

## La<sub>8-x</sub>Sr<sub>x</sub>Cu<sub>8</sub>O<sub>20</sub>: An Oxygen-Deficient Perovskite Built of CuO<sub>6</sub>, CuO<sub>5</sub>, and CuO<sub>4</sub> Polyhedra

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Received July 17, 1987

A new oxygen-deficient perovskite corresponding to the formulation La<sub>8-x</sub>Sr<sub>x</sub>Cu<sub>8</sub>O<sub>20-ε</sub> (1.28 ≤ x ≤ 1.92) has been isolated. The results of chemical analysis show that copper exhibits a mixed valence in this oxide. This perovskite crystallizes in a tetragonal cell with parameters related to the a<sub>p</sub> parameter of the cubic perovskite by: a ≈ a<sub>p</sub> 2√2, c ≈ a<sub>p</sub>. The structure has been determined by neutron powder diffraction in the space group *p4/mbm*. This study shows that the oxygen vacancies are ordered, forming rows parallel to (001). The [Cu<sub>8</sub>O<sub>20</sub>] framework is built of corner-sharing CuO<sub>6</sub> octahedra, CuO<sub>5</sub> pyramids, and CuO<sub>4</sub> square planar groups forming hexagonal tunnels in which are located the La<sup>3+</sup> and Sr<sup>2+</sup> ions. The slight oxygen substoichiometry with regard to the formulation A<sub>8</sub>Cu<sub>8</sub>O<sub>20</sub> is discussed in terms of a superstructure along the c axis (c ≈ 2a<sub>p</sub>), which was observed in some crystals by electron diffraction. © 1988 Academic Press, Inc.

### Introduction

Mixed-valence copper oxides form an important family of oxygen-deficient perovskites (1-5) which have been extensively studied these last 6 years for their metallic conductivity (4, 6-9) and more recently for their superconducting properties (10-16). The phase diagram of those compounds and especially their oxygen stoichiometry is not completely understood. It is known that the amount of oxygen vacancies and their ordering depend on the nature of the alkaline-earth element A (Ba, Sr, or Ca), which is substituted for lanthanum and also on the molar ratio of La to Ba, as shown, for instance, for the barium oxides La<sub>3</sub>Ba<sub>3</sub>Cu<sub>6</sub>O<sub>14+δ</sub> (3), LaBa<sub>2</sub>Cu<sub>3</sub>O<sub>8-ε</sub> (13), and La<sub>4</sub>BaCu<sub>5</sub>O<sub>13+δ</sub> (4, 5). No oxygen-deficient perovskite involving

copper and strontium has been isolated up to the present, in spite of the ability of copper to exhibit mixed-valence [Cu(II)-Cu(III)]. The present work deals with the synthesis and the structural study of a new oxygen-deficient ordered perovskite La<sub>8-x</sub>Sr<sub>x</sub>Cu<sub>8</sub>O<sub>20</sub>, which is closely related to the oxide La<sub>4</sub>BaCu<sub>5</sub>O<sub>13</sub>.

### Experimental

#### Synthesis

Samples were prepared by solid-state reaction in platinum crucible from appropriate mixtures of dried La<sub>2</sub>O<sub>3</sub>, CuO, and SrCO<sub>3</sub>. The mixtures were heated in air, first for a few hours at 900°C, then at 1000°C for 24 hr, and finally quenched to room temperature.

TABLE I  
ANALYTICAL DATA OF THE OXIDES La<sub>8-x</sub>Sr<sub>x</sub>Cu<sub>8</sub>O<sub>20-ε</sub>

Composition	ε	a (Å)	c (Å)	V (Å <sup>3</sup> )	d <sub>exp</sub>	d <sub>calc</sub>
La <sub>6.72</sub> Sr <sub>1.28</sub> Cu <sub>8</sub> O <sub>19.92</sub>	0.08	10.868(4)	3.856(3)	455.4	6.84	6.86
La <sub>6.40</sub> Sr <sub>1.28</sub> Cu <sub>8</sub> O <sub>19.84</sub>	0.16	10.840(4)	3.861(2)	453.7	6.82	6.83
La <sub>6.08</sub> Sr <sub>1.92</sub> Cu <sub>8</sub> O <sub>19.68</sub>	0.32	10.825(4)	3.863(3)	452.6	6.77	6.78

### Chemical Analysis

In order to determine the mean oxidation state of the copper ions and consequently the oxygen content, chemical analysis was carried out by redox back titration: a known amount of the sample is dissolved in an aqueous solution of hydrochloric acid containing a known volume of a standard solution of Fe(II). Fe(II) is partly oxidized into Fe(III) if Cu<sup>3+</sup> ions are present in the sample; the excess Fe(II) is titrated with a standard solution of potassium dichromate.

### Structural Analysis

The cell parameters were determined from X-ray powder diffraction patterns obtained with a Philips goniometer using CuKα radiation. The space group was determined by electron diffraction using a JEOL 120CX electron microscope. For the structural study, powder neutron data were collected on the DIA high-resolution diffractometer at the Institute Laue-Langevin with λ = 1.9575 Å, from 10 to 150° in steps of 0.05° (2θ). Calculations were made by profile refinement of diffraction lines (17, 18). The following scattering amplitudes (all × 10<sup>-12</sup> cm) were used (19): 0.772 (Cu), 0.824 (La), 0.702 (Sr), 0.580 (O).

### Results and Discussion

The scanning of the system La<sub>2</sub>O<sub>3</sub>-SrO-CuO for the compositions corresponding to the molar ratio (La + Sr)/Cu = 1 allowed a new perovskite to be isolated for the composition La<sub>8-x</sub>Sr<sub>x</sub>Cu<sub>8</sub>O<sub>20-ε</sub>, with x ranging

from 1.28 to 1.92 and ε ranging from 0.08 to 0.32. From the X-ray powder and electron diffraction investigation it appears that the crystal symmetry is tetragonal; the parameters of the tetragonal cell are related to the a<sub>p</sub> parameter of the perovskite cubic cell in the following way: a ≈ 2a<sub>p</sub>√2, c = a<sub>p</sub> with the reflection condition 0kl: k = 2n. Another superstructure was observed by electron diffraction for a small number of crystals, differing from the first by the c parameter, c = 2a<sub>p</sub> (reflection condition 0kl: k + 1 = 2n). No extra line corresponding to this latter superstructure was observed on the X-ray diffraction and neutron diffraction patterns. The cell parameters obtained from indexing the X-ray powder diffractograms (Table I) show that a decreases and c increases slightly as x increases, leading to a slight decrease in the cell volume. The chemical analysis shows the mixed-valence of copper, the number of oxygen atoms per cell tending toward 20. Nevertheless it must be pointed out that the number of oxygen vacancies (ε) with respect to the formulation A<sub>8</sub>M<sub>8</sub>O<sub>20</sub> increases as the strontium content increases. The measured densities confirm the presence of one A<sub>8</sub>M<sub>8</sub>O<sub>20-ε</sub> species per cell.

The oxides La<sub>8-x</sub>Sr<sub>x</sub>Cu<sub>8</sub>O<sub>20-ε</sub> exhibit a composition close to the one of La<sub>4</sub>BaCu<sub>5</sub>O<sub>13+δ</sub> (5) and can be described like this compound as an ordered oxygen-deficient perovskite. However, they differ from this latter oxide by the nature of the superstructure and the amount of oxygen vacancies with respect to the stoichiometric perovskite ABO<sub>3</sub>. The barium oxide indeed

TABLE II  
STARTING PARAMETERS (*a*) AND FINAL PARAMETERS (*b*) IN SPACE GROUP *P4/mbm*

Atom	Sites	$x^a$	$y^a$	$z^a$	$x^b$	$y^b$	$z^b$	$B (\text{Å}^2)^b$
La(Sr)	8(j)	0.25	0.5	0.5	0.2621(2)	0.4693(2)	0.5	1.16(5)
Cu(1)	2(a)	0.0	0.0	0.0	0.0	0.0	0.0	0.5(1)
Cu(2)	2(d)	0.5	0.0	0.0	0.5	0.0	0.0	1.5(1)
Cu(3)	4(g)	0.25	$0.5 + x$	0.0	0.2196(2)	$0.5 + x$	0.0	0.58(6)
O(1)	2(b)	0.0	0.0	0.5	0.0	0.0	0.5	1.6(2)
O(2)	2(c)	0.5	0.0	0.5	0.5	0.0	0.5	1.5(1)
O(3)	4(h)	0.25	$0.5 + x$	0.5	0.2169(3)	$0.5 + x$	0.5	2.0(1)
O(4)	4(g)	0.375	$0.5 + x$	0.0	0.3757(3)	$0.5 + x$	0.0	1.1(1)
O(5)	8(i)	0.125	0.125	0.0	0.1615(3)	0.0960(3)	0.0	1.57(7)
O(6)	4(g)	0.125	$0.5 + x$	0.0				

exhibits the following parametric relationships with the perovskite:  $a \approx a_p \sqrt{5}$  and  $c \approx a_p$ ; one observes about 11% of oxygen vacancies in the barium perovskite against 17% in the strontium compound. These observations suggest clearly that the oxygen ordering is again responsible for the superstructure in the strontium compound. A neutron diffraction study of the oxide  $\text{La}_{6.4}\text{Sr}_{1.6}\text{Cu}_8\text{O}_{19.84}$  was undertaken in order to determine the distribution of the oxygen vacancies in the structure.

Owing to the absence of extra lines corresponding to  $c = 2a_p$ , this structural study has been carried out in the cell with  $c = a_p$ . The observed condition of reflection  $0kl$ :  $k = 2n$  leads to three possible space groups,  $P4bm$ ,  $P\bar{4}b2$ ,  $P4/mbm$ . To minimize the number of variable parameters the most symmetrical group,  $P4/mbm$ , was chosen. In the range  $10\text{--}150^\circ$  ( $2\theta$ ), 57 diffraction lines were measured. For calculations all the allowed reflections (150  $hkl$ ) were included. The refined cell parameters deduced from the neutron diffraction powder pattern ( $a = 10.8461(8)$ ,  $c = 3.8631(10)$ ) are found to be very close to those calculated from X-ray diffraction (Table I).

The first calculation was carried out with a composition corresponding to a nonoxygen-deficient perovskite, i.e. for " $\text{La}_{6.4}\text{Sr}_{1.6}\text{Cu}_8\text{O}_{24}$ ," with starting positions for the

different atoms corresponding to those they would have in a cubic cell (Table II). Lanthanum and strontium were distributed statistically on equivalent positions; all the thermal parameters were fixed to  $1 (\text{Å}^2)$ . Refinements of the atomic parameters allowed the nuclear  $R$  factor  $R_N$  ( $R$  factor on the integrated intensities) to be lowered from 0.70 to 0.265, but during these refinements Cu(3) and O(6) draw nearer together leading to a Cu(3)–O(6) distance of 1.15 Å. At this point, oxygen vacancies were considered: with regard to the formulation  $\text{La}_{6.4}\text{Sr}_{1.6}\text{Cu}_8\text{O}_{24}$ , about four oxygen atoms are missing which correspond to the number of O(6) oxygen. The occupancy of this oxygen site was then refined. Rapid convergence was obtained with occupancy converging to 0.0 ( $R_N = 0.157$ ). O(6) was therefore removed completely from the structure for the final refinements. Table II lists the final positional and thermal parameters obtained after the final refinement ( $R_N = 0.068$ ,  $R_p = 0.149$ ,  $R_e = 0.060$ ).

Calculations carried out in the supercell  $2a_p \sqrt{2} \times 2a_p \sqrt{2} \times 2a_p$  with the three possible space groups  $P4_2nm$ ,  $P\bar{4}n2$ ,  $P4_2/mnm$  did not allow the  $R$  factors to be lowered. This result is in agreement with the fact that only a small number of crystals exhibit a superstructure along  $c$ .

The projection of the structure onto the

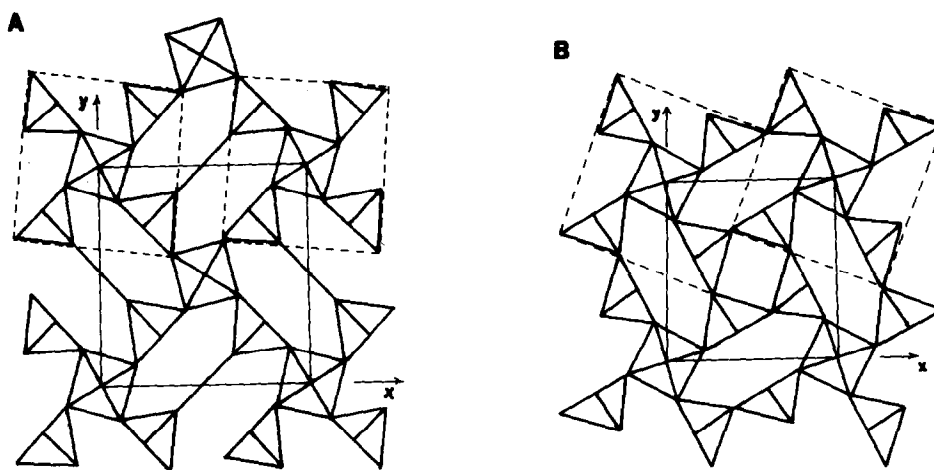


FIG. 1. Projection onto the (001) plane of the framework of the oxygen-deficient perovskite La<sub>6.4</sub>Sr<sub>1.6</sub>Cu<sub>8</sub>O<sub>20</sub> (A) and La<sub>4</sub>BaCu<sub>5</sub>O<sub>13</sub> (B). Some of the [Cu<sub>5</sub>O<sub>22</sub>] groups are surrounded by dotted lines.

(001) plane (Fig. 1A) shows a great similarity with the one of La<sub>4</sub>BaCu<sub>5</sub>O<sub>13+δ</sub> (Fig. 1B): one can recognize in both structures [Cu<sub>5</sub>O<sub>22</sub>] groups of five corner-sharing polyhedra built up from one CuO<sub>6</sub> octahedron and four CuO<sub>5</sub> pyramids, forming hexagonal tunnels running along *c*. However the [Cu<sub>5</sub>O<sub>22</sub>] groups are arranged in a different way in the two structures: they share the corners of their pyramids in BaLa<sub>4</sub>Cu<sub>5</sub>O<sub>13</sub>, whereas they are linked through CuO<sub>4</sub> square planar groups and CuO<sub>6</sub> octahedra in the strontium oxide. It is also worth pointing out that the CuO<sub>4</sub> groups exhibit two perpendicular orientations, parallel to (110) and (1 $\bar{1}$ 0), respectively. Each CuO<sub>5</sub> pyramid is linked to one CuO<sub>4</sub> group, two CuO<sub>6</sub> octahedra, and two CuO<sub>5</sub> pyramids in La<sub>6.4</sub>Sr<sub>1.6</sub>Cu<sub>8</sub>O<sub>20</sub>, whereas it is surrounded by four other pyramids and one octahedron in BaLa<sub>4</sub>Cu<sub>5</sub>O<sub>13</sub>. Consequently the hexagonal tunnels are orientated differently in the two structures: they share only their corners in La<sub>4</sub>BaCu<sub>5</sub>O<sub>13</sub>, whereas they form pairs by sharing one CuO<sub>4</sub> group in La<sub>6.4</sub>Sr<sub>1.6</sub>Cu<sub>8</sub>O<sub>20</sub>. The fact that La<sup>3+</sup> and Sr<sup>2+</sup> ions are randomly distributed over the same crystallographic sites is dictated by

the space group. Attempts to create an ordering between those cations by using less symmetrical space groups did not allow the *R* factor to be lowered. This statistical distribution of the strontium and lanthanum ions is quite in agreement with the similarity of their size as shown for other perovskites like oxides such as La<sub>2-x</sub>Sr<sub>x</sub>CuO<sub>4-x/2+δ</sub> (2) and La<sub>2-x</sub>Sr<sub>1+x</sub>Cu<sub>2</sub>O<sub>6-x/2+δ</sub> (1).

All the calculated *M*-O distances (Table III) are compatible with the ionic radii (20) and are close to those usually observed. The CuO<sub>6</sub> octahedra are compressed along the *c* axis as observed in the perovskite BaLa<sub>4</sub>Cu<sub>5</sub>O<sub>13+δ</sub>; the Cu-O distances are exactly the same in the two compounds. The geometry of the CuO<sub>5</sub> pyramids with four mean Cu-O distances (1.88–1.93 Å) and one longer (2.39 Å) has often been observed in copper square pyramids. With four O-O distances of 2.71 Å and two Cu-O distances of 1.93 Å and two of 1.91 Å, the CuO<sub>4</sub> polyhedron is approximately square planar; the Cu-O distances are close to those observed in the superconductor YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (14) for the same coordination (1.85–1.94 Å).

TABLE III  
 INTERATOMIC DISTANCES

M-O distances (Å)		O-O distances (Å)	
La(Sr)-O <sub>10</sub> polyhedron			
La(Sr)-O(1)	2.602(3) × 1		
La(Sr)-O(2)	2.862(3) × 1		
La(Sr)-O(3)	2.730(4) × 1		
La(Sr)-O(3)	2.747(4) × 1		
La(Sr)-O(4)	2.645(3) × 2		
La(Sr)-O(5)	2.511(3) × 2		
La(Sr)-O'(5)	2.848(3) × 2		
Cu(1)-O <sub>6</sub> octahedron			
Cu(1)-O(1)	1.932(1) × 2	O(1)-O(5)	2.808(3) × 8
Cu(1)-O(5)	2.038(4) × 4	O(5)-O(5)	2.881(5) × 4
Cu(2)-O <sub>4</sub> square planar			
Cu(2)-O(2)	1.932(1) × 2	O(2)-O(4)	2.714(3) × 4
Cu(2)-O(4)	1.906(4) × 2		
Cu(3)-O <sub>5</sub> pyramid			
Cu(3)-O(3)	1.932(1) × 2	O(3)-O(4)	3.109(4) × 2
Cu(3)-O(4)	2.395(4) × 1	O(3)-O(5)	2.682(3) × 4
Cu(3)-O(5)	1.860(4) × 2	O(4)-O(5)	3.333(5) × 2

The oxygen defect  $\varepsilon$ , with respect to the formulation  $\text{La}_{6.4}\text{Sr}_{1.6}\text{Cu}_8\text{O}_{20-\varepsilon}$ , is too low to be refined, even by neutron diffraction; the occupancy factor of all the oxygen sites always tends toward 1.0. These additional oxygen vacancies are probably distributed over the O(1) sites: the creation of oxygen vacancies on those sites lead to the formation of  $\text{CuO}_5$  pyramids, whereas the creation of oxygen vacancies on the other sites would involve an unusual coordination of copper. The doubling of the  $c$  parameter of a minority of crystal suggests that those additional vacancies are ordered along  $c$ .

These results confirm the ability of copper to form various oxygen-deficient perovskites and show that strontium induces a different framework from that obtained for barium. The mixed-valence character of copper is responsible for the electron transport properties of this oxide, which is a metallic conductor (21). However, this compound cannot be a high  $T_c$  supercon-

ductor owing to the three-dimensional character of its frameworks, according to Labbé and Bok's model (22).

### Acknowledgment

The authors thank Dr. M. Hervieu for electron microscopy observations and helpful discussions.

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