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New family of layered copper oxide compounds with ordered cations: Prospective high-temperature superconductors

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A new family of layered copper oxide compounds with ordered rare-earth cations has been designed and synthesized. The compounds are partially Sr-substituted $L_1La_1CuO_4$, where L (=Sm, Eu, and Gd) and La ions are sequentially ordered thus: [$-L-L-$La$-$La$-$]. As a result, the Cu-O network of the new compound forms single-layer sheets of CuO_5 pyramids, which is essentially the same as in the 30-K superconductor $(Nd,Ce,Sr)_2CuO_4$ discovered recently by Akimitsu *et al.* Extensive oxygen annealing makes the new compounds metallic, indicating their possibility as a new class of high-temperature superconductors with hole-type charge carriers.

Since the discovery of high-temperature superconductivity (high T_c) in copper oxide compounds by Bednorz and Müller,[1] unprecedented extensive efforts have been devoted to synthesizing new superconducting copper oxide compounds with higher T_c. Some of those attempts have succeeded as is well known, realizing higher-T_c compounds with new structures. Most of the new superconductors, e.g., Y-Ba-Cu-O (Ref. 2) and Bi(Tl)-Sr(Ba)-Ca-Cu-O (Refs. 3 and 4) systems, are characterized by the layered structures which comprise Cu-O pyramidal sheets, as a common structural unit, and also sequentially ordered noncopper cations along the normal to the CuO_2 planes. In this Brief Report, we describe the design and synthesis of a new family of layered copper oxide compounds, partially Sr-substituted $L_1La_1CuO_4$, where L stands for Sm, Eu, and Gd: The new compounds are composed of the single-layer sheets of Cu-O pyramids, as shown in Fig. 1(a), and show the sequential ordering of the cations in such a way as [$-$La$-$La$-L-L-$]. We have found that the Sr-doping into the mother compound $LLaCuO_4$ stabilizes the new structure, which we will call the T^* phase hereafter, and makes the compounds metallic (and possibly superconducting, if we can diminish oxygen vacancies). The new compounds form essentially the same Cu-O network as the 30-K superconductor $Nd_{2-x-z}Ce_xSr_zCuO_4$ discovered by Akimitsu *et al.*,[5] which shows the partial ordering of Nd and Sr as shown in Fig. 1(b). The T^* phase compound is possibly the simplest system among the Cu-O pyramidal sheet compounds and, hence, will provide a unique opportunity for investigating basic physical properties relating to the existing multisheet compounds with higher T_c but with more complicated structures.

Our synthetic strategy for the new single-layer Cu-O pyramidal sheet compounds was as follows: There are two well-known examples of copper oxide compounds with single-layer sheets:[6] The K_2NiF_4 structure or the so-called T phase [shown in Fig. 1(c)] as observed in La_2CuO_4 and the Nd_2CuO_4 structure or the so-called T' phase [shown in Fig. 1(d)] as in L_2CuO_4, L being Pr, Nd, Sm, Eu, and Gd. Whether rare-earth metal copper oxides with single-layer CuO_2 sheets have the T or T' phase structure seems to be critically dependent on the ionic radius of constituent rare-earth ion. In particular, the T phase is only stabilized for the largest La ion among rare-earth trivalent ions. The relatively large Pr (and Nd) ions can form the solid solution with the largest La ions, $La_{2-x}Pr_xCuO_4$ and $La_{2-x}Nd_xCuO_4$, over the whole

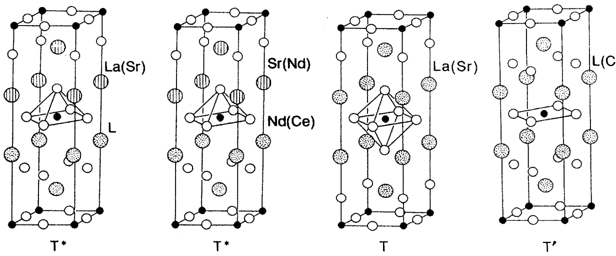

FIG. 1. Crystal structures of metallic (and possibly superconducting) copper oxide compounds with single-layer CuO_2 sheets: (a) $L_{1-x}La_{1+x-z}Sr_zCuO_4$ (T^* phase; L =Sm, Eu, and Gd); (b) $Nd_{2-x-z}Ce_xSr_zCuO_4$ (T^* phase); (c) $La_{2-x}Sr_xCuO_4$ (T phase); and (d) $L_{2-x}Ce_xCuO_4$ (T' phase; L =Pr, Nd, Sm, Eu, and Gd).

composition range, but undergoes the T-to-T' phase transformation at critical concentration.[7] On the other hand, the large La ions can hardly be dissolved in the smaller ion sites (Sm, Eu and Gd sites) in the T' phase structures, and vice versa in the T phase structure. The key to get a new structure is to mix the large La ions and small Sm (or Eu or Gd) ions, which are mutually insoluble, approximately with the 1:1 ratio. This is essential for realizing the sequential ordering of the large and small cations, just as in the case of Y (small)-Ba_2 (large)-Cu_3O_7. Then, the resultant structure is expected to be a hybrid of the T phase (characteristic of La sites) and T' phase (L sites), that is the T^* phase structure shown in Fig. 1(a), composed of two-dimensional (2D) sheets of the Cu-O pyramids.

Materials were synthesized from a mixture of prescribed amounts of La_2O_3, Sm_2O_3 (or Eu_2O_3 or Gd_2O_3), CuO, and $SrCO_3$. Mixed powder was first calcined at 950 °C in air for 10 h, then pressed into pellets, and finally sintered at 1130 °C in air for 15 h. The pellets were quenched to room temperature in air, and subsequently annealed at 550 °C in the atmosphere with various oxygen pressures up to 80 atm.

A series of new compounds with the chemical formula of $L_{1-x}La_{1+x-z}Sr_zCuO_{4-y}$, could be obtained in the nearly single-phase form for the composition ranges, $0<x<0.20$ and $0.10<z<0.30$. In these compounds the stoichiometric ratio of La to L is kept around 1 to realize the sequential ordering of these cations as described above. To stabilize the new T^* phase, however, a small amount of Sr is necessary, supposedly due to the condition of the stable Cu valence slightly above 2.0.

The x-ray-diffraction pattern of the new compound, for example, $Sm_{1.0}La_{0.75}Sr_{0.25}CuO_{4-y}$, differs evidently in peak positions from those of the typical compounds of the T phase (e.g., $La_{2-x}Sr_xCuO_4$) with 2D sheets of Cu-O octahedra and of the T' phase (e.g., Nd_2CuO_4) with 2D sheets of Cu-O squares. The Rietveld analysis of the x-ray pattern has been carried out for the new-phase sample, for example, $Sm_{1.0}La_{0.75}Sr_{0.25}CuO_{4-y}$, as shown in Fig. 2. In an initial refinement, occupation factors of Sm, La, and Sr were varied freely. It was proven that the occupation factor of the L-ion site in Fig. 1(a) exceeds unity. Then this site was assumed to be fully occupied by the Sm with the largest atomic number of three. The oxygen content of the present sample has been determined by an iodometric titration technique[8] as $4-y=3.95$, and occupation factors for O(1), O(2), and O(3) sites were fixed at 1, 0.95, and 1, respectively. We also used isotropic thermal parameters of 0.4 Å^2 for metal atoms and 0.5 Å^2 for oxygen. In the diffraction pattern, traces of impurity peaks (less than 5%) were observed, and intensity data in these regions were excluded in the refinement. Table I lists final structure parameters determined in the present Rietveld analysis. The R factors are $R_{wp}=11.9\%$, $R_p=8.8\%$, $R_I=4.8\%$, and $R_F=4.1\%$.

Unfortunately, the large neutron absorbance of Sm prevents us from carrying out the neutron-diffraction study for the more accurate determination of positions of oxygen and its vacancy. However, the above structure model is also supported by the high-resolution lattice image by the transmission electron microscope operated at 400 kV. The micrograph for the same compound, $Sm_{1.0}La_{0.75}Sr_{0.25}CuO_{4-y}$, is shown in Fig. 3 together with the interpretation of the lattice image. In particular, fairly large separation between two lines of La ions is clearly seen in the micrograph, which is in accord with the x-ray analysis.

Reflecting the hybrid character between the T and T' phase, the new tetragonal compound of the T^* phase structure shows the intermediate values of the lattice constants, $a=3.86$ Å, $c=12.6$ Å, which are to be compared with the values in the T phase ($a=3.78$ Å, $c=13.2$ Å) and in the T' phase ($a=3.96$ Å, $c=12.1$ Å). Reasonably, the x-ray pattern and lattice parameters of the new compounds are nearly identical to those of the 30-K superconductor $Nd_{2-x-z}Ce_xSr_zCuO_4$, having the same T^* phase structure.[9-11] In the case of $Nd_{2-x-z}Ce_xSr_zCuO_4$, however, the compound is stabilized by a subtle balance of the electric charge of cations, which can be obtained in a narrow compositional range of Ce^{4+} ions and Sr^{2+} ions.[11] By contrast, the present new series of compounds appear

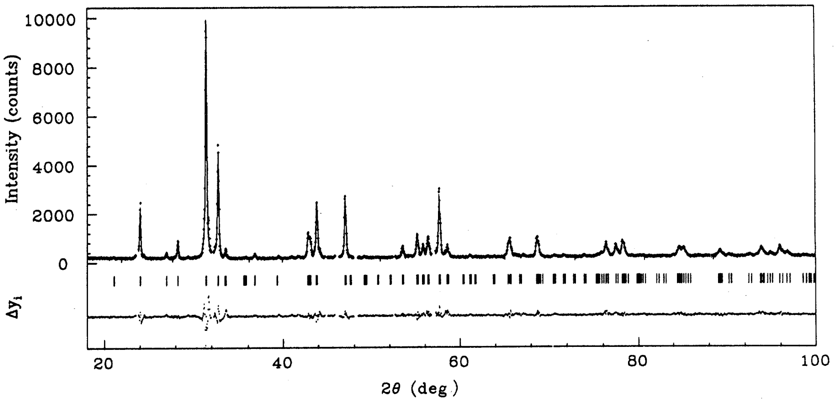

FIG. 2. Rietveld refinement pattern of $Sm_{1.0}La_{0.75}Sr_{0.25}$- CuO_{4-y}. Positions of 172 Bragg reflections for CuK_1 and K_2 radiations are indicated by markers, and y_i is the difference between observed and calculated intensities.

TABLE I. Structure parameters of $Sm_{1.0}La_{0.75}Sr_{0.25}CuO_{3.95}$. Space group *P*4/*nmm*. $a=3.8588(2)$ Å and $c=12.5725(7)$ Å. *g* is the occupation factor. Numbers in parentheses are standard deviations of the last significant digit.

Atom	Site	*x*	*y*	*z*	*g*
La	2*c*	0	$\frac{1}{2}$	0.390(2)	0.75
Sr	2*c*	0	$\frac{1}{2}$	0.390(2)	0.25
Sm	2*c*	0	$\frac{1}{2}$	0.106(1)	1
Cu	2*c*	$\frac{1}{2}$	0	0.244(4)	1
O(1)	4*f*	0	0	0.243(11)	1
O(2)	2*c*	$\frac{1}{2}$	0	0.422(8)	0.85
O(3)	2*a*	0	0	0	1

to be realized essentially by the simple order of the large (La) and small (Sm, Eu, and Gd) rare-earth ions having the same valence (3+).

In Fig. 4, we show the temperature dependence of resistivity in the T^* phase compounds, $Sm_{1.0}La_{0.70}Sr_{0.30}CuO_{4-y}$, which were quenched from 1130 °C in air or annealed in different oxygen atmospheres as indicated in the figure. The transport properties in the T^* phase sample were found to be quite sensitive to the annealing treatment, as clearly seen in Fig. 4. To characterize each sample, the effective Cu valence $(2+p)$, or the concentration (p) of the doped holes per [Cu-O] unit was determined by an iodometric titration technique.[7] In Fig. 4 are indicated the p value as well as the oxygen vacancy (y). The latter value was determined by the condition of electric neutrality in the sample $L_{1+x}{}^{3+}La_{1-x-z}{}^{3+}Sr_z{}^{2+}Cu^{2+p}O_{4-y}$. In the sample quenched from 1130 °C in air $(y=0.10, p=0.10)$ and the sample annealed at 900 °C in N_2 gas flow $(y=0.11, p=0.08)$, behaviors of resistivity are semiconducting. With decrease of oxygen vacancy y, or with increase of hole concentration p by the annealing procedure, the resistivity at low temperature is greatly reduced. In particular, the extensively oxygenated sample $(p=0.14, y=0.08)$, which was annealed at 550 °C in the atmosphere of 80 atm oxygen for 20 h, shows the metallic (i.e., $d\rho/dT>0$) behavior over the whole temperature region below 300 K. Although a resistivity drop was observed at around 20 K in this sample, the measurement of the Meissner signal (field-cooling run) indicated that its volume fraction at 2 K was as small as 10^{-2} of the ideal value and, hence, the observed trace of superconductivity is not of bulk nature.

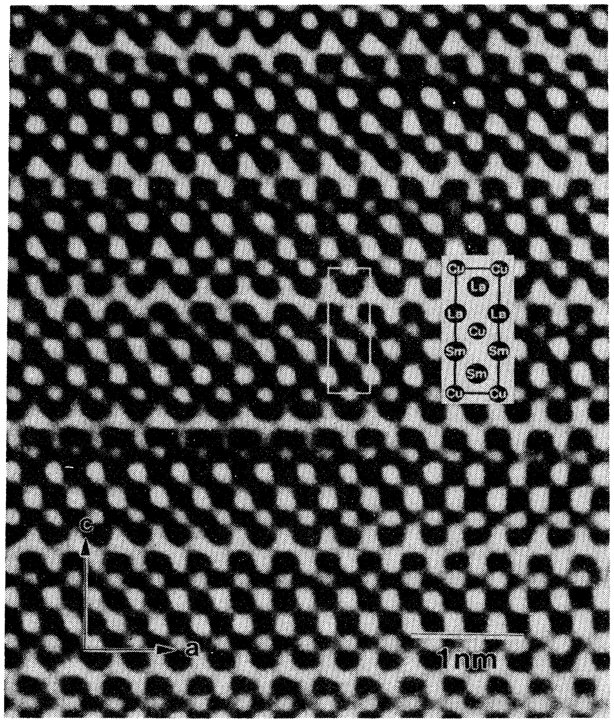

FIG. 3. High-resolution transmission electron micrograph of $Sm_{1.0}La_{0.75}Sr_{0.25}CuO_{4-y}$.

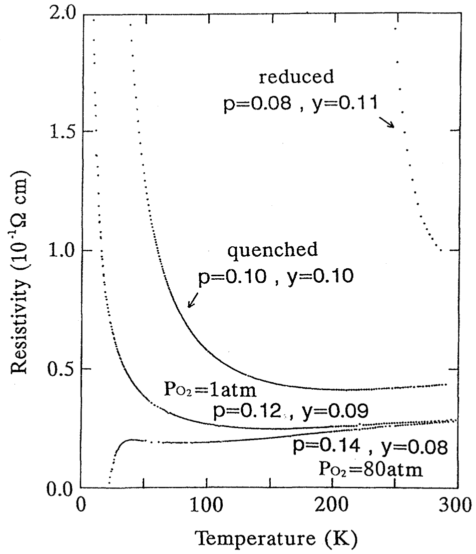

FIG. 4. Temperature dependence of resistivity in $Sm_{1.0}La_{0.70}Sr_{0.30}CuO_{4-y}$. The values of p and y represent the nominal hole concentration per [Cu-O] unit and oxygen vacancy, respectively. The resistivity drop in the $p=0.14$ sample around 20 K is not due to the bulk superconductivity (see text).

The Hall coefficient of this sample was also measured, which shows the positive value of $+2\times10^{-3}$ cm^3/C at room temperature. This confirms the hole-type charge carriers in this T^* phase structure with the Cu-O pyramidal sheets. The similar positive value was also obtained in the superconducting T^* phase compound, $Nd_{2-x-z}Ce_xSr_zCuO_{4-y}$.[11] The situation in this T^* phase is similar to the cases of the T phase La-based compounds with octahedral sheets [Fig. 1(c)] and also of other high-T_c copper oxide compounds with pyramidal sheets, but sharply contrasts with the T' phase [for example, $Nd_{2-x}Ce_xCuO_4$ shown in Fig. 1(d)] in which the charge carriers are electrons.[12]

The observed resistivity behavior in the new compounds appears to be strongly correlated with the hole concentration and oxygen vacancies, although it is difficult in the present case to separate their respective contribution from each other. As compared with the case of $La_{2-x}Sr_xCuO_4$ (T phase) with similar values of $p(\sim 0.2)$ or of Sr content,[13] even the most oxygenated sample shown in Fig. 4 still includes considerable amounts of oxygen vacancies ($y=0.06$), which does not seem to be easily fulfilled by the usual oxygen treatment. Nevertheless, the observed systematic change of resistivity behavior in the course of decreasing oxygen vacancies implies that the new T^* phase compounds, $L_{1-x}La_{1+x-z}Sr_zCuO_{4-y}$, will be a new family of high-T_c oxide compounds if the oxygen vacancies can be properly fulfilled. For this purpose, higher-pressure (>100 atm) oxygen annealing and/or substitution of other divalent ions for Sr may be useful, which are currently being tested.

Note added in proof. After submission of this paper, we have obtained the bulk superconducting T^*-phase sample, $Sm_{1.0}La_{0.75}Sr_{0.25}CuO_4$, by annealing the compound under the partial O_2 pressure of 400 atm for 5 h at 900 °C. The clear onset of Meissner signal (field cooled) was observed around 20 K and its magnitude exceeded 10% of the ideal value at 5 K.

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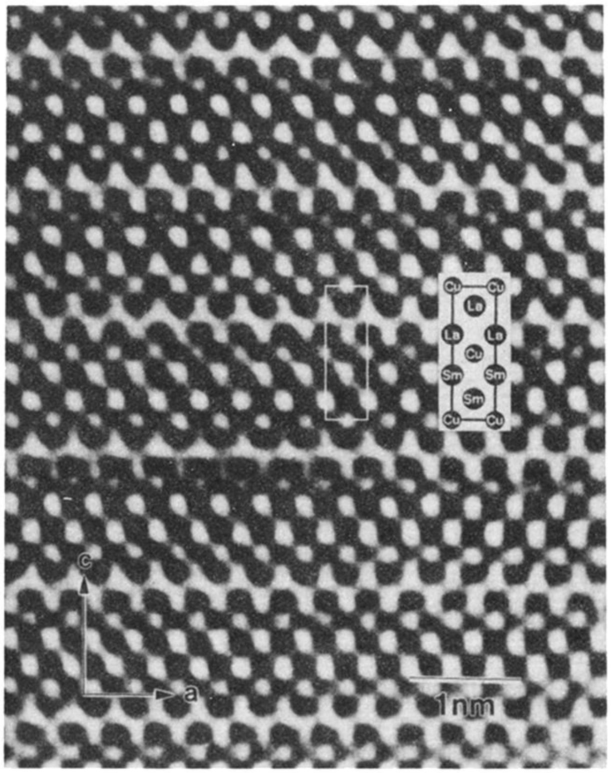
[1] J. G. Bednorz and K. A. Müller, Z. Phys. B **64**, 189 (1986).
[2] M. K. Wu *et al.*, Phys. Rev. Lett. **58**, 908 (1987).
[3] H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. **27**, L209 (1988).
[4] Z. Z. Sheng and A. M. Hermann, Nature (London) **332**, 138 (1988).
[5] J. Akimitsu, S. Suzuki, M. Watanabe, and H. Sawa, Jpn. J. Appl. Phys. **27**, L1859 (1988).
[6] Hk. Muller-Buschbaum, Angew. Chem. Int. Ed. Engl. **16**, 674 (1977).
[7] K. K. Singh, P. G. Ganguly, and J. B. Goodenough, J. Solid State Chem. **53**, 254 (1984).
[8] A. I. Nazzal *et al.*, Physica C **153–156**, 1367 (1988).
[9] E. Takayama-Muromachi *et al.*, Jpn. J. Appl. Phys. **27**, L2283 (1988).
[10] H. Sawa *et al.*, Nature (London) **337**, 347 (1989).
[11] Y. Tokura *et al.*, Phys. Rev. B (to be published).
[12] Y. Tokura, H. Takagi, and S. Uchida, Nature (London) **337**, 345 (1989).
[13] J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Parkin, Phys. Rev. Lett. **61**, 1127 (1988).



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