The Unconventional Copper Oxide Superconductor with Conventional Constitution

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Abstract
A new Ba2CuO4-δ superconductor with critical temperature (Tc) exceeding 70 K was discovered. The X-ray absorption measurement gives evidence that this cuprate resembles La2CuO4 but is doped with a fairly large amount of holes, while in contrast to the so far known hole-doped high-Tc cuprates, the new cuprate possesses a much shorter local apical oxygen distance as well as much expanded in-plane Cu–O bond, leading to unprecedented compressed local octahedron. In compressed local octahedron, the Cu3d3z2−r2 orbital level will be lifted above the Cu3dx2−y2 orbital level with more three-dimensional features, implying that pairing symmetry may carry admixtures from more than one gap, suggesting that Ba2CuO4-δ composed of alkaline earth copper oxides that are the essential elements to form cuprate superconductors may belong to a new branch of cuprate superconductors.

Keywords Unconventional cuprates · Compressed octahedron · High pressure

1 Introduction
Searching for superconductors with higher Tc has attracted great interest since cuprate superconductors was discovered [1–9]. It is widely accepted that the superconducting critical temperature (Tc) is a function of carrier doping level, i.e., Tc becomes maximum at optimal doping while gradually diminishing at both sides of underdoped or overdoped regions [10, 11]. Consensus is currently that a Tc dome in the low p region (optimum doping around p ~ 0.15) is born out of the Mott insulator with antiferromagnetic (AF) order [12, 13], and high Tc superconductivity (HTS) emerges from around p ~ 0.08 [14]. In the overdoping region, Tc vanishes again when the doping level is larger than a critical value pmax ~ 0.27 [11]. The material is deemed a Fermi-liquid-like metal in which electronic correlations become weak in heavily overdoped regions. But a growing number of researches in recent years suggest that it shows not a simply Fermi liquid behavior even in very highly overdoped copper oxides [15, 16].

Prof. T. H. Geballe is the pioneer who paid much attention to the unusual phenomenon in the heavily doped region of cuprates [1, 17, 18]. Some cuprates synthesized at a high pressure show very high Tc in the strongly overdoped region well beyond the normal superconducting phase diagram for the established cuprate superconductors [18–20]. This raised the question to the paradigm where the high Tc of cuprates actually originates from [17]. One typical system is Cu0.75Mo0.25Sr2YCu2O7.54 with double CuO layers in the unit cell similar to YBCO123 phase which is in the heavily overdoped regime (p ~ 0.46) but shows a Tc up to 87 K [19, 21]. Another system is a monolayer CuO2 deposited on a single crystal of Bi2Sr2CaCu2O8+δ which is thought to be heavily overdoped (p ~ 0.9) due to charge transfer at the interface [22, 23]. Besides, a very important system is Sr2CuO3+δ...
The hole-doped Sr$_2$CuO$_{3+\delta}$ superconductor crystallizes into an oxygen-deficient La$_2$CuO$_4$ (i.e., K$_2$NiF$_4$) structure. Our previous studies show that the maximum $T_c$ of Sr$_2$CuO$_{3+\delta}$ can reach 95 K with a nominal $\delta \sim 0.4 \ (p \sim 0.8)$ which will be located in the very heavily overdoped region [20, 25]. Further, $T_c^{\text{max}} = 98$ K is achieved in the Ba-substituted material Sr$_{2-x}$Ba$_x$CuO$_{3+\delta}$ ($0 \leq x \leq 0.6$) with $x = 0.6$ that reaches the record value among the single-layer copper oxide superconductors—even higher than that of Hg1201 [26]. These materials are all synthesized at high oxygen pressure and characterized as heavily overdoping cuprates.

To deal with the topic, we have been focusing for long time on the alkaline earth and copper oxide system that is the simplest composition to build up cuprate superconductors [18, 20, 25–29]. However, high pressure is usually required in order to get the structure by design. Recently, we discovered a new type of superconductor Ba$_2$CuO$_{4.5}$ (briefly coined Ba214) with the oxygen-deficient La$_3$CuO$_4$ (La214) structure [18]. It has so far the only compressed local octahedron, in sharp contrast to the elongated octahedron for all previously known cuprate superconductors. Moreover, it is in an extremely overdoped state as well. The new superconductor shows superconductivity with $T_c$ up to 73 K. It is generally believed that orbital reversal and extreme overdoping will suppress superconductivity in cuprates [11]. These suggest that Ba214 is a member of a new branch of high $T_c$ cuprate superconducting materials with unconventional features that challenge the established wisdom of HTS [30].

2 Experiments

The polycrystalline sample of Ba214 was synthesized at high pressure (~ 18 GPa) and high temperature (~ 1000 °C) conditions with a highly self-oxidizing atmosphere [27–29] using a 6 over 8 double-stage type multianvil high-pressure facility. Phase purity of the obtained high-pressure products was examined by both powder X-ray diffraction (XRD) at room temperature and neutron at low temperature. Rietveld refinements were performed using the GSAS software package. The direct-current magnetic susceptibility was measured using a commercial SQUID-VSM (Quantum Design). Soft X-ray
absorption spectroscopy (XAS) at the Cu $L_{2,3}$ edges and O-$K$ edge was measured at beamline BL11A of the NSRRC in Taiwan.

3 Results and Discussion

High-$T_c$ superconducting Ba214 samples can be synthesized only in a narrow range of the nominal oxygen deficiency $y \approx 0.8$. Powder Ba214 compound crystallizes into the La$_2$CuO$_4$-type structure with space group $I4/mmm$ and gives rise to the lattice parameters $a = 4.0030(3)$ Å and $c = 12.942(1)$ Å. The Cu–O bond lengths for Ba214 are estimated to be 2.0015(2) Å in the plane and 1.861(8) Å along the c-axis (corresponding to the apical O distance $d_A$). It yields both records of the longest in-plane Cu–O bond length and shortest apical-O distance among hole-doped cuprates as known so far. This may be attributed to the extremely large A site cation Ba$^{2+}$ dramatically expanding the in-plane Cu–O bond to the unprecedented length ever reported. As a consequence, the octahedron in turn becomes compressed instead of elongated as shown in Fig. 1. The locally compressed octahedron of Ba214 is exceptionally opposite to the previously “conventional” cuprates [31], which strongly suggests Ba214 may belong to a new type of “non-conventional” high-$T_c$ cuprate superconductor.

Temperature dependence of field-cooling (FC) dc magnetic susceptibility of the Ba214 compound is shown in Fig. 2a together with optimum doped isostructural La$_{1.85}$Sr$_{0.15}$CuO$_4$ taken from ref. 32. The Ba214 sample shows a $T_c^{\max} \approx 73$ K after post annealing under O$_2$ flow. The bulk superconductivity behavior of the Ba214 sample was also confirmed by the muon-spin-rotation (μSR) and the specific heat measurements.

X-Ray absorption spectroscopy (XAS) is a very useful tool to detect the doped hole numbers and the distribution in cuprate superconductors [33]. The result obtained from both the study of the Cu-$L_3$ edge and O-$K$ edge spectrum indicated a very high doping level in the Ba214 sample, consistent with the estimated $\delta$ values and the XRD spectrum Rietveld refinements. We take the bulk-sensitive fluorescence-yield (FY) mode measurement results. Figure 2b shows the Cu-$L_3$ spectra of Ba$_2$CuO$_{4-y}$ together with spectra for the overdoped La$_{1.66}$Sr$_{0.34}$CuO$_4$ [33] and perovskite LaCuO$_3$ [34] as references. Two peaks are observed in Ba214. Peak A around 931.3 eV, assigned to a $2p^63d^{10}$ final state (upper Hubbard band) coming from a $2p^63d^{10}$ initial state, and peak B at the high-energy side of peak A, around 932.9 eV, are assigned to a $2p^63d^{10}$ states. In the Cu-$L_3$ XAS spectrum, the intensity of B peak for
Ba$_2$CuO$_4$-$y$ is stronger than that for highly overdoped La$_{1.66}$Sr$_{0.34}$CuO$_4$ even if it is still weaker than that for “all-Cu” La$_2$CuO$_4$ ($p = 1$) while they all have a nearly 180° Cu–O–Cu bond with bond angle. The result explicitly indicates a very high doping level in Ba214, consistent with the estimated $\delta$ values.

In copper oxides, the octahedrons are generically elongated due to both Jahn–Teller effect and strong interlayer Coulomb interactions which push the 3$d^x$-$2$ orbital topmost and the doped holes to reside primarily on the 3$d^x$-$2$ orbital, forming the so-called Zhang–Rice (Z–R) singlet [35] via strong hybridization with oxygen 2$p$ orbital. It is very fascinating that the overdoped cuprates synthesized at high-pressure and high-oxidizing atmosphere as mentioned before usually possess a short apical oxygen distance $d_A$ compared with the normal or “conventional” cuprates (the typical value of 2.42 Å in La$_2$CuO$_4$): $d_A = 2.165$ Å for double-layered Cu$_{0.75}$Mo$_{0.25}$Sr$_2$YCu$_2$O$_{7.54}$ (Mo–Y123), $d_A = 2.11$ Å for monolayer Cu$_2$O$_2$ (Mono-Cu$_2$O$_2$), and $d_A = 2.085$ Å for Sr$_2$CuO$_{2.5}$ (Sr214), respectively [19, 20, 22]. Figure 3 shows the ratio of the bond lengths of in-plane Cu–O and copper apical oxygen of Mo–Y123 (double layered), Mono-Cu$_2$O$_2$, and Sr214, compared with Ba214. Nonetheless, the octahedrons (pyramid for Mo–Y123) of all above non-conventional-like cuprates are still elongated which result in an ordinary degenerate of Cu $e_g$ orbitals split into a higher 3$d^x$-$2$ orbital vs a lower 3$d^x$-$2$ orbital except Ba214.

The Ba214 sample possesses a compressed octahedron which is completely different from the conventional cuprates. In a compressed octahedron, the Cu3d$3z^2$-$r^2$ orbital will be pushed higher than the Cu3d$3x^2$-$y^2$ orbital level. This suggests that the doped holes may reside preferentially in the 3$d^x$-$2$ orbital and considerable 3$d^x$-$2$ orbital character might be mixed up in the states near the Fermi level that has been thought to be harmful for high-$T_c$ superconductivity. It also means pairing symmetry of Ba214 may carry admixtures from more than one gap, and the system becomes more three-dimensional. It renders this new HTS cuprate a multi-band system like the iron-based superconductors [36–38]. K. Liu et al. suggested that the AFM fluctuations in one-dimensional Cu–O chains may play an important role in the superconducting pairing of electrons [36]. T. Maier et al. found two domes of pairing strength while one corresponds to the extremely overdoped regime and there is significant pairing strength in both the $d$-wave and $s^\pm$ channels in the overdoped regime [37]. M. Jiang et al. provided a new model featuring in a Cu-3$d$ multiplet structure that only the ligand O-2$p$ orbitals play an essential role [38].

The unique structure features of compressed octahedron in extremely overdoped Ba$_2$CuO$_4$-$y$, with conventional constitution of alkaline earth copper oxides kindled keen interest in a deeper understanding of the unconventional copper oxide superconductor.

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