Electronic Structures, Hole-Doping, and Superconductivity of the s = 1, 2, 3, and 4 Members of the (Cu,Mo)-12s2 Homologous Series of Superconductive Copper Oxides

Inga Grigoraviciute,[†] Maarit Karppinen,*,[†,‡] Ting-Shan Chan,[§] Ru-Shi Liu,[§] Jin-Ming Chen,[∥] Omar Chmaissem,[⊥,#] and Hisao Yamauchi[†,‡]

Materials and Structures Laboratory, Tokyo Institute of Technology, Yokohama 226-8503, Japan, Laboratory of Inorganic Chemistry, Department of Chemistry, Helsinki University of Technology, Espoo 02150, Finland, Department of Chemistry, National Taiwan University, Taipei 106, Taiwan, Republic of China, National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan, Republic of China, Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, and Physics Department, Northern Illinois University, DeKalb, Illinois 60115

Received October 21, 2009; E-mail: maarit.karppinen@tkk.fi

Abstract: We demonstrate that the T_c value of superconductive copper oxides does not depend on the distance between two adjacent CuO$_2$ planes as long as the hole-doping level and the immediate (crystal) chemical surroundings of the planes are kept the same. Experimental evidence is accomplished for the homologous series of (Cu,Mo)-12s2, the member phases of which differ from each other by the number (s) of cation layers in the fluorite-structured (Ce,Y)−[O$_2$−(Ce,Y)]$_{s-1}$ block between the CuO$_2$ planes. X-ray absorption near-edge structure spectroscopy is employed as a probe for the hole states of these phases. The s = 1 member appears to be more strongly doped with holes than other phases of the series and accordingly to possess the highest T_c value of 87 K. For $s \geq 2$, unexpectedly, both the CuO$_2$ plane hole concentration and the value of T_c (∼55 K) remain constant, being independent of s.

Introduction

High-T_c superconductors possess a multilayered crystal structure where the superconductive CuO$_2$ planes are alternatively piled up with nonsuperconductive (or blocking) layers of various types. The dimensionality, the inter-CuO$_2$-plane coupling, and the role of the blocking layer as a spacer, carrier supplier, and/or mediator for the inter-CuO$_2$-plane coupling have been discussed ever since the first report on high-T_c superconductivity. Answers have been searched for by, e.g., growing artificial superlattices such as YBa$_2$Cu$_3$O$_{7-\delta}$/PrBa$_2$Cu$_3$O$_{7-\delta}$ and Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_x$/Bi$_2$Sr$_2$CuO$_x$.[1] Similar but naturally assembled superlattices are accomplished with the M_mA_2(Ce,R)$_s$-Cu$_2$O$_{m+4+2s\pm\delta}$ [or M−$m2s$2 for short] type layered copper oxides.[2] The members of the M−$m2s$2 homologous series characteristically contain an insulating fluorite-structured (Ce,R)−[O$_2$−(Ce,R)]$_{s-1}$ layer block between adjacent CuO$_2$ planes.[3−5] In an ideal case, the CuO$_2$ plane spacing over the fluorite-structured block is then controlled by the choice of the number (s) of (Ce,R) cation layers in the M−$m2s$2 unit cell (or

half unit cell for s = 2, 4, ...).[6,7] However, once the (Ce,R)−[O$_2$−(Ce,R)]$_{s-1}$ block gets thicker it becomes increasingly difficult to prepare high-quality superconductive samples.

Recently we succeeded in synthesizing single-phase samples of the first four members of the (Cu,Mo)-12s2 homologous series with compositions given by (Cu$_{0.75}$Mo$_{0.25}$)Sr$_2$(Ce,Y)$_s$-Cu$_2$O$_{5+2s+\delta}$ and making them all superconductive through a postsynthesis high-oxygen-pressure annealing.[8] Figure 1 shows schematic crystal structures of the four phases with the layer sequence of SrO−(Cu,Mo)O$_{1+\delta}$−SrO−CuO$_2$−(Ce,Y)−[O$_2$−(Ce,Y)]$_{s-1}$−CuO$_2$. Excitingly, it was found that, upon insertion of an additional (Ce,Y)−O$_2$ cation−oxygen double-layer unit between two adjacent CuO$_2$ planes, that is, upon increasing s, the value of T_c initially decreases, i.e., as s goes from 1 to 2, but then it remains constant for s = 2−4. In the present work we have employed X-ray absorption near-edge structure (XANES) spectroscopy at both Cu L$_{2,3}$ and O K edges to probe the

† Tokyo Institute of Technology.
‡ Helsinki University of Technology.
§ National Taiwan University.
∥ National Synchrotron Radiation Research Center.
⊥ Argonne National Laboratory.
Northern Illinois University.

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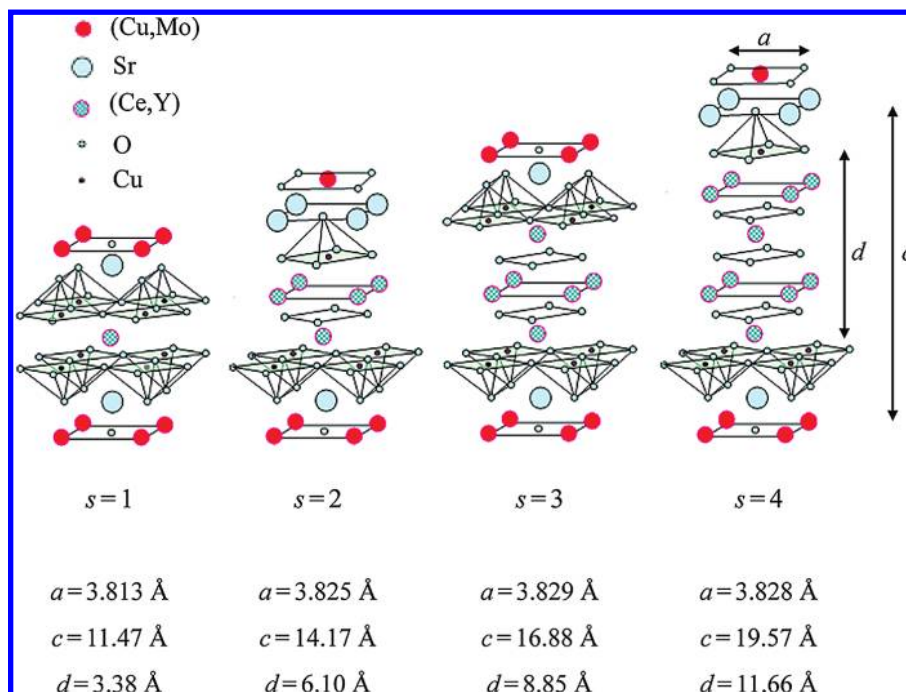
Figure 1. Crystal structures of the $s = 1-4$ members of the homologous series (Cu,Mo)-12s2 or (Cu,Mo)Sr$_2$(Ce,Y)$_s$Cu$_2$O$_{5+2s+\delta}$ (at $\delta = 0$). The excess oxygen should be located in the (Cu,Mo)O layer. With the parameter s increasing from 1 to 4, the adjacent CuO$_2$ planes are separated by a single Y cation layer for $s = 1$ and a fluorite-structured layer block of (Ce,Y)−[O$_2$−(Ce,Y)]$_{s-1}$ for $s \geq 2$. Note that, for $s = 2$ and 4, "c" represents only half of the lattice parameter c.

electronic structures of the four (Cu,Mo)-12s2 phases and to determine the total amount of doped holes and their distribution between the two crystallographically distinct Cu-containing layers, i.e., the (Cu,Mo)O$_{1+\delta}$ charge reservoir and the CuO$_2$ planes. On the basis of the XANES data, we are able to conclude that within the (Cu,Mo)-12s2 homologous series T_c does not depend on the number of (Ce,Y)−O$_2$ layers between the CuO$_2$ planes as long as the hole-doping level of the planes remains constant; the high T_c value of the $s = 1$ phase is concluded to be due to the higher hole-doping level of the phase than those for the higher s members of the series.

Experimental Section

Samples of all four (Cu,Mo)-12s2 phases were synthesized in a parallel manner, starting from wet-chemically prepared nitrate precursors with cation compositions corresponding to the formulas (Cu$_{0.75}$Mo$_{0.25}$)Sr$_2$YCu$_2$O$_{7+\delta}$ ($s = 1$), (Cu$_{0.75}$Mo$_{0.25}$)Sr$_2$(Ce$_{0.5}$Y$_{0.5}$)$_2$-Cu$_2$O$_{9+\delta}$ ($s = 2$), (Cu$_{0.75}$Mo$_{0.25}$)Sr$_2$(Ce$_{0.67}$Y$_{0.33}$)$_3$Cu$_2$O$_{11+\delta}$ ($s = 3$), and (Cu$_{0.75}$Mo$_{0.25}$)Sr$_2$(Ce$_{0.75}$Y$_{0.25}$)$_4$Cu$_2$O$_{13+\delta}$ ($s = 4$). High-quality samples were obtained through a sequence of heat treatments in air first by calcination at 220−900 °C followed by (Cu,Mo)-12s2 phase formation firings at 930−1005 °C. Details of the heat treatments have been reported elsewhere.[8] To induce superconductivity, the as-air-synthesized (AS) samples were annealed under high oxygen pressures. These high-pressure oxygenation (HPO) treatments were carried out in a cubic-anvil-type high-pressure apparatus at 5 GPa and 500 °C in the presence of 33 mol % KClO$_3$, which decomposes to KCl and thereby acts as an efficient in situ oxygen generator. All the AS and HPO samples were confirmed to be essentially single-phase (except for the small KCl residues in the HPO samples) by powder X-ray diffraction (XRD; Rigaku RINT2550 V equipped with a rotating anode, Cu Kα radiation).

Superconductivity properties of the HPO samples were determined using a superconducting-quantum-interference device (SQUID) magnetometer (Quantum Design MPMS-XL, applied magnetic field 10 Oe). The HPO samples were all confirmed to be bulk superconductors: the superconducting volume fraction calculated

Table 1. T_c Values and Values for the Average Valence of Copper [V(Cu)] and the CuO$_2$ Plane Hole Concentration [p(CuO$_2$)] As Estimated for the (Cu,Mo)-12s2 Phases on the Basis of Cu L$_{2,3}$ Edge and O K Edge Data, Respectively[a]

phase	V(Cu), AS	V(Cu), HPO	p(CuO$_2$), HPO	T_c (K)
$s = 1$	2.16[b]	2.46	0.53	87
$s = 2$	2.13	2.24	0.28	56
$s = 3$	2.14	2.25	0.26	54.5
$s = 4$	2.14	2.26	0.27	55.5

[a] The V(Cu) values were determined for both AS and HPO samples, and the p(CuO$_2$) values were determined only for the superconductive HPO samples. [b] Iodometric titration gave a value of 2.15 for the same sample.

from the zero-field-curve data at 5 K exceeded 20% for each of the four samples. As for T_c (defined as the onset of the diamagnetic signal), the values were very close to those previously seen for our similarly synthesized samples,[8] i.e., 87 K for $s = 1$ and 55 ± 1 K for the other three phases (Table 1).

The XANES spectra were collected at both Cu L$_{2,3}$ and O K edges in X-ray fluorescence yield mode at the 6 m HSGM beamline of the National Synchrotron Radiation Research Center in Hsinchu, Taiwan; experimental details are reported elsewhere.[9] The recorded spectra were corrected for the energy-dependent incident photon intensity as well as for self-absorption effects and normalized to the tabulated standard absorption cross sections.[10]

Results and Discussion

The Cu L$_{2,3}$ edge measurements were carried out for both the AS and HPO samples; Figure 2 displays the spectra for the HPO samples. The Cu L$_3$ area has been commonly used to

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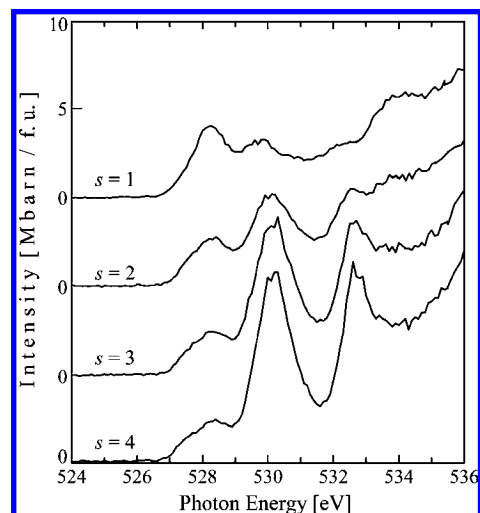
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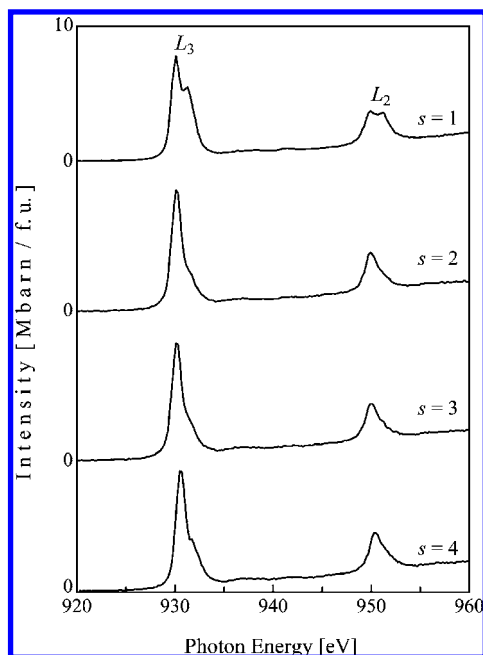
Figure 2. Cu L$_{2,3}$ edge XANES spectra for the HPO samples of the four (Cu,Mo)-12s2 phases.

Figure 3. O K edge XANES spectra for the HPO samples of the four (Cu,Mo)-12s2 phases.

estimate the average valence of copper in superconductive copper oxides: the narrow peak centered about 931.2 eV is due to divalent copper, Cu^{II} (i.e., transitions from the Cu $(2p_{3/2})3d^9$ ground state to the Cu $(2p_{3/2})^{-1}3d^{10}$ excited state, where $(2p_{3/2})^{-1}$ denotes a $2p_{3/2}$ hole), and its high-energy shoulder around 932.4 eV is due to trivalent copper states, Cu^{III} (i.e., transitions from the Cu $(2p_{3/2})3d^9L$ ground state into the Cu $(2p_{3/2})^{-1}3d^{10}L$ excited state, where L denotes a ligand hole in the O 2p orbital).[9,11] The spectral features about the Cu L$_3$ edge were analyzed following the model reported in ref 9. In short, after subtraction of the background (modeled by a straight line), the two peaks were fitted using combined Lorentzian and Gaussian functions, and the average valence of copper was calculated from the integrated intensities of the peaks, i.e., $I(Cu^{II})$ and $I(Cu^{III})$, as $V(Cu) = 2 + I(Cu^{III})/[I(Cu^{II}) + I(Cu^{III})]$. The analysis results are given in Table 1.

From Table 1, it is seen that the value of $V(Cu)$ does not vary significantly among the AS samples, being just slightly higher for $s = 1$ (2.16) than for the rest of the samples (2.13−2.14). The $s = 1$ sample was found to be soluble enough in diluted acid solutions. Hence, it was possible to analyze its oxygen content by means of wet-chemical analysis. Iodometric titration revealed the amount of excess oxygen at $\delta = 0.21(2)$ and consequently a copper oxidation state, $V(Cu)$, of 2.15 (assuming Mo^{VI}), which is in good agreement with the value of 2.16 determined by XANES for the same sample. For the HPO samples the $V(Cu)$ values are, as expected, significantly higher in comparison with the values for the corresponding AS samples (Table 1). Moreover, a significantly higher $V(Cu)$ is observed for the $s = 1$ phase (2.46) compared with the three other higher s members of the series. Surprisingly, for the $s = 2$, 3, and 4 HPO samples, the $V(Cu)$ values were nearly identical, being 2.25 ± 0.01. Hence, we conclude that the (Cu,Mo)-1212 phase made superconductive through an HPO treatment is more

strongly doped with holes [to show a higher $V(Cu)$ value] than similarly HPO-treated samples of the higher s members of the same (Cu,Mo)-12s2 homologous series. Most importantly, the trend is essentially parallel to that seen for the T_c values of the same samples.

Since the Cu L edge XANES data do not allow us to differentiate between the two types of Cu-containing layers in the (Cu,Mo)-12s2 phase, i.e., the (Cu,Mo)O$_{1+\delta}$ charge reservoir and the CuO$_2$ planes, we employed O K edge XANES spectroscopy, which allows us to distinguish the CuO$_2$ plane hole states from those of the (Cu,Mo)O$_{1+\delta}$ charge reservoir. O K edge spectra were collected for the HPO samples (see Figure 3). Three or four peaks are distinguished below approximately 532 eV. Two of the peaks are straightforwardly identified on the basis of accumulated knowledge on XANES spectra for various superconductive copper oxide phases: the broad peak slightly below 530 eV is due to transitions into the upper Hubbard band (predominantly formed by the hybridization in the ground state of the Cu $3d^9$ and Cu $3d^{10}L$ states), and the peak with a maximum at ∼528.3 eV is due to the excitations of O 1s electrons to O 2p holes located in the CuO$_2$ planes.[9,11] Then, with increasing s (i.e., increasing Ce content), a shoulder grows on the higher energy side of the UHB peak about 530 eV, which most likely originates from Ce 5d and/or Ce 4f states hybridized with O 2p states. Note that a similar feature has already been seen for the electron-doped $(R,Ce)_2CuO_4$ super-conductors.[12,13] Finally, partly overlapping with the 528.3 eV peak, the fourth peak is discerned at ∼527.5 eV. Taking an analogy to the case of the CuBa$_2$YCu$_2$O$_{7-\delta}$ (or Cu-1212) phase,[11] we here assign the 527.5 eV peak to the hole states in the (Cu,Mo)O$_{1+\delta}$ charge reservoir block. To derive a quantitative estimation for the distribution of holes between the (Cu,Mo)O$_{1+\delta}$ charge reservoir and the CuO$_2$ planes, the spectral features were analyzed by fitting the three pre-edge peaks at 527.5, 528.3, and 530 eV with a combination of Lorentzian and Gaussian functions after subtracting the background intensity (approximated with a straight line within 527−532 eV). The thus obtained integrated intensities, $I(527.5)$ and $I(528.3)$, for the 527.5 and 528.3 eV peaks are assumed to be proportional to

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the relative hole concentrations of the $(Cu,Mo)O_{1+\delta}$ charge reservoir and the two CuO_2 planes, respectively. Hence, we calculate an estimate for the CuO_2 plane hole concentration as $p(CuO_2) \equiv p_{tot}\{0.5I(528.3)/[I(528.3) + I(527.5)]\}$, where the ratio $0.5I(528.3)/[I(528.3) + I(527.5)]$ defines the share of one CuO_2 plane of the total hole content, p_{tot}, which is estimated on the basis of the Cu L_3 edge XANES data as $p_{tot} = (0.75 + 2.00)[V(Cu) - 2]$. The $p(CuO_2)$ values obtained for the four HPO samples are given in Table 1. The absolute values ranging from 0.26 to 0.53 look somewhat too high; however, the relative comparison among the four phases is possible in a rather accurate way. From Table 1, it is clearly seen that the CuO_2 plane hole concentration is much higher for the $s = 1$ phase than for the other three phases. On the other hand, for the three phases with $s = 2, 3,$ and 4, nearly the same $p(CuO_2)$ values have been obtained. Herewith we have shown that the $p(CuO_2)$ behavior determined from the XANES data is similar to the T_c behavior for the (Cu,Mo)-12s2 series: both decrease initially when the single Y cation layer in the $s = 1$ phase is replaced by the double-fluorite-layer block of $(Ce,Y)-O_2-(Ce,Y)$ in the $s = 2$ phase, but remain constant when the fluorite-structured $(Ce,Y)-[O_2-(Ce,Y)]_{s-1}$ block gets thicker and thicker for the $s = 3$ and 4 phases. Finally, we should mention that recently the same samples were characterized for their precise crystal structures by means of neutron powder diffraction to reveal that for the $s = 2, 3,$ and 4 phases the immediate (crystal)chemical surroundings of the CuO_2 planes are nearly the same. In other words, for these phases the three-layer unit of $SrO-CuO_2-(Ce,Y)$ was found to be essentially identical in regard to both the cation composition (i.e., Ce/Y ratio) and the Cu−O bond lengths (whereas the $s = 1$ phase was found to be clearly different).

Conclusion

In the present work we have demonstrated that the similarly synthesized and oxygenated $s = 2, 3,$ and 4 members of the (Cu,Mo)-12s2 homologous series of superconductive copper oxides are essentially identical in regard to the total hole-doping level [i.e., $p_{tot} = V(Cu) - 2$], the CuO_2 plane hole concentration [i.e., $p(CuO_2)$], and the value of T_c, whereas the first member of the series (with $s = 1$) is somewhat different (being more heavily hole-doped and having a higher T_c). Hence, we conclude that the T_c value of a high-T_c superconductive copper oxide is independent of the distance between adjacent CuO_2 planes as long as their hole-doping level and immediate chemical surroundings remain unchanged.

Supporting Information Available: Complete ref 12. This material is available free of charge via the Internet at http://pubs.acs.org.

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