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Hole doping and superconductivity characteristics of the $s = 1$, 2 and 3 members of the (Cu,Mo)-12s2 homologous series of layered copper oxides

M. Karppinen[a,*], Y. Morita[a], T. Kobayashi[a], I. Grigoraviciute[a], J.M. Chen[b], R.S. Liu[c], H. Yamauchi[a]

[a] *Materials and Structures Laboratory, Tokyo Institute of Technology, 4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan*
[b] *National Synchrotron Radiation Research Center (NSRRC), Hsinchu, Taiwan, ROC*
[c] *Department of Chemistry, National Taiwan University, Taipei, Taiwan, ROC*

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Abstract

Superconductivity characteristics have been systematically evaluated for a two-CuO_2-plane copper oxide system, (Cu,Mo)-12s2, upon increasing the number of fluorite-structured layers, s, between the two CuO_2 planes. Essentially single-phase samples of $(Cu_{0.75}Mo_{0.25})Sr_2YCu_2O_{7+\delta}$ ($s = 1$), $(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.45}Y_{0.55})_2Cu_2O_{9+\delta}$ ($s = 2$) and $(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.67}Y_{0.33})_3Cu_2O_{11+\delta}$ ($s = 3$) were synthesized through a conventional solid-state route in air. To make the samples superconductive an additional high-pressure oxygenation (HPO) treatment was required. Such treatment (carried out at 5 GPa and 500 °C in the presence of 75 mol% Ag_2O_2 as an oxygen source to maximize the T_c) compressed the crystal lattice for the three members of the $(Cu_{0.75}Mo_{0.25})$-12s2 series equally, i.e., by 0.01 Å for the a parameter and by 0.07 Å for the c parameter per formula unit. From both Cu L-edge and O K-edge XANES spectra the $s = 1$ sample was found to possess the highest overall hole-doping level among the HPO samples. Accordingly it exhibited the best superconductivity characteristics. With increasing s, both the T_c ($s = 1$: 88 K, $s = 2$: 61 K, $s = 3$: 53 K) and H_{irr} values got depressed, being well explained by the trend of decreasing CuO_2-plane hole concentration with increasing s as revealed from O K-edge XANES spectra for the same samples. Hence, the present results do not suggest any significant (negative) impact on the superconductivity characteristics from the gradually thickened fluorite-structured block itself.

Keywords: High-T_c superconductive copper oxides; Fluorite-structured layers; Homologous series; Oxygen content; Cu valence; XANES spectroscopy

1. Introduction

The crystal structure of a high-T_c superconductive copper oxide is composed of an ordered stack of superconductive CuO_2 plane(s) and nonsuperconductive layers of various types. The nonsuperconductive layers not only provide the (proper) spacing between the CuO_2 planes but also control the hole-doping level of the planes. Here an interesting group of phases is recognized, having two distinct blocks of piled nonsuperconductive layers. One of the blocks is the conventional "blocking block" of rock-salt (RS) and/or perovskite (P) structured layers, i.e. $[AO]_{RS}$-$[(MO_{1\pm\delta/m})_m]_{P/RS}$-$[AO]_{RS}$ where A = Ba, Sr, etc. and M = Cu, Bi, Pb, Tl, Hg, etc. This block is glued through the AO layer to a CuO_2 plane by sharing the apical oxygen atom of the CuO_5 pyramid that constitutes the CuO_2 plane. The other layer-piling block of (Ce,R)-$[O_2$-(Ce,R)$]_{s-1}$ (R = rare earth element) in which the valence states of Ce^{IV} and R^{III} are assumed is of the fluorite (F) structure, being inserted between the basal CuO_2 planes of the pyramids. The phase that contains both the two types of blocking block repeats the layer sequence of $[AO]_{RS}$-$[(MO_{1\pm\delta/m})_m]_{P/RS}$-$[AO]_{RS}$-$[CuO_2]_P$-$[$(Ce,$R$)-$\{O_2$-(Ce,$R$)$\}_{s-1}]_F$-$[CuO_2]_P$ and accordingly obeys a general formula of $M_mA_2(Ce,R)_sCu_2O_{m+4+2s\pm\delta}$ expressed as M-$m^{(A)}2s2$ in

*Corresponding author. Fax: +81 45 924 5365.
E-mail address: karppinen@msl.titech.ac.jp (M. Karppinen).

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short [1]. Such phases with F-structured layers are classified as "Category-B" phases, whereas the more common phases with a single nonsuperconductive block only and a general formula of $M_mA_2(Ca,R)_{n-1}Cu_nO_{m+2+2n\pm\delta}$ [M-$m^{(A)}(n-1)n$] belong to "Category-A" [2].

For Category-A phases, a widely adopted practice [1,3–6] has been to discuss both the chemical (oxygen content, hole doping, etc.) and superconductivity (T_c and H_{irr}) characteristics in terms of the number of consecutively stacked CuO_2 planes within one "homologous series", i.e., a group of phases for which the $[AO]_{RS}$-$[(MO_{1\pm\delta/m})m]_{P/RS}$-$[AO]_{RS}$ block is common but the number, n, of the CuO_2 planes in the superconductive $[CuO_2$-$\{(Ca,R)$-$CuO_2\}_{n-1}]_P$ block varies [7]. For instance, it has been empirically well established that for each homologous series of Category-A, the highest T_c achieved is due to the $n=3$ member [1]. Here an interesting question arises, concerning possible systematics among the Category-B phases. Note that for an M-$m^{(A)}2s2$ (M, m and A are fixed) homologous series of Category-B, the members differ from each other in terms of the number of the F-structured cation layers, i.e., s [1,8]. Despite the potential interest, systematic studies on Category-B phases have been rather rare, one of the most apparent reasons being the fact that superconductivity—for a long time—could not be induced into phases with $s \geqslant 3$ [9–12].

Recently we synthesized a three-fluorite-layer phase of (Cu,Mo)-$1^{(Sr)}232$ with the composition of $(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.67}Y_{0.33})_3Cu_2O_{11+\delta}$ [13]. Samples synthesized in air did not superconduct, but superconductivity was successfully induced in the as-synthesized samples by means of high-pressure oxygenation. Here we recognize that together with the two earlier established phases, (Cu,Mo)-$1^{(Sr)}212$ and (Cu,Mo)-$1^{(Sr)}222$ [14], this $s=3$ phase forms a homologous series of (Cu,Mo)-$1^{(Sr)}2s2$ of Category-B. With the parameter s increasing from 1 to 3 the members of the (Cu,Mo)-$1^{(Sr)}2s2$ series have adjacent two CuO_2 planes separated from each other by a single Y-cation layer for $s=1$, a "double-fluorite-layer" block of (Ce,Y)-O_2-(Ce,Y) for $s=2$, and a "triple-fluorite-layer" block of (Ce,Y)-O_2-(Ce,Y)-O_2-(Ce,Y) for $s=3$; for the schematic crystal structures, see Fig. 1. In the present contribution, we present our systematic characterization results for these three phases in terms of both the doping state of the phase and the superconductivity parameters, T_c and H_{irr}.

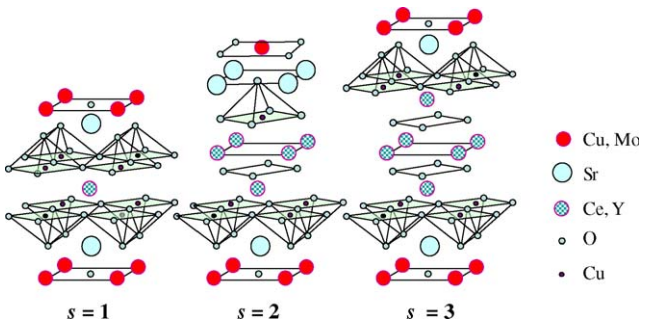

Fig. 1. Schematic presentation of the crystal structures of the first three members of the homologous series, (Cu,Mo)-$1^{(Sr)}2s2$.

2. Experimental

Polycrystalline samples of $(Cu_{0.75}Mo_{0.25})Sr_2YCu_2O_{7+\delta}$ ($s=1$), $(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.45}Y_{0.55})_2Cu_2O_{9+\delta}$ ($s=2$) and $(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.67}Y_{0.33})_3Cu_2O_{11+\delta}$ ($s=3$) were synthesized through a solid-state reaction route from appropriate mixtures of high-purity powders of CuO, MoO_3, $SrCO_3$, CeO_2, and Y_2O_3. The mixed powders were calcined at 950 °C and sintered at 1020 °C in air with several intermediate grindings. Portions of these as-air-synthesized (AS) samples were then high-pressure oxygenated (HPO) at 5 GPa and 500 °C for 30 min in a cubic-anvil-type high-pressure apparatus in the presence of 75 mol% Ag_2O_2 (against (Cu,Mo)-$1^{(Sr)}2s2$ formula unit) as an excess-oxygen source [13]. It should be noted that from preliminary experiments we had confirmed that for all the three phases the lattice parameters decreased and the values of T_c and V(Cu) (= average valence of copper) increased with increasing amount of Ag_2O_2 only up to 50–75 mol% of Ag_2O_2, and then levelled off. Hence, our HPO samples (that are either underdoped or optimally doped but not overdoped) exhibit the highest T_c values achieved for the three phases so far. Also confirmed was from SEM–EDX analysis (for $s=3$) that the Mo content in a sample that had undergone all the heat-treatment steps yet agreed well with the nominal value. (This was considered important, since MoO_3 is prone to evaporation.)

The samples were characterized by powder X-ray diffraction (XRD; Rigaku: RINT2550VK/U; Cu K_α radiation) for phase purity and lattice parameters. Oxygen content of the AS (Cu,Mo)-$1^{(Sr)}212$ ($s=1$) sample was analyzed by means of iodometric titration, whereas for the other AS samples of the $s=2$ and 3 phases oxygen-content analysis was not possible by the presently employed standard iodometric titration technique, since the samples did not dissolve in 1 M HCl solution. In the case of the HPO samples, titration experiments were not even tried due to the presence of Ag and/or Ag_2O (originating from Ag_2O_2) in these samples.

For the estimation of the average valence state of copper X-ray absorption near-edge structure (XANES) spectra were collected for the samples at the Cu $L_{2,3}$ edge. Additionally for the HPO samples O K-edge XANES spectra were collected for the layer-specific hole concentrations. The XANES experiments were performed at the 6-m HSGM beam-line of NSRRC in Hsinchu (Taiwan) in X-ray fluorescence-yield mode; experimental details were as previously given elsewhere [15].

Superconductivity/magnetic properties were measured for all the samples down to 4 K in both field-cooled (FC) and zero-field-cooled (ZFC) modes using a superconducting-quantum-interference-device (SQUID) magnetometer (Quantum Design: MPMS-XL) under 10 Oe. The value of