when further increasing the annealing temperature above 250 °C [7]. This is in consistent with the observation in Ref. [15]. However, our TEM investigations suggest that the enhancement of T_C is mainly caused by the apical oxygen reordering [7,8]. In this paper, TEM and electron energy-loss spectroscopy (EELS) techniques are utilized to study the as prepared superconducting samples of $Sr_2CuO_{3+\delta}$ with different nominal δ, further suggesting that the ordering of apical oxygen has effects on T_C.

2. Experimental

To make the phase as pure as possible, we synthesized the $Sr_2CuO_{3+\delta}$ samples under high pressure using SrO_2 as an oxidizer. The starting material, Sr_2CuO_3, was prepared from high purity $SrCO_3$ and CuO raw materials mixed at a molar ratio of 2:1. The powder mixture was calcined at 950 °C for 24 h with several intermediate grindings. Then, Sr_2CuO_3, SrO_2 and CuO were mixed to yield the nominal composition $Sr_2CuO_{3+\delta}$ at various molar ratios and subjected to high-pressure synthesis (6 GPa and 1100 °C for 1 h) using a cubic-anvil-type apparatus. More detailed process and discussion of the sample preparation are given in Ref. [7].

A series of superconducting samples of $Sr_2CuO_{3+\delta}$ with different nominal δ were prepared by changing the initial amount of SrO_2. The sample structures detected from XRD using Cu Kα radiation gradually transform to tetragonal form from orthorhombic structure with increasing nominal δ, and a single-phase tetragonal form is formed when nominal $\delta = 0.4$. Superconductivity of these samples was examined by dc magnetic susceptibility measurements using a SQUID magnetometer in an external magnetic field of 20 Oe, and the results reveal that the samples for nominal $\delta = 0.1$ and 0.2 display a 60 K superconductivity, while the samples for nominal $\delta = 0.3$ and 0.4 exhibit, respectively, a 68 K and a 75 K superconductivity. In order to further identify the superconducting phase and reveal