J|A|C|S
ARTICLES

Published on Web 02/07/2007

Layer-Engineering of High-T_c Superconductors: $(Cu,Mo)Sr_2(Ce,Y)_4Cu_2O_{13+\delta}$ with a Quadruple-Fluorite-Layer Block Between CuO_2 Planes

Inga Grigoraviciute, Hisao Yamauchi, and Maarit Karppinen*,†

Contribution from the Materials and Structures Laboratory, Tokyo Institute of Technology,
Yokohama 226-8503, Japan

Received October 5, 2006; E-mail: maarit.karppinen@tkk.fi

Abstract: Among high-T_c superconductive copper oxides, there have been known phases that contain fluorite-structured layers as an additional “blocking block” between adjacent CuO_2 planes. Here, we report that even a phase with the CuO_2 planes separated by a 12-Å thick quadruple-fluorite-layer block can be synthesized in a single phase and strongly oxygenated form to exhibit superconductivity with a T_c value as high as 55 K. The new phase is the fourth member of the $(Cu,Mo)Sr_2(Ce,Y)_sCu_2O_{5+2s+\delta}$ or (Cu,Mo)-12s2 homologous series. Comparison with the previously known $s = 1$, 2, and 3 members of the series reveals the amazing conclusion that T_c remains essentially unaffected upon inserting additional fluorite-structured layers between the two CuO_2 planes as long as the hole-doping level of the planes is kept constant.

Introduction

A high-T_c superconductive copper-oxide crystal is an ordered stack of superconductive CuO_2 plane(s) and nonsuperconductive layers, being nothing but a series of naturally assembled nanoscopic superconductor−insulator−superconductor Josephson junctions.[1] Having the eye on potential applications, on-demand control of such natural junctions is highly desired; an apparent prerequisite for this is that the thickness and properties of each structure block may be individually tailored. Revealing the material limits of the high-T_c superconductor family, that is, finding the simplest members and also the most complex ones, is of definite scientific interest, too. Hence, we should search for advanced layer-engineering approaches, which would enable us to layer-by-layer design the superconductor crystal.

One of the structurally simplest phases is the very first high-T_c superconductor, $(La,Ba)_2CuO_4$ or A_2CuO_4 (A = La, Ba, Sr, etc.), with a single CuO_2 plane alternating with two insulating rock-salt (RS)-structured AO layers. As for the more complex ones, it is well known that the double-layer $(AO)_2$ block readily accepts additional $MO_{1\pm\delta/m}$ (M = Cu, Bi, Pb, Tl, Hg, etc.) layers to form a thicker insulating “blocking block” of AO-$(MO_{1\pm\delta/m})_m$-AO type between adjacent CuO_2 planes. The blocking block not only provides the (proper) spacing between the CuO_2 planes but also controls their hole-doping level. The superconductive block itself may also get thickened to have multiple CuO_2 planes piled up alternatively with layers of Q cation (Q = Ca, rare earth element (R), etc.) in a perovskite (P)-type arrangement. This is the way the most common superconductive copper oxides with a layer sequence of AO-$(MO_{1\pm\delta/m})_m$-AO-CuO_2-(Q-$CuO_2)_{n-1}$ and chemical formula of $M_mA_2Q_{n-1}Cu_nO_{m+2+2n\pm\delta}$ (or M-$m2(n-1)n$ in short) are formed.[2,3] The M-$m2(n-1)n$ family has been extended to 3 in m[4] and to 9 in n,[5] and also derived down to the parent $m = 0$ phases.[6]

To yet increase the structural complexity, there should be recognized another interesting category of copper-oxide phases that, besides the conventional AO-$(MO_{1\pm\delta/m})_m$-AO block, accommodates an additional blocking block of B-$(O_2\text{-}B)_{s-1}$ of fluorite (F) structure (B = Ce, R).[7−9] From the resultant layer sequence of $[AO]_{RS}$-$[(MO_{1\pm\delta/m})_m]_{P/RS}$-$[AO]_{RS}$-$[CuO_2]_P$-$[B\text{-}(O_2\text{-}B)_{s-1}]_F$-$[CuO_2]_P$ (see Figure 1), the chemical formula of such phases is derived to be $M_mA_2B_sCu_2O_{m+4+2s\pm\delta}$ or M-$m2s2$.[3] (Here, the subscripts RS, P, and F refer to the crystal structure of the layer/block.) Among the known M-$m2s2$ phases, m varies from 0 to 3 and s can be increased to 7 or 8.[10−12] However, phases with $s > 2$ are rather rare and usually not obtained in phase-pure form. Moreover, the $s > 2$ phases

---

† Present address: Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, FI-02015 TKK, Finland.

(1) Kleiner, R.; Steinmeyer, F.; Kunkel, G.; Müller, P. *Phys. Rev. Lett.* **1992**, *68*, 2394−2397. Kleiner, R.; Müller, P. *Phys. Rev. B* **1994**, *49*, 1327−1341.

(2) Marezio, M.; Antipov, E. V.; Capponi, J. J.; Chaillout, C.; Loureiro, S.; Putilin, S. N.; Santoro, A.; Tholence, J. L. *Physica B* **1994**, *197*, 570−578.

(3) For a review, see: Karppinen, M.; Yamauchi, H. *Mater. Sci. Eng., R* **1999**, *26*, 51−96.

(4) Cava, R. J.; et al. *Nature* **1988**, *336*, 211−214.

(5) Loureiro, S. M.; Matsui, Y.; Takayama-Muromachi, E. *Physica C* **1998**, *302*, 244−256.

(6) For a review, see: Yamauchi, H.; Karppinen, M. *Physica C* **2000**, *335*, 273−278.

(7) Akimitsu, J.; Suzuki, S.; Watanabe, M.; Sawa, H. *Jpn. J. Appl. Phys.* **1988**, *27*, L1859−L1860. Sawa, H.; Suzuki, S.; Watanabe, M.; Akimitsu, J.; Matsubara, H.; Watabe, H.; Uchida, S.; Kokusho, K.; Asano, H.; Izumi, F.; Takayama-Muromachi, E. *Nature* **1989**, *337*, 347−348.

(8) Tokura, Y.; Takagi, H.; Uchida, S. *Nature* **1989**, *337*, 345−347.

(9) Sawa, H.; Obara, K.; Akimitsu, J.; Matsui, Y.; Horiuchi, S. *J. Phys. Soc. Jpn.* **1989**, *58*, 2252−2255.

(10) Tokiwa, A.; Oku, T.; Nagoshi, M.; Syono, Y. *Physica C* **1991**, *181*, 311−319.

(11) Wada, T.; Nara, A.; Ichinose, A.; Yamauchi, H.; Tanaka, S. *Physica C* **1992**, *192*, 181−190.

(12) Ikegawa, S.; Nakayama, K.; Motoi, Y.; Arai, M. *Phys. Rev. B* **2002**, *66*, 14536-1−11.

10.1021/ja0671316 CCC: $37.00 © 2007 American Chemical Society

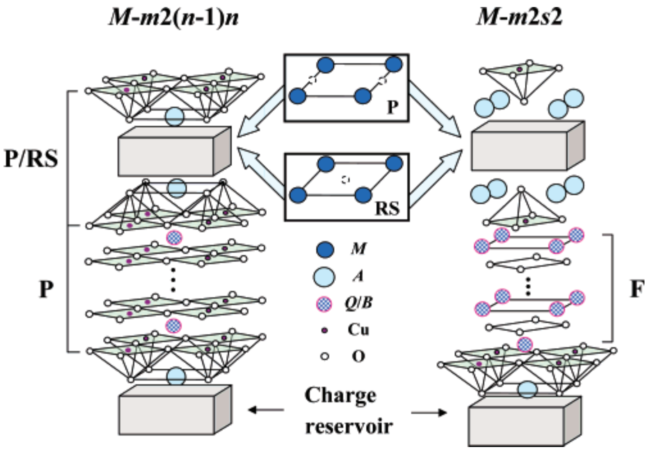

Figure 1. Crystal structures of multilayered copper oxides with one (left) and two (right) blocking blocks: the former phases, $M_mA_2Q_{n-1}Cu_nO_{m+2+2n\pm\delta}$ or M-$m2(n-1)n$, consist of rock-salt (RS)- and perovskite (P)-structured layers only, whereas the latter phases, $M_mA_2B_sCu_2O_{m+4+2s\pm\delta}$ or M-$m2s2$, contain fluorite (F)-structured layers as well. The so-called charge-reservoir block, $M_mO_{m\pm\delta}$, which contains m layers of $MO_{1\pm\delta/m}$ is represented by a rectangular solid.[3]

remained for long nonsuperconductive.[12] Recently, we synthesized the first $s = 3$ superconductors, (Hg,W)-1232 and (Cu,Mo)-1232.[13,14] Together with the two previously established phases, (Cu,Mo)-1212 and (Cu,Mo)-1222,[15] the latter phase forms a homologous series of (Cu,Mo)-12s2.[16] The present work now demonstrates that even the fourth member of the series with an almost 12-Å thick quadruple-fluorite-layer block between adjacent CuO_2 planes can be synthesized in single-phase form and doped with enough holes to show high-T_c superconductivity with a T_c as high as 55 K. Moreover, comparison with the previously known $s = 1$, 2, and 3 members of the series reveals the amazing conclusion that T_c remains essentially unaffected upon inserting additional fluorite-structured layers between the two CuO_2 planes as long as the hole-doping level of the planes is kept constant.

Experimental Section

Synthesis. All of the samples were synthesized from a homogeneous nitrate precursor prepared from appropriate amounts of CeO_2, Y_2O_3, CuO, MoO_3, and $SrCO_3$ powders. The starting powders were dissolved one by one in a solution of HNO_3 (2 M) and H_2O_2 (0.04 M). A clear solution was obtained in approximately 10 h with the help of heating (∼100 °C). It was then dried at 100 °C, and the thus obtained solid nitrate residue was carefully decomposed first through 2-h heating periods at 220, 450, and 650 °C with intermediate grindings and then for the final calcination at 850 °C for 5 h and at 900 °C for 24 h. After the calcination, the sample powder was fired several times at 930−995 °C with intermediate grindings. All of the heat treatments were carried out in air. The cation compositions and final firing conditions for the samples are summarized in Table 1.

High-Pressure Oxygenation. The air-synthesized samples were high-pressure oxygenated in a cubic-anvil-type high-pressure apparatus at 5 GPa and 500 °C for 30 min in the presence of 33 mol % $KClO_3$ as an excess-oxygen source. For the high-pressure treatment, a small portion (∼70 mg) of the sample powder (together with $KClO_3$) was packed in an Au capsule.

Characterization. Powder X-ray diffraction (XRD) patterns were collected at room temperature on a Rigaku RINT2550VK/U diffractometer equipped with a rotating Cu anode. High-resolution transmission electron microscopy (HRTEM) images were taken with a Hitachi H900NR equipment. Magnetization measurements were carried out in a field-cooled mode under 10 Oe using a superconducting-quantum-interference device (SQUID) magnetometer, Quantum Design: MPMS-XL. The superconductivity transition temperature, T_c, was defined at the onset of diamagnetic signal.

Results and Discussion

The choice of proper synthesis route was essentially important for obtaining the $s = 4$ member of the (Cu,Mo)-12s2 series. For related layered oxide systems, a common experimental fact has been that with increasing number of various types of intervening layers completion of the synthesis requires elongated heat-treatment periods or alternatively increased temperatures to speed up the reaction kinetics. Initially, we therefore attempted to obtain the (Cu,Mo)-1242 phase through conventional solid-state synthesis at temperatures higher than those used for the lower members of the series. Synthesis from ordinary oxide and carbonate starting materials at temperatures somewhat higher than ∼1000 °C (used for the $s = 3$ phase) yielded a mixture of (Cu,Mo)-1232 and CeO_2 only, underlining the fact that the members of the (Cu,Mo)-12s2 series apparently are energetically very close to each other. A solution to the problem that turned out to be successful was to look for more reactive precursors. We ended up with a rather simple nitrate method, in which the simple oxide and carbonate raw materials are dissolved in a HNO_3 solution to obtain a homogeneous nitrate precursor for the final synthesis of the desired (Cu,Mo)-1242 phase realized then through several repeated heat treatments in air at 950−985 °C. From XRD patterns recorded for the sample after each heat treatment, it was clearly seen that the $s = 4$ phase forms upon gradual intercalation of CeO_2 into the structures of the lower members of $s = 2$ and 3, rationalizing the fact that successful synthesis of high-quality (Cu,Mo)-1242 samples is promoted by using a well-homogenized precursor mixture and long synthesis periods. The final product after a 264-h firing was of XRD-pure (Cu,Mo)-1242 phase. Figure 2 depicts the XRD pattern and a representative HRTEM image for the sample. In the HRTEM image, the layer repetition of SrO-(Cu,Mo)$O_{1+\delta}$-SrO-CuO_2-(Ce,Y)-O_2-(Ce,Y)-O_2-(Ce,Y)-O_2-(Ce,Y)-CuO_2 expected for a 1242-type crystal structure is clearly revealed. No sign of any stacking faults is seen.

Like the cases of the previously established $s = 1$, 2, and 3 phases of the (Cu,Mo)-12s2 series,[14,16] samples of the $s = 4$ phase synthesized in air were not superconductive. Superconductivity could, however, be induced in the air-synthesized (AS) samples of the phase (again, like the cases of the lower members of the series) through a high-pressure oxygenation (HPO) treatment. From the magnetic susceptibility versus temperature data shown for the HPO sample in Figure 3, a sharp superconductivity transition is seen at 55 K.

To enable a detailed comparison of the basic structural and superconductivity characteristics among the different (Cu,Mo)-

---

(13) Watanabe, T.; Karppinen, M.; Motohashi, T.; Nagai, T.; Matsui, Y.; Yamauchi, H. *Phys. Rev. B* **2004**, *70*, 174514-1−4.

(14) Morita, Y.; Nagai, T.; Matsui, Y.; Yamauchi, H.; Karppinen, M. *Phys. Rev. B* **2004**, *70*, 174515-1−6. Karppinen, M.; Morita, Y.; Chen, J. M.; Liu, R. S.; Yamauchi, H. *Phys. Rev. B* **2005**, *72*, 12501-1−4. Grigoraviciute, I.; Arai, M.; Yamauchi, H.; Karppinen, M. *Solid State Commun.* **2006**, *137*, 601−605.

(15) Ono, A. *Jpn. J. Appl. Phys.* **1993**, *32*, 4517−4520.

(16) Karppinen, M.; Morita, Y.; Kobayashi, T.; Grigoraviciute, I.; Chen, J. M.; Liu, R. S.; Yamauchi, H. *J. Solid State Chem.* **2005**, *178*, 3464−3470.

Table 1. Cation Composition and Synthesis/Sintering Protocol (after the Initial Calcination Steps Common to Each Phase) of Single-Phase Samples of the (Cu,Mo)-12*s*2 Series

phase	composition	synthesis/sintering
$s = 1$	$(Cu_{0.75}Mo_{0.25})Sr_2YCu_2O_{7+\delta}$	930 °C (2 × 24 h) + 960 °C (24 h)
$s = 2$	$(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.50}Y_{0.50})_2Cu_2O_{9+\delta}$	950 °C (24 h), 970 °C (2 × 24 h), 995 °C (24 h), 1005 °C (24 h)
$s = 3$	$(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.67}Y_{0.33})_3Cu_2O_{11+\delta}$	950 °C (24 h), 970 °C (3 × 24 h), 995 °C (2 × 24 h), 1005 °C (24 h)
$s = 4$	$(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.75}Y_{0.25})_4Cu_2O_{13+\delta}$	950 °C (24 h), 970 °C (2 × 24 h), 980 °C (7 × 24 h), 985 °C (24 h)

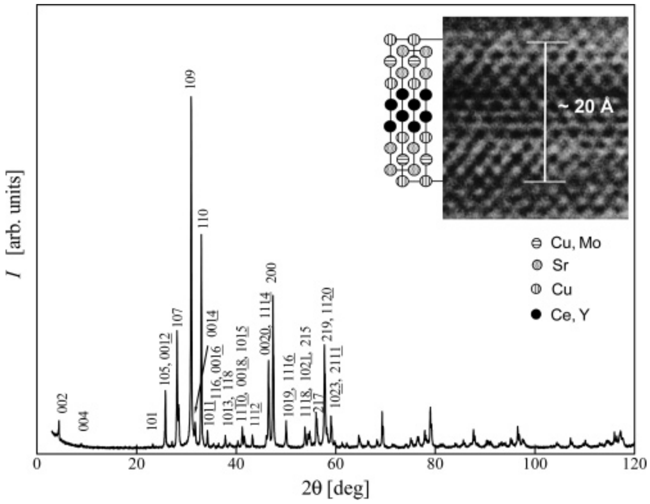

Figure 2. XRD pattern (indexed for the 1242 structure in space group *I*4/*mmm*) for a sample of $(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.75}Y_{0.25})_4Cu_2O_{13+\delta}$ synthesized from a nitrate precursor through several repeated heat treatments in air at 950−985 °C. The inset shows an HRTEM image for the same sample.

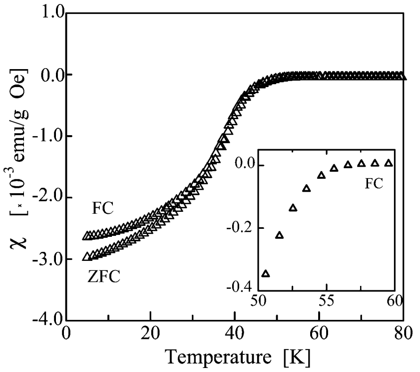

Figure 3. Temperature dependence of magnetic susceptibility (χ) measured for a XRD-pure $(Cu_{0.75}Mo_{0.25})Sr_2(Ce_{0.75}Y_{0.25})_4Cu_2O_{13+\delta}$ sample after its high-pressure oxygenation treatment.

12*s*2 phases, we synthesized single-phase samples of all four phases (with $s = 1$, 2, 3, and 4) through parallel synthesis steps. An important fact to note is that for the present samples the overall positive charge of the fluorite-structured blocking block, (Ce,Y)-$[O_2\text{-}(Ce,Y)]_{s-1}$, between the two CuO_2 planes is exactly the same for all four phases, that is, +3 (as calculated from the nominal cation composition of the block and assuming the valence states of Ce^{IV} and Y^{III}). Each of the AS and HPO samples was found to contain the target phase in phase-pure form within the detection limit of the XRD measurement. We moreover used the XRD data to refine the lattice parameters and cation positions, in the tetragonal space group, *P*4/*mmm* (*I*4/*mmm*), expected for 1212 and 1232 (for 1222 and 1242)-type structures. For each phase, the HPO treatment was found to result in lattice contraction in both the in-plane and the out-of-plane directions, whereas the refined Cu−Cu distance, *d*(Cu−Cu), over the F-structured block was found to increase (by ~0.05 Å) upon the HPO treatment. These trends are parallel to those observed for many other high-T_c superconductors, for example, $CuBa_2YCu_2O_{7-\delta}$,[17] upon oxygenation. In Figure 4, the lattice parameters, *a* and *c*, calculated here per (Cu,Mo)-12*s*2 structural unit are plotted against *s* for the HPO samples. Also given is the Cu−Cu distance, *d*(Cu−Cu), for the four

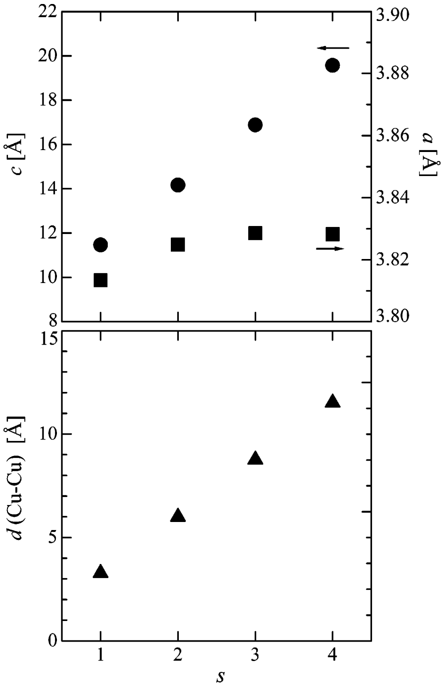

Figure 4. Evolution of lattice dimensions within the (Cu,Mo)-12*s*2 series in terms of *s*: with increasing *s*, both the lattice parameter *c* (●) and the CuO_2-plane separation distance *d*(Cu−Cu) (▲) increase in a linear manner, whereas the lattice parameter *a* (■) saturates for $s \geq 2$. Note that the lattice parameters are given for each phase per (Cu,Mo)-12*s*2 structural unit.

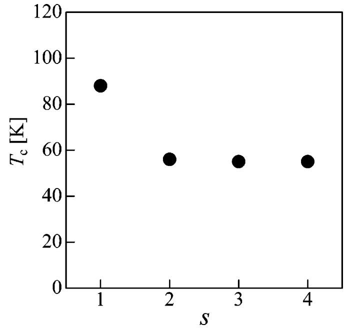

Figure 5. T_c values for the first four members of the (Cu,Mo)-12*s*2 series. The given values are for similarly high-pressure-oxygenated samples.

---

(17) Jorgensen, J. D.; Veal, B. W.; Paulikas, A. P.; Nowicki, L. J.; Crabtree, G. W.; Claus, H.; Kwok, W. K. *Phys. Rev. B* **1990**, *41*, 1863−1877.

phases. With increasing number (s) of F-structured layers in the (Ce,Y)-[O_2-(Ce,Y)]$_{s-1}$ block, the c and d(Cu−Cu) values both increase in a linear manner. The a-axis parameter, on the other hand, behaves differently: it is clearly shorter for the $s = 1$ phase in comparison with the values for the higher members of the series, suggesting that the $s = 1$ phase is more strongly doped with holes than are the other three phases. Preliminary electronic structure study by means of X-ray absorption spectroscopy techniques has revealed highly parallel results: from Cu L-edge absorption spectra average Cu valence was estimated for the samples at 2.46 ($s = 1$), 2.24 ($s = 2$), 2.25 ($s = 3$), and 2.25 ($s = 4$).[18]

Magnetization measurements confirmed that the XRD-pure HPO samples of the four (Cu,Mo)-12s2 phases are all bulk superconductors. The volume fraction of superconductivity (at 5 K) exceeded 20% for each case. In Figure 5, the value of T_c is plotted against s. It is seen that T_c first decreases when the single Y cation layer in the $s = 1$ phase is replaced by the F-structured (Ce,Y)-O_2-(Ce,Y) block in $s = 2$, but then remains constant even though the F-structured (Ce,Y)-[O_2-(Ce,Y)]$_{s-1}$ block gets thicker for $s = 3$ and 4. The observed T_c values are in line with our belief that we had synthesized the $s = 1$ phase in a more strongly oxygenated/hole-doped form than the other three phases. On the other hand, comparison among the $s = 2$, 3, and 4 phases provides us with strong evidence for the "not-necessarily expected" conclusion that once the hole-doping level of the CuO_2 planes remains constant the distance between the superconductive CuO_2 planes has no significant effect on the value of T_c.

Conclusion

We have successfully realized the (Cu,Mo)-12s2 homologous series of copper-oxide high-T_c superconductors, for which the insulating spacing or blocking block (of a constant charge of +3) between two adjacent superconductive CuO_2 planes can be gradually thickened from the ~3 Å thick "single-cation-layer" block in (Cu,Mo)-1212 to the ~12 Å thick "quadruple-fluorite-layer" block in (Cu,Mo)-1242 without significantly affecting the value of T_c as long as the hole-doping level of the CuO_2 planes remains constant. The discovery has demonstrated the power of layer-by-layer-engineering techniques in on-demand design of new high-T_c superconductors and related multilayered materials.

Acknowledgment. This work was supported by a Grant-in-aid for Scientific Research (No. 15206002) from the Japan Society for the Promotion of Science and also by the Academy of Finland (Decision Nos. 110433 and 116254). I.G. acknowledges the Scholarship (ID 043145) from the Ministry of Education, Culture, Sports, Science, and Technology of Japan. K. Sakai is thanked for his assistance in HRTEM experiments.

Supporting Information Available: Complete ref 4. This material is available free of charge via the Internet at http://pubs.acs.org.

JA0671316

---

[18] Grigoraviciute, I.; Chen, J. M.; Liu, R. S.; Yamauchi, H.; Karppinen, M. Unpublished work at the National Synchrotron Radiation Research Center, Taiwan.