

High pressure studies of high T_c superconductors in A–Cu–O system: The role of apical oxygen

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Abstract

We address the role of apical oxygen that plays the bridges linking charge reservoir and CuO_2 conducting layers for high T_c superconductors (HTS). The presentation will introduce our recent work on high pressure synthesis of novel superconductors in the A–Cu–O simple system by tuning apical oxygen content and arrangement (A represents alkaline earth element). The topic will focus on 214 type compounds highlighting apical oxygen as a novel doping mechanism in oxychloride HTS, or dopant at a partially occupied apex, especially the unusual enhancement of T_c up to 95 K in a monolayered HTS by improving ordering state.

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1. Introduction

Since the historical discovery of high T_c superconductors (HTS) of cuprate oxide in 1986 by Bednorz and Muller [1], a lot of HTS compounds have been synthesized [2–18]. Crystallographically HTS consists of periodic stacking of charge reservoir and $[\text{CuO}_2]$ conducting layers, respectively. They are usually bridged via apical oxygen as shown in Fig. 1 [1–6]. Charge reservoir is responsible for generating carriers to the $[\text{CuO}_2]$ superconducting plane through an appropriate doping. According to the geometric relationship with the $[\text{CuO}_2]$ plane, the charge reservoir block can be further classified into two sub blocks: the nearest neighbor to $[\text{CuO}_2]$ plane; and the next nearest neighbor to $[\text{CuO}_2]$ plane as shown in Fig. 2. The oxygen which connects the nearest neighbor charge reservoir layer in turn is named “apical oxygen” since it is located at the apical position relative to the $[\text{CuO}_2]$ plane (this is validate to p type HTS). Tuning the oxygen content at the charge reservoir layer is the most fundamental chemical doping mechanism of HTSs [2].

It is noted that most of oxygen doping are taking place at the next nearest neighbor charge reservoir block. One can expect that T_c will be even more sensitive to the oxygen evolution at the nearest charge reservoir block via the apical bonding nature [3,6,11]. It was found that the distance of apical oxygen with the $[\text{CuO}_2]$ plane has an essential effect on the hopping integral t' between the second nearest Cu–Cu within the $[\text{CuO}_2]$ plane [6], and consequently it is crucial to modify T_c value of p-type HTS. However almost all typical HTSs have a fully occupied oxygen site, leaving the apical oxygen amount stoichiometrically unchangeable. Searching compounds with tunable apical oxygen content is thus of fundamental physical interests in terms of deeply understanding the unknown doping effects of oxygen at the nearest charge reservoir block.

Since HTS is of perovskite crystal nature [2,3], high pressure is thus thermodynamically favorable to stabilize novel HTSs [11]. High oxygen pressure can effectively modulate the copper valence. The obvious merit of high pressure is to build up novel HTS, which otherwise will be hard to approach in ambient conditions. On the other hand, the positive pressure effect on T_c , such as the record 160 K T_c of Hg-1223 above 20 GPa will shed lights on pursuing new HTS with higher T_c as well as solving mechanism puzzle. Here we will briefly introduce our recent

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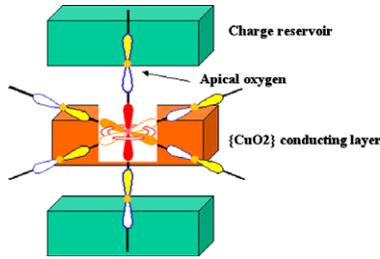


Fig. 1. A schematic view of the crystal structure of HTS, being composed of the charge reservoir and the [CuO₂] conducting block, which are usually connected via apical oxygen.

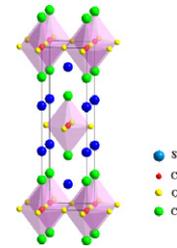


Fig. 3. The crystal structure of Sr₂CuO₂Cl₂.

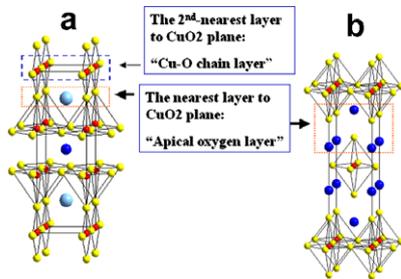


Fig. 2. The charge reservoir layer can be further viewed into the nearest layer and the 2nd nearest layer with respect to [CuO₂] plane as shown for YBa₂Cu₃O₇ (a). The oxygen at the nearest layer is named “apical oxygen” since it is located at the apex site of the [CuO₂] plane. Crystallographically, 214 (i.e., 0201) type only has the nearest charge reservoir layer as indicated for La₂CuO₄ (b).

research progress on the high pressure studies of high T_c superconductors in A–Cu–O system (A is alkaline earth element) highlighting the role apical oxygen as a dopant mechanism in 0201 type Sr₂CuO_{2+δ}Cl_{2-x} series, the ordering effects to enhance T_c up to 95 K in Sr₂CuO_{3+δ}.

2. The “apical oxygen doping” to introduce p type superconductivity

So far there are two major types of hole carrier doping mechanisms for a pure oxide HTS. One is to apply hetero-valence metallic ions substitution as very well established in (La_{2-x}Sr_x)CuO₄. The other is to tune oxygen nonstoichiometry as classically performed for YBa₂Cu₃O_{7-δ} or other 12($n-1$) n or 22($n-1$) n homologous series. But those oxygen modifications all happen in the 2nd nearest charge reservoir layer. The stoichiometric oxychloride A₂CuO₂X₂ (A = Ca, Sr) is an antiferromagnetic insulator similar to that of La₂CuO₄ as shown in Fig. 3. This affinity makes A₂CuO₂X₂ (A = Ca, Sr) favorable prototype candidates for new HTS. Considering the crystal structural characteristics, we established a new hole doping mechanism to induce carriers in oxyhalide cuprates. The doping is realized through a heterovalent anion substitution, i.e., a partial replacement of monovalent halide with divalent oxygen at the apical site. Since all Cl ions reside at the apex anion position, it is called “apical oxygen doping” [9], to

address the doping nature that introduces apical oxygen otherwise absent into the pristine A₂CuO₂X₂.

The apical oxygen doping was first realized in the double-[CuO₂]-layer compound (Sr, Ca)₃Cu₂O_{4+δ}Cl_y [9,10] which is isostructural to (La, Sr)₂CaCu₂O₆.

Using high pressure synthesis, we also found a new homologous series (Sr,Ca)_{n+1}Cu_nO_{2n+δ}Cl_{2-x}, or termed as Cl- $02(n-1)n$. Cl-02($n-1$) n crystallizes into tetragonal phase with space group I4/mmm. The unique crystal structure of Cl-02($n-1$) n oxyhalide cuprates enables more to modify the apical oxygen amount, studying its effects on superconductivity.

3. The Sr₂CuO_{2+δ}Cl_{2-x} superconductor induced by “apical oxygen doping”

Using apical oxygen doping, we recently have been able to get the new Sr₂CuO_{2+δ}Cl_{2-x} superconductors using high pressure synthesis [13]. Bulk superconductivity was realized with T_c up to 30 K.

The sample was synthesized under high pressure high temperature at 5 GPa and 1000 °C. Fig. 4 shows the temperature dependence of the DC magnetic susceptibility of

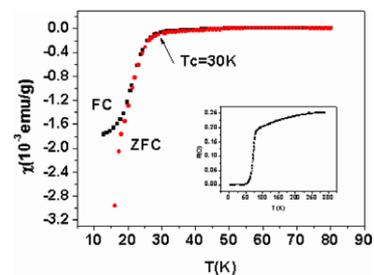


Fig. 4. The superconducting transition of Sr₂CuO_{2+δ}Cl_{1.2}.

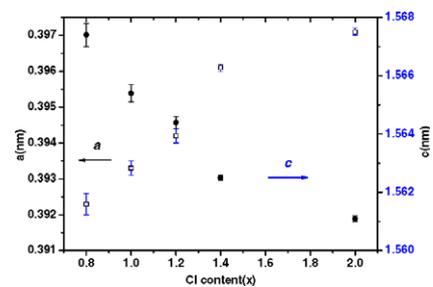


Fig. 5. The change of lattice parameters as a function of apical oxygen doping in Sr₂CuO_{2+δ}Cl_{2-x}.

$\text{Sr}_2\text{CuO}_{2+\delta}\text{Cl}_{1.2}$ sample, indicating the bulk superconducting nature. The inset of Fig. 4 presents the temperature dependence of the resistivity of the sample.

Fig. 5 shows the lattice parameters versus apical oxygen content in $\text{Sr}_2\text{CuO}_{2+\delta}\text{Cl}_{2-x}$. The a axis shrunken with the increase of apical oxygen amount, indicating the hole doping nature.

4. The enhanced superconductivity up to 95 K in 214 type $\text{Sr}_2\text{CuO}_{3+\delta}$ by apical oxygen ordering

$\text{Sr}_2\text{CuO}_{3+\delta}$ was synthesized under high pressure high temperature crystallizing into La_2CuO_4 structure. More interestingly as a dopant mechanism its apical oxygen site is partially occupied and the amount is adjustable as shown in Fig. 6.

Previously Hiroi et al. [7] synthesized a tetragonal form of $\text{Sr}_2\text{CuO}_{3+\delta}$ superconductor in 1993. They suggested that the main phase in this material is a highly apical oxygen-deficient K_2NiF_4 -type tetragonal structure. Later, some $\text{Sr}_2\text{CuO}_{3+\delta}$ type superconductors were subsequently synthesized and the superconducting transition can be enhanced above 90 K after post annealing [8]. But there are uncertainty on which phase is real responsible for the superconducting transition [3,8,12,14,15].

To make the phase as pure as possible, we synthesized the $\text{Sr}_2\text{CuO}_{3+\delta}$ sample under high pressure high temperature using an improved approach with $\text{Sr}_2\text{CuO}_3 + \text{SrCuO}_2 + \text{SrO}_2$ as the starting materials for high pressure synthesis. The role of SrO_2 peroxide is to create an oxygen atmosphere during the high-pressure synthesis that will not introduce third element or other phases containing chlorine [12].

In order to further “optimize” the superconducting phase through tuning the apical oxygen distribution, the high pressure synthesized $\text{Sr}_2\text{CuO}_{3+\delta}$ sample of optimally doping with $\delta = 0.4$ was post heat treated in the temperatures range of 150 °C to 300 °C for 12 h in 1 atm N_2 atmosphere. X-ray diffraction shows that the sample keeps the

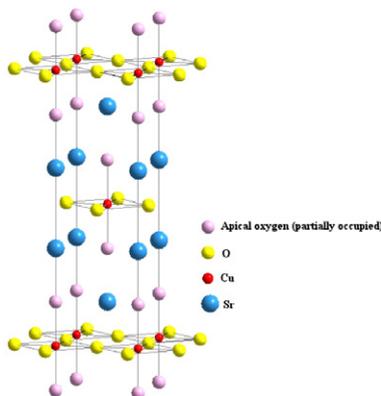


Fig. 6. The crystal structure of $\text{Sr}_2\text{CuO}_{3+\delta}$, isostructural to La_2CuO_4 , but with partially occupied apical oxygen that also serves as the dopant mechanism.

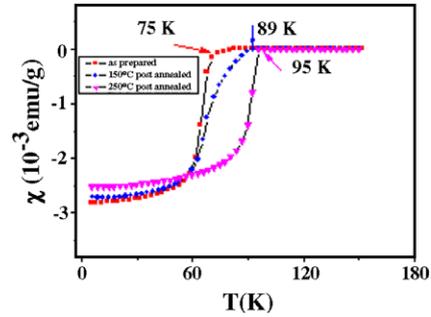


Fig. 7. The magnetic susceptibility of $\text{Sr}_2\text{CuO}_{3+\delta}$ superconductor with different post annealing temperature, showing an increase of T_c .

tetragonal single phase unchanged up to 300 °C heat treatment, before becoming mixture of tetragonal and the ambient orthorhombic chain phase at 350 °C.

Fig. 7 illustrates the magnetic susceptibility measurement at a Meissner mode for the high pressure as-prepared and those after different heat treatments of $\text{Sr}_2\text{CuO}_{3+\delta}$ superconductors. It is shown as increasing the annealing temperature, T_c increases monotonically up to 95 K which is the highest T_c observed in the single-layer copper oxide superconductors.

ED and HRTEM investigations showed that almost all grains in the superconducting samples exhibited modulated structures at a - b plane based on the K_2NiF_4 structure. In the as-prepared sample, two types of modulated structures were found. One is the already reported face-centered orthorhombic modulated structure (space group $Fmmm$) with the lattice constants of about $5\sqrt{2}a_p \times 5\sqrt{2}a_p \times c_p$ [12].

The other is a new base-centered monocline 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 $\beta = 101.3^\circ$. Fig. 8a shows the ED patterns taken along $[001]_p$ zone-axis of the $C2/m$ modulated phase. After heat treatment at 150 °C, parts of $C2/m$ modulated phase was found to convert to another new modulated phase as shown in Fig. 8b (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 almost remains the same. As the post annealed temperature was increased to 250 °C, all the $C2/m$ and $Cmmm$ modulated phases converted to another modulated phase as shown in Fig. 8c (space group $Pmmm$) with the unit-cell parameters $a \approx b = 4\sqrt{2}a_p$ and $c = c_p$ which was previously reported.

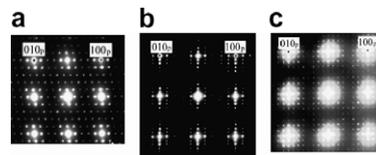


Fig. 8. The TEM images of $\text{Sr}_2\text{CuO}_{3+\delta}$ samples, (a) the $C2/m$ superlattice for the as prepared sample with T_c 75 K, (b) the $Cmmm$ superlattice appeared in the sample with T_c 89 K, (c) the $Pmmm$ superlattice observed in the sample with T_c 95 K.

The results of our experiments strongly suggest that the observed superconductivities in $\text{Sr}_2\text{CuO}_{3+\delta}$ samples are related to these modulated phases. The as-prepared sample with an onset T_c at 75 K contained two types of modulated phases ($Fmmm$ and $C2/m$), respectively. Therefore, it is likely that the $Fmmm$ or/and the $C2/m$ modulated phase is responsible for T_c at 75 K. However, the $Fmmm$ modulated phase has always existed in the as-prepared and heat treated superconducting samples. This means if the $Fmmm$ modulated phase is responsible for the T_c at 75 K, the same T_c (75 K) could be observed in the heat-treated samples either, but it did not. Therefore only the $C2/m$ modulated phase is responsible for the T_c at 75 K. The evolution route of superconductivity and the relation with modulation structure of the $\text{Sr}_2\text{CuO}_{3+\delta}$ superconductor are thus following the rationale: starting from the 75 K original superconducting transition with $C2/m$ modulation structure in the high pressure as prepared sample \rightarrow 89 K superconducting transition with $Cmmm$ modulation structure in the 150 °C post annealed sample \rightarrow 95 K superconducting transition with $Pmmm$ modulation structure in the 300 °C post annealed sample, respectively. The $Pmmm$ modulated phase was in fact the *optimally* ordered phase associated with the highest T_c (95 K) for the optimally doped $\text{Sr}_2\text{CuO}_{3+\delta}$ superconductor.

The TG-DTA experiments of $\text{Sr}_2\text{CuO}_{3+\delta}$ superconductor indicate little weight evolution below 300 °C. Since the modulation is taking place at a - b plane, assuming a perfect $[\text{CuO}_2]$ plane as it is a very well established consensus, the oxygen vacancy should be on the rock salt type $[\text{SrO}]$ layer, i.e., the apical oxygen layer. It is in fact found that oxygen can even migrate at room temperature. Thus the modulation is reasonably related to the apical oxygen rearrangement at the low annealing temperature. It is consequently inferred that the modulation structure related to the apical oxygen ordering state has an additional contribution to enhance superconducting transition temperature for an optimally doped sample. These further support the recent research that the quenched order disorder of dopant atom has sufficient effects on the superconductivity [16,17]. The results indicate that T_c might be significantly enhanced by ordering dopant such as the apical oxygen [18].

5. Summary

The high pressure synthesized 214 type superconductors with partially occupied oxygen at the nearest charge reservoir provide opportunities to understand the role of apical oxygen atoms and to further identify the intrinsic feature of ordering effects on superconducting transition temperature in the high T_c cuprate superconductors.

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