JOURNAL OF SOLID STATE CHEMISTRY **80**, 276–285 (1989)

Compounds and Phase Compatibilities in the System La_2O_3–SrO–CuO at 950°C

D. M. DE LEEUW, C. A. H. A. MUTSAERS, G. P. J. GEELEN,
AND C. LANGEREIS

*Philips Research Laboratories, P.O. Box 80000,
5600 JA Eindhoven, The Netherlands*

Received December 5, 1988; in revised form Feburary 28, 1989

The subsolidus phase diagram of the system La_2O_3–SrO–CuO at 950°C under 1 bar of pure oxygen has been investigated and a new ternary compound, $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$ with $0.05 \leq x \leq 0.15$, was isolated. This compound crystallizes in an orthorhombic unit cell with lattice constants related to the lattice constant of the perovskite cubic unit cell, a_p, by $a = 3.80$ Å $\cong a_p$, $b = 11.48$ Å $\cong 3a_p$, and $c = 20.23$ Å $\cong 5a_p$. The structure is isotypical to that of $LnSr_2Cu_2O_{5.5+\delta}$ with Ln = Sm, Eu, or Gd. Reported data on the crystal chemistry of the equilibrium compounds in the system La_2O_3–SrO–CuO have been summarized and compared with the present data. The structure of all compounds is built up of a La–O rock-salt layer separated by a number of $LaCuO_3$ perovskite layers. The general formula is $(La–O)(LaCuO_3)_n$ where La can be replaced either partly or completely by Sr. Compounds are found for n = 1, 2, and ∞. The structures of the compounds show different types of oxygen vacancy ordering.

Introduction

Compounds in the system La_2O_3–SrO–CuO have been extensively studied over the last decade by Raveau (*1*), Müller-Buschbaum (*2*), and their co-workers. Interest in the structure and properties of these cuprates has grown tremendously due to the discovery of superconductivity (*3*) at 30 K in one of them, $La_{2-x}Ba_xCuO_4$ ($x \cong 0.15$) (*4, 5*). Replacement of La by Sr was found to increase the T_c to 40 K (*6, 7*). Considerable efforts have also been devoted to identifying the phases in the system La_2O_3–SrO–CuO, resulting in the recent identification of the binary compounds $La_{n+1}Cu_nO_{3n+1-y}$ with $n > 2$ (*8, 9*) and $Sr_{14}Cu_{24}O_{41}$ (*10, 11*) and the ternary compound $La_{8-x}Sr_xCu_8O_{20-\delta}$ with ($1.28 \leq x \leq 1.92$) (*12*). The last compound was independently reported with $x = 1.33$ (*13*) and with $1.6 \leq x \leq 2.0$ (*14*). Investigations on the phase compatibilities can exclude the existence of other stable ternary compounds. Only a preliminary subsolidus phase diagram has been reported, however (*15*). We investigated the compounds and phase compatibilities in the system La_2O_3–SrO–CuO. The results are presented in this report.

The subsolidus phase diagram was investigated at 950°C. At higher temperatures experiments are complicated due to the presence of cuprooxide-based compounds. At much lower temperatures equilibrium is difficult to obtain due to hampered kinetics in solid-state diffusion reactions.

La–Sr–Cu oxides can exhibit a reversible

0022-4596/89 $3.00

uptake and release of oxygen (*1*). The oxygen content is also fixed by the temperature and atmospheric partial oxygen pressure. We equilibrated the samples under 1 bar of pure oxygen so that in the present study the system La_2O_3–SrO–CuO can be treated as a pseudo-ternary system.

Experimental

La–Sr–Cu oxide powders were prepared by solid-state reaction starting from La_2O_3, CuO, and $Sr(NO_3)_2$ or $Sr(OH)_2 \cdot 8H_2O$. All the compounds discussed below could be prepared at 950°C. However, due to hampered kinetics, firing times of more than a week could be necessary. In order to reach equilibrium some samples were therefore fired at temperatures up to 1150°C. The firing temperature was chosen below the decomposition temperature of the compounds as checked by X-ray diffraction measurements on quenched samples. After firing, the samples were annealed under 1 bar of pure oxygen for 4 hr at 950°C and subsequently cooled to room temperature in about 4 hr. Smaller cooling rates had no influence on the structure of the compounds.

The oxygen contents of samples were obtained from a determination of the oxidizing power (*10*). Although the oxidizing power may be ascribed to a formal valency of Cu above 2+, it is probably due to the presence of O^{1-} (*16, 17*). Phase identification of the samples was carried out with an X-ray diffractometer using Cu$K\alpha$ radiation.

Results and Discussion

First the limiting pseudo-binary systems are discussed. No new pseudo-binary compounds were found. In the ternary system a new compound was isolated, $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$ with $0.05 \leq x \leq 0.15$. The structure was found to be closely related to that of $Ln_{2-x}Sr_{1+x}Cu_2O_{6-\delta}$ with $0.70 \leq x \leq 0.90$ and Ln = Sm, Eu, or Gd (*18*). Reported data and our data on the crystal chemistry of the ternary compounds are summarized below. Finally the phase equilibrium relations in the system La_2O_3–SrO–CuO are presented. The subsolidus phase diagram obtained is discussed within the framework of cuprate compounds as reported by Goodenough and Longo (*19*) and Torrance *et al.* (*9*).

The System La_2O_3–SrO

Investigations of the phase diagram of the system La_2O_3–SrO ly Lopato (*20*) show that the compound $La_4Sr_3O_9$ is formed at 1860°C. This compound was isolated by Schulze and Müller-Buschbaum (*21*) using a CO_2 laser annealing technique, and crystallizes in a monoclinic unit cell, Cc (9), $Z = 4$, with $a = 11.657$ Å, $b = 7.348$ Å, $c = 13.471$ Å, and $\beta = 115.6°$. The metastable compound $La_4Sr_3O_9$ decomposes at 1500°C (*20*) and was also not detected in our investigations on the La_2O_3–SrO–CuO phase diagram at 950°C. The mutual solubility of SrO and La_2O_3 can be neglected at 950°C (*20*).

The System SrO–CuO

In the system SrO–CuO the binary compounds Sr_2CuO_3, $SrCuO_2$, $SrCu_2O_2$ (*2, 22–24*), and $Sr_{14}Cu_{24}O_{41}$ (*11*) have been reported. The compound Sr_2CuO_3 crystallizes in an orthorhombic unit cell, space group *Immm* (71), with $a = 12.68$ Å, $b = 3.91$ Å, and $c = 3.48$ Å (*22*). It has an orthorhombically distorted K_2NiF_4-type structure with ordered oxygen vacancies in the copper oxygen planes which results in copper ions coordinated in infinite $[CuO_3]_n$ chains (*2, 22*). The structure is isotypical to that of Ca_2CuO_3 (*2, 23*) and $Ba_2CuO_{3+\delta}$ (*25*). The oxygen content of Ca_2CuO_3 and Sr_2CuO_3 cannot be increased, while for samples $Ba_2CuO_{3+\delta}$ slowly cooled to room temperature an oxygen content of 3.3 has been measured (*25*).

The compound $SrCuO_2$ crystallizes in an orthorhombic unit cell, space group *Cmcm* (63), with $a = 3.56$ Å, $b = 16.32$ Å, and $c = 3.92$ Å (*23*), and contains square planar configurations of O^{2-} ions around Cu^{2+} ions. The $[CuO_2]_n$ squares are connected to form isolated infinite double zigzag ribbons (*2, 23*).

The compound $SrCu_2O_2$ crystallizes in a tetragonal unit cell, space group $I4_1/amd$ (141), with $a = 5.48$ Å and $c = 9.82$ Å (*24*). It has copper ions with two oxygen neighbors forming infinite zigzag chains. $SrCu_2O_2$ was made by firing reactive SrO and Cu_2O at 700–800°C in Ar. This monovalent copper compound does not exist at 950°C in oxygen of 1 bar and hence was not detected in the present investigations.

In the subsolidus phase diagram of the system Y_2O_3–SrO–CuO a compound with composition close to $Sr_8Cu_{13}O_{22.6}$ has been reported and a list of interplanar spacings, *hkl* indices, and relative intensities as determined from powder X-ray diffraction measurements has been presented (*10*). Recently, the composition was identified as $Sr_{14}Cu_{24}O_{41}$ (*11*). Single-crystal X-ray diffraction investigations showed that the incommensurate structure is built up of layers of $Sr_2Cu_2O_3$ and layers of CuO_2 chains (*11*).

The System La_2O_3–CuO

In the system La_2O_3–CuO the compound $LaCuO_2$ and a homolog series of binary compounds $La_{n+1}Cu_nO_{3n+1-y}$ have been reported. The monovalent copper compound $LaCuO_2$ crystallizes in the rhombohedral $Na(HF_2)$ structure, $R\bar{3}m$ (166), with $a = 6.11$ Å and $\alpha = 36.5°$ (*26*). The copper ions are linearly coordinated by two oxygen ions and the lanthanum ions are octahedrally surrounded by oxygen ions. This monovalent copper compound does not exist at 950°C under 1 bar of pure oxygen and hence was not detected in the present investigations.

The homolog series $La_{n+1}Cu_nO_{3n+1-y}$ can be considered as intergrowing a La–O rock-salt layer with an increasing number of ideal perovskite layers with composition $LaCuO_3$. The unit cell consists of two identical halves related to each other by a translation vector of $\frac{1}{2}(\vec{a} + \vec{b})$. The first member of the homolog series, $n = 1$, is the well-known compound La_2CuO_4. It exhibits an orthorhombically distorted K_2NiF_4-type structure, *Cmca* (64), with $a = 5.363$ Å, $b = 5.409$ Å, and $c = 13.17$ Å (*27, 28*), and contains single sheets of Jahn–Teller distorted octahedra sharing corners in two directions. At temperatures above 530 K La_2CuO_4 transforms into the tetragonal, *I4/mmm*, regular K_2NiF_4 structure (*27*). The compounds for $n = 3$ and $n = 4$, $La_4Cu_3O_{10-y}$ and $La_5Cu_4O_{13-y}$, were first identified in TEM specimens by Davies and Tilley (*8*) and were obtained as nearly single phase materials by Torrance *et al.* (9). The TEM data showed evidence for phases up to $n = 7$ (*8*). The end member of the series, $n = \infty$, $LaCuO_3$, was isolated by Demazeau *et al.* (*29*) and has a rhombohedrically distorted perovskite structure, $R\bar{3}c$ (167), with $a = 5.431$ Å and $\alpha = 60.51°$.

In the homolog series the formal oxidation number of copper increases from 2+ in La_2CuO_4 to 3+ in $LaCuO_3$. At a given temperature the equilibrium oxygen pressure increases with the formal oxidation number and accordingly $LaCuO_3$ can be made only under oxygen pressures of >65 kbar (*29*). At 950°C and under 1 bar of oxygen only the compound La_2CuO_4 was detected. Also, as found by Davies and Tilley, the series $La_{n+1}Cu_nO_{3n+1-y}$ with $n > 1$ appears to be stable up to about 800°C under 1 bar of oxygen (*8*), and hence was not detected in the present investigations. However, as is discussed in the next section, compounds with $n = 2$ and $n = \infty$ can be stabilized at 950°C by partly replacing La by Sr. The re-

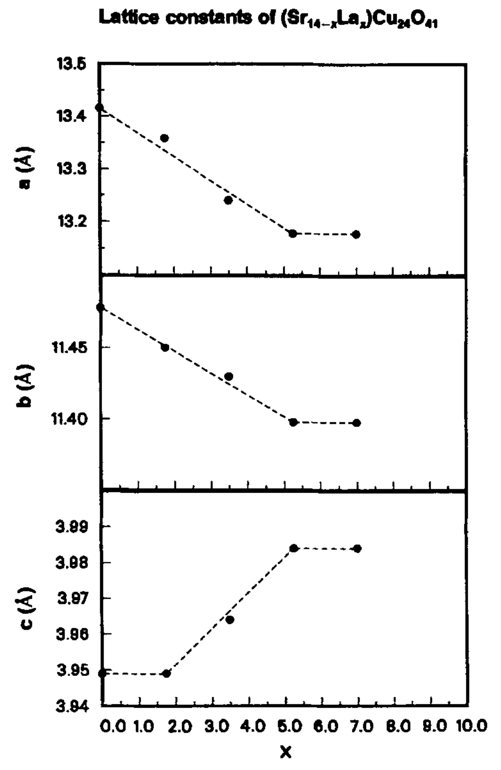

FIG. 1. Lattice constants of the compound $(Sr_{14-x}La_x)Cu_{24}O_{41}$ as a function of the La content, x. After firing, the samples were slowly cooled to room temperature under 1 bar of pure oxygen.

sulting compounds are, for $n = 2$, $La_{2-x}Sr_{1+x}Cu_2O_{6+\delta}$ and $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$, and for $n = \infty$, $La_{8-x}Sr_xCu_8O_{20-\delta}$.

The Ternary System La_2O_3–SrO–CuO

The following ternary compounds are discussed below: $Sr_{14}Cu_{24}O_{41}$ with Sr partly replaced by La, $La_{8-x}Sr_xCu_8O_{20-\delta}$, $La_{2-x}Sr_{1+x}Cu_2O_{6+\delta}$, $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$, and $La_{2-x}Sr_xCuO_{4-\delta}$.

In the compound $Sr_{14}Cu_{24}O_{41}$, Sr can be partially replaced not only by Y (*10*) but also by La. The lattice constants of $(Sr_{14-x}La_x)Cu_{24}O_{41}$ as a function of La content, x, are presented in Fig. 1. The oxygen content was measured to be independent of the La content. Therefore a simple solid solution behavior is expected for the replacement of Sr by La which is confirmed by the almost linear dependence of the lattice constants on the La content. As can be seen from Fig. 1, about 35% of Sr can be replaced by La. At higher La contents the compounds CuO and $La_{8-x}Sr_xCu_8O_{20-\delta}$ with x about 1.9 (*12*) were detected as second phases. Due to the constant oxygen content the formal valency of Cu decreases with increasing La content. The maximum La content of 35% corresponds to $Sr_9La_5Cu_{24}O_{41}$ with a formal copper valency of about 2+.

As expected, the stability increases with the increasing content of La. Above 950°C under an atmosphere of 1 bar O_2 the compound $Sr_{14}Cu_{24}O_{41}$ decomposes into CuO and $SrCuO_2$. However, the decomposition temperature of $(Sr_{14-x}La_x)Cu_{24}O_{41}$ increases with La content up to about 1100°C for $x = 5$.

In the system La_2O_3–SrO–CuO a new oxygen-deficient perovskite-type compound with composition $La_{8-x}Sr_xCu_8O_{20-\delta}$ $(1.28 \leq x \leq 1.92)$ has recently been isolated by Er-Rakho *et al.* (*12*). The compound with $x = 1.33$ has independently been reported by Tokura *et al.* (*13*) and with $1.6 \leq x \leq 2.0$ by Murayama *et al.* (*14*). The compound $La_{8-x}Sr_xCu_8O_{20-\delta}$ has been investigated by neutron diffraction measurements (*12*) and crystallizes in a tetragonal unit cell, *P4/mbm* (127), with $a \cong 2\sqrt{2}\, a_p$ and $c \cong a_p$, where a_p is the lattice constant of the perovskite cubic unit cell. The structure is derived from a hypothetical $LaCuO_3$ perovskite with perfect La–O planes and ordered oxygen vacancies in the formal $[CuO_2]$ planes. The oxygen ordering leading to the superstructures shows great similarity to that of $La_4BaCu_5O_{13.4}$ (*30*). Measurements of the electron transport properties, magnetic susceptibility, and thermoelectric power as a function of temperature (*31*) also indicate similar metallic behavior for both compounds.

The compound $La_{8-x}Sr_xCu_8O_{20-\delta}$, fired at temperatures above 1000°C and subsequently quenched to room temperature, appeared to be decomposed into CuO, $La_{2-x}Sr_xO_{4-\delta}$ and $(Sr_9La_5)Cu_{24}O_{41}$. This low decomposition temperature is typical for a highly oxidized cuprate. Single phase materials to investigate the phase region and equilibrium relations were obtained by annealing the samples at 950°C. In agreement with the results of Murayama *et al.* (*14*) a phase region of $1.6 \leq x \leq 2.0$ was found. Contrary to results of Er-Rakho *et al.* (*12*) and Tokura *et al.* (*13*), single phase compounds with lower Sr contents were not obtained.

The compound $La_{2-x}Sr_{1+x}Cu_2O_{6+\delta}$ with $0 \leq x \leq 0.14$ was isolated by Nguyen *et al.* (*32*) and crystallizes in a tetragonal unit cell, space group *I4/mmm* (139), with $a \cong 3.90$ Å and $c \cong 20$ Å. The structure as obtained from refined X-ray diffraction spectra on samples with $\delta = 0$ is comparable to that of $Sr_3Ti_2O_7$ and consists of two sheets of corner-sharing $[CuO_5]^{8-}$ pyramids separated by La(Sr) layers without oxygen (*32*). The distribution of the La and Sr ions over the (2*a*) and (4*e*) sites is not yet resolved. A neutron diffraction study to determine positions and site occupancies of all constituents of the unit cell of $La_{2-x}Sr_{1+x}Cu_2O_{6+\delta}$ is in progress (*33*). We found a phase region of $0.05 \leq x \leq 0.15$ which is slightly smaller than reported by Nguyen *et al.* (*32*).

Oxygen can be incorporated in the La(Sr) plane sandwiched between the Cu–O_2 sheets (*33*) by annealing in oxygen. The compound $La_2SrCu_2O_{6+\delta}$ fired in air at about 1000°C and subsequently quenched to room temperature is a semiconductor with $\delta = 0$. After annealing for 16 hr at 650°C at 6.5 bar of O_2, δ increases to about 0.2 and a metallic resistivity behavior is observed (*1*).

The compound $Ln_{2-x}Sr_{1+x}Cu_2O_{6+\delta}$ with higher Sr content, viz. $0.70 \leq x \leq 0.90$, has been isolated by Nguyen *et al.* for the lanthanides Sm, Eu, and Gd (*18*). We obtained the corresponding La compound, $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$, by firing at 1050°C and annealing at 950°C under 1 bar of pure oxygen. This compound is obtained at 950°C as well, but the formation is then hampered kinetically. We found that the phase region for $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$ is given by $0.05 \leq x \leq 0.15$. The unit cell of $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$ is orthorhombic with $a = 3.80$ Å $\cong a_p$, $b = 11.48$ Å $\cong 3a_p$, and $c = 20.23$ Å $\cong 5a_p$. For samples $La_{1.1}Sr_{1.9}Cu_2O_{5.5+\delta}$ slowly cooled to room temperature, an oxygen content of 5.8 was determined. A list of interplanar spacings, relative intensities, and *khl* indices of $La_{1.1}Sr_{1.9}Cu_2O_{5.8}$ as determined from X-ray powder diffraction measurements is presented in Table I. The crystal structure was refined in the orthorhombic unit cell, *Immm* (71), $Z = 6$, starting from the atomic parameters $Eu_{1.3}Sr_{1.7}Cu_2O_{5.65}$ (*18*). In the refinement an overall temperature factor of 1.0 Å^2 was used. The atomic positions as obtained from the refinement are presented in Table II. A residue of 9.4% was obtained, which suggests that the crystal structure $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$ is isotypical to that of $Ln_{2-x}Sr_{1+x}Cu_2O_{6+\delta}$ with $0.70 \leq x \leq 0.90$ and Ln = Sm, Eu, or Gd and that the crystal structure of $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$ is derived from that of $La_2SrCu_2O_{6+\delta}$ with additional ordered oxygen vacancies in the basal copper oxygen planes leading to a tripled *b*-axis. A neutron powder diffraction study to determine the atomic positions and site occupancies of all constituents of the unit cell of $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$ with $0.05 \leq x \leq 0.15$ is in progress.

The oxygen content and structure of the solid solution $La_{2-x}Sr_xCuO_{4-\delta}$ was first reported by Nguyen *et al.* (*34*). The compound crystallizes for $0 \leq x \leq 0.10$ in the La_2CuO_4 structure, and for $0.1 \leq x \leq 1.0$ in the tetragonal, *I4/mmm*, regular K_2NiF_4 structure. For samples with $1 \leq x \leq 1.34$ additional superstructures due to oxygen vacancy ordering in the basal plane of the

TABLE I

List of Interplanar Spacings, Relative Intensities, and *hkl* Indices of $La_{1.1}Sr_{1.9}Cu_2O_{5.8}$ as Determined from X-Ray Powder Diffraction Measurements

No.	*d* (Å)	Intensity	*hkl*	No.	*d* (Å)	Intensity	*hkl*
1	10.11	15	0 0 2	60	1.527	1	0 6 8 / 1 1 12
2	5.91	<1	0 1 3	61	1.521	1	2 0 8 / 0 7 5
3	5.75	<1	0 2 0	62	1.513	1	2 2 4
4	5.05	1	0 0 4	63	1.506	1	1 7 0
5	5.00	1	0 2 2	64	1.4897	<1	1 7 2
6	3.82	2	0 1 3	65	1.4712	1	1 6 7
7	3.79	1	0 2 4	66	1.4683	2	2 3 7 / 2 2 8
8	3.76	4	0 3 1	67	1.4613	1	2 5 1
9	3.74	7	1 0 1	68	1.4443	1	0 0 14 / 1 7 4
10	3.61	2	1 1 0	69	1.4407	2	0 3 13 / 1 0 13 / [a]
11	3.40	1	1 1 2	70	1.4359	2	1 4 11 / 0 5 11 / [a]
12	3.373	11	0 0 6	71	1.4300	4	1 3 12 / 2 5 3
13	3.329	1	0 3 3	72	1.3970	1	1 2 13
14	3.312	<1	1 0 3	73	1.3901	4	0 6 10
15	3.133	2	1 2 1	74	1.3868	6	2 0 10
16	2.940	1	1 1 4	75	1.3757	1	2 5 5 / 1 7 6
17	2.908	2	0 2 6	76	1.3585	1	2 3 9 / 1 6 9
18	2.781	83	0 3 5	77	1.3496	5	2 6 0
19	2.773	100	1 0 5	78	1.3416	1	1 1 14 / 1 8 1
20	2.699	93	1 3 0	79	1.3251	1	0 7 9
21	2.608	1	1 3 2	80	1.3219	1	0 8 6
22	2.531	1	0 0 8	81	1.2904	1	0 4 14
23	2.497	5	0 4 4 / 1 2 5	82	1.2719	2	0 3 15 / 1 0 15
24	2.463	1	1 1 6	83	1.2650	1	0 6 12 / 0 0 16
25	2.380	2	1 3 4	84	1.2621	2	2 0 12
26	2.307	7	0 3 7	85	1.2525	2	0 9 3 / 2 6 6 / [a]
27	2.302	10	1 0 7	86	1.2497	2	2 3 11
28	2.282	4	0 5 1	87	1.2403	1	2 7 1
29	2.277	6	1 4 1	88	1.2247	1	0 7 11
30	2.207	3	0 1 9	89	1.2171	1	0 9 5
31	2.186	2	0 4 6	90	1.2099	4	3 0 5 / 1 9 0
32	2.137	1	1 2 7	91	1.2038	3	3 3 0
33	2.107	21	1 3 6	92	1.1904	1	2 6 8
34	2.070	1	1 1 8	93	1.1875	1	2 7 5
35	2.024	16	0 0 10	94	1.1710	<1	3 3 4
36	1.993	2	0 0 5 / 1 4 5	95	1.1620	1	3 0 7
37	1.936	2	0 3 9 / 1 0 9	96	1.1458	1	1 3 16
38	1.913	13	0 6 0	97	1.1386	1	1 9 6
39	1.902	17	2 0 0	98	1.1362	2	0 3 17 / 1 0 17
41	1.879	1	0 6 2	99	1.1339	1	3 3 6
42	1.869	<1	2 0 2 / 2 1 1	100	1.1227	3	2 6 10 / 0 0 18
43	1.845	1	1 3 8	101	1.1157	<1	3 4 5
44	1.834	1	1 2 9 / 1 5 4	102	1.1038	<1	3 5 2
45	1.797	<1	0 5 7 / 1 4 7	103	1.0982	1	1 10 1
46	1.765	1	1 1 10	104	1.0872	1	3 3 8
47	1.704	<1	1 6 1 / 2 1 5	105	1.0846	1	1 8 11 / 3 5 4
48	1.698	3	2 3 1 / 1 5 6	106	1.0733	<1	1 1 18
49	1.686	3	0 0 12	107	1.0681	<1	2 4 17
50	1.664	2	0 6 6	108	1.0603	1	0 1 19
51	1.657	6	2 0 6 / 1 6 3 / [a]	109	1.0575	1	2 3 15 / 1 6 15
52	1.635	1	0 7 1	110	1.0535	1	2 6 12 / 2 0 16
53	1.620	15	1 3 10	111	1.0429	1	1 7 14
54	1.606	2	1 4 9 / 0 5 9	112	1.0384	1	1 9 10
55	1.592	1	2 2 6 / 1 2 11	113	1.0350	1	3 3 10
56	1.585	<1	2 4 0	114	1.0251	1	2 9 5
57	1.575	13	1 6 5	115	1.0229	2	3 6 5
58	1.571	22	2 3 5	116	1.0111	<1	0 0 20
59	1.541	1	0 1 13				

Note. The unit cell is orthorhombic, *Immm* (71), $Z = 6$, with $a = 3.806$ Å, $b = 11.484$ Å, and $c = 20.234$ Å.

[a] Additional indices are possible.

TABLE II

ATOMIC POSITIONS IN THE ORTHORHOMBIC UNIT CELL, *Immm* (71), $Z = 6$, FOR $La_{1.1}Sr_{1.9}Cu_2O_{5.8}$ AS OBTAINED FROM REFINED X-RAY POWDER DIFFRACTION MEASUREMENTS

Atom	Position	x	y	z	Occupancy
La	(2*a*)	0	0	0	1.0
La	(4*g*)	0	0.309(3)	0	1.0
La	(4*i*)	0	0	0.187(4)	0.15
Sr	(4*i*)	0	0	0.187(4)	0.85
Sr	(8*l*)	0	0.324(3)	0.183(2)	1.0
Cu	(4*i*)	0	0	0.590(4)	1.0
Cu	(8*l*)	0	0.342(4)	0.602(2)	1.0
O	(8*l*)	0	0.105(9)	0.397(9)	1.0
O	(8*l*)	0	0.17(4)	0.12(1)	0.35
O	(4*j*)	$\frac{1}{2}$	0	0.11(1)	1.0
O	(4*j*)	$\frac{1}{2}$	0	0.446(10)	1.0
O	(4*i*)	0	0	0.683(11)	1.0
O	(8*l*)	0	0.415(8)	0.729(6)	1.0
O	(4*h*)	0	0.33(3)	$\frac{1}{2}$	1.0

Note. The residue is 9.4%.

octahedra have been identified by both X-ray diffraction and electron microscopy measurements (*34*).

The oxygen content depends on Sr content, temperature, and partial oxygen pressure. Under 1 bar of oxygen the stoichiometry parameter δ is 0 for $0 \leq x \leq 0.2$. At higher Sr content the oxygen content decreases. Oxygen can be incorporated by annealing at temperatures in the range 400 to 600°C under oxygen pressure (*1*). Upon annealing at 600°C under 100 bar the onset Sr content at which oxygen vacancies are formed increases from $x = 0.2$ to about $x = 0.4$ (*35*). This onset can be shifted to much higher Sr content by applying higher oxygen pressures. At 800°C under 3 kbar of O_2 the stoichiometric compound for $x = 1$, $LaSrCuO_4$, could be obtained (*36*).

An indication of the oxygen content can be obtained from X-ray diffraction measurements. For a given Sr content the *c*-axis increases with oxygen content (*1*, *35*).

At a firing temperature of 950°C we obtained single phase compounds for $0 \leq x \leq 0.5$ and for $1 \leq x \leq 1.5$. However, by firing at 1150°C and subsequent annealing at 950°C a complete solid solution was obtained for $0 \leq x \leq 1.5$.

The orthorhombic to tetragonal phase transition temperature decreases with increasing Sr content (*37*, *38*). We found the unit cell to be tetragonal for $x \geq 0.06$. The lattice constants for samples slowly cooled (12°C/hr) to room temperature under 1 bar of O_2 are presented in Fig. 2. The dependence of the lattice constants on the Sr content, x, is comparable to that reported by Nguyen *et al.* (*34*) and Tarascon *et al.* (*6*). The *c*-axis lattice constant decreases at about $x > 0.3$ indicating the onset of oxygen vacancy formation (*35*).

Subsolidus Phase Diagram

The compatibility triangles were determined from X-ray diffraction measure-

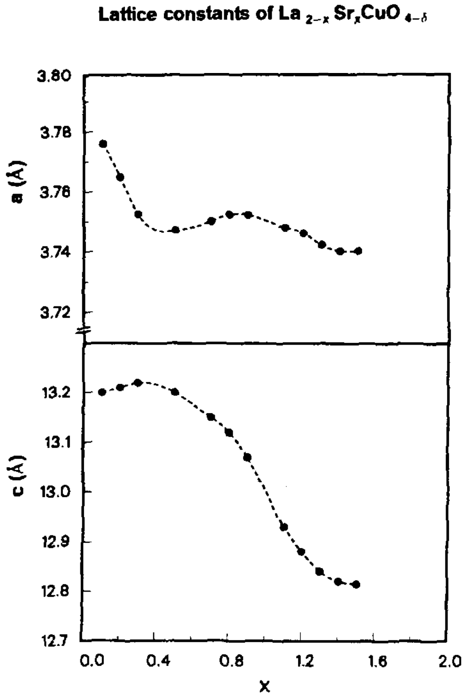

FIG. 2. Lattice constants of the compound $La_{2-x}Sr_xCuO_{4-\delta}$ as a function of the Sr content, x. After firing, the samples were slowly cooled to room temperature under 1 bar of pure oxygen.

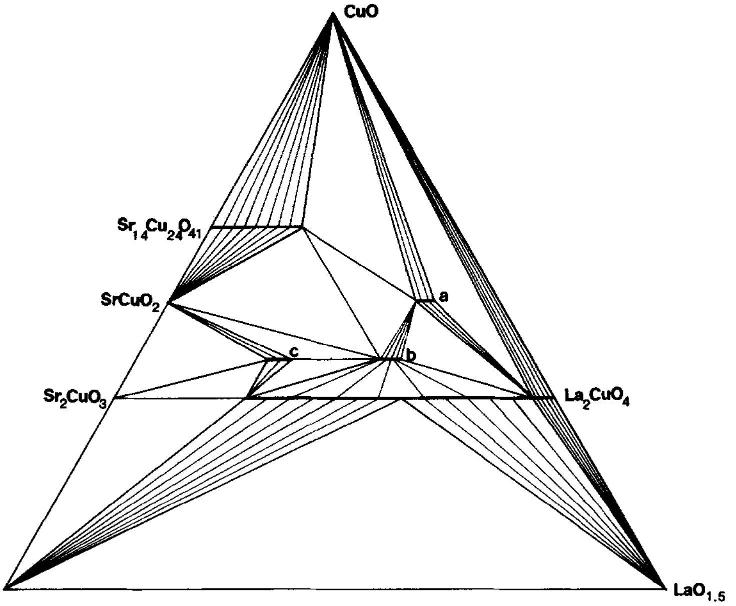

FIG. 3. Subsolidus phase diagram of the system La_2O_3–SrO–CuO at 950°C under 1 bar of oxygen. Solid solutions are indicated by thick lines. The ternary compounds indicated by a, b, and c are $La_{8-x}Sr_xCu_8O_{20-\delta}$ with $1.6 \leq x \leq 2.0$, $La_{2-x}Sr_{1+x}Cu_2O_{6+\delta}$ with $0.05 \leq x \leq 0.15$, and $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$ with $0.05 \leq x \leq 0.15$, respectively.

ments on about 200 samples with different La, Sr, and Cu contents. For each composition the influence of firing times and firing temperatures was investigated. Due to hampered kinetics at 950°C some samples had to be fired for more than a week. In order to reach equilibrium some samples were therefore fired at temperatures up to 1150°C. The phase analyses of all samples resulted in the subsolidus phase diagram of the system La_2O_3–SrO–CuO at 950°C under 1 bar of pure oxygen, which is presented in Fig. 3. In Fig. 3 solid solutions are presented as thick lines and tie lines are indicated by thin lines.

Discussion

The structure of the compounds in the system La_2O_3–SrO–CuO can conveniently be described as a primary structure of the cations and a secondary structure due to the ordering of oxygen anion vacancies (*9, 19*).

Apart from $(Sr,La)_{14}Cu_{24}O_{41}$ the primary structure of the compounds in the system La_2O_3–SrO–CuO consists of a number of ideal $LaCuO_3$ perovskite layers sandwiched between two La–O rock-salt layers. The general formula of the compounds is $(La\text{–}O)(LaCuO_3)_n$ or $La_{n+1}Cu_nO_{3n+1}$, where La can either partly or completely be replaced by Sr. As *n* increases, the rock-salt layer is separated by a larger number of perovskite layers. The unit cell consists of two identical halves related to each other by a translation vector of $\frac{1}{2}(\vec{a} + \vec{b})$.

At 950°C under 1 bar of pure oxygen the compounds $(La,Sr)_2CuO_{4-\delta}$ and Sr_2CuO_3 are obtained for $n = 1$, $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$ with $0.05 \leq x \leq 0.15$, and $La_{2-x}Sr_{1+x}Cu_2O_{6+\delta}$ with $0.05 \leq x \leq 0.15$ for $n = 2$, and $SrCuO_2$ and $La_{8-x}Sr_xCu_8O_{20-\delta}$ for $n = \infty$.

The secondary structure of these compounds is related to the ordering of oxygen vacancies. The formal valency of copper increases from 2+ for $n = 1$ to 3+ for $n = \infty$. At a given temperature the equilibrium partial oxygen pressure increases with increasing formal copper valency. Materials fired under 1 bar partial oxygen pressure then become oxygen deficient. La can be replaced by Sr. To compensate for the charge difference oxygen vacancies are formed. The oxygen vacancies can be randomly distributed but are, however, often ordered. In the absence of oxygen vacancies the copper is coordinated in a Jahn–Teller distorted octahedron, e.g., La_2CuO_4. In the oxygen-deficient compounds the coordination of the copper ions changes into square planar and square pyramidal.

In the $n = 1$ compound $La_{2-x}Sr_xCuO_{4-\delta}$ oxygen vacancies are formed in the basal CuO_2 plane under 1 bar partial oxygen pressure for $x \geq 0.2$. The vacancies are disordered up to about $x = 1$ and give rise to ordered superstructures for $1 \leq x \leq 1.3$. The onset oxygen content at which oxygen vacancies are formed can be shifted to $x = 0.4$ by annealing at 600°C under 100 bar partial oxygen pressure (*35*). The compound with $x = 2$, Sr_2CuO_3, exhibits a fully ordered substructure of isolated infinite $[CuO_3]_n$ chains.

All the $n = 2$ and $n = 3$ compounds exhibit ordered secondary substructures. In the $n = 2$ compound $La_2SrCu_2O_6$ the oxygens are absent from the (La,Sr)O rock-salt layer between the two CuO_2 layers, leading to an empty (La,Sr) layer. Additional vacancies in the CuO_2 planes occur in the compound $La_{1+x}Sr_{2-x}Cu_2O_{5.5+\delta}$, leading to a superstructure indicated by a tripled *b*-axis. In the $n = \infty$ compound $La_{8-x}Sr_x Cu_8O_{20-\delta}$ the occurrence of ordered oxygen vacancies in the CuO_2 basal plane leads to a tetragonal unit cell with $a \cong 2\sqrt{2}a_p$. Vacancy ordering in $SrCuO_2$ leads to a chain structure of double zigzag ribbons.

The degree of oxygen vacancy ordering determines in first approximation the phase region. As can be seen from Fig. 3, compounds with a secondary structure of ordered oxygen vacancies have a limited phase region, while the disordered defect structures exhibit extended phase regions.

In pseudo-binary Sr–Cu oxides with a formal copper valency larger than 2+, Sr can be replaced by La, e.g., $(Sr_{14-x}La_x)Cu_{24}O_{41}$. The maximum content of La corresponds to a formal copper valency of 2+. The oxygen content and hence the formal valence of copper in the compounds $SrCuO_3$ and Sr_2CuO_3 cannot be increased and Sr thus cannot be replaced by La. For samples of the isotypical compound $Ba_2CuO_{3+\delta}$ slowly cooled to room temperature an oxygen content of 3.3 has been measured (*25*). As expected Ba can be replaced by La, and an extended phase region is observed (*39*).

Acknowledgments

Grateful acknowledgment is due to Mr. H. Smoorenburg and Mrs. A. Mouwen-Tijssen for the X-ray diffraction measurements.

References

1. C. Michel and B. Raveau, *Rev. Chim. Miner.* **21,** 407 (1984).

2. H. Müller-Buschbaum, *Angew. Chem.* **89,** 704 (1977).

3. J. G. Bednorz and K. A. Müller, *Z. Phys.* **64,** 189 (1986).

4. J. G. Bednorz, M. Takashige, and K. A. Müller, *Europhys. Lett.* **3,** 379 (1987).

5. H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, *J. Appl. Phys. Japan* **26,** L123 (1987).

6. J. M. Tarascon, L. M. Greene, W. R. McKinnon, G. W. Hull, and T. H. Geballe, *Science* **235,** 1373 (1987).

7. R. J. Cava, R. van Dover, B. Batlogg, and E. A. Rietman, *Phys. Rev. Lett.* **55,** 408 (1987).

8. A. H. Davies and J. D. Tilley, *Nature* (*London*) **326,** 859 (1987).

9. J. B. Torrance, Y. Tokura, and A. Nazzal, *Chemtronics* **2,** 120 (1987).

10. D. M. de Leeuw, C. A. H. A. Mutsaers, G. P. J.

Geelen, H. C. A. Smoorenburg, and C. Langereis, *Physica C* **152,** 508 (1988).

11. E. M. McCarron, M. A. Subramanian, J. C. Calabrese, and R. L. Harlow, *Mater. Res. Bull.* **23,** 1355 (1988).
12. L. Er-Rakho, C. Michel, and B. Raveau, *J. Solid State Chem.* **73,** 514 (1988).
13. Y. Tokura, J. B. Torrance, A. I. Nazal, T. C. Huang, and C. Orttiz, *J. Amer. Chem. Soc.* **109,** 7555 (1987).
14. N. Murayama, S. Sakaguchi, F. Wakai, E. Sudo, A. Tsuzuki, and Y. Torii, *J. Appl. Phys. Japan* **27,** L55 (1988).
15. J. Hahn, T. O. Mason, S. J. Hwu, and R. K. Poeppelmeier, *Chemtronics* **2,** 126 (1987).
16. H. Verweij, *Solid State Commun.* **64,** 1213 (1987).
17. P. Kuyper, G. Kruizinga, J. Ghijsen, M. Grioni, P. J. W. Weis, F. M. F. de Groot, G. A. Sawatsky, H. Verweij, L. F. Feiner, and H. Petersen, *Phys. Rev. B* **38,** 6483 (1988).
18. N. Nguyen, J. Choisnet, and B. Raveau, *Mater. Res. Bull.* **17,** 567 (1982).
19. J. B. Goodenough and J. M. Longo, *in* "Landolt-Bornstein" (K. H. Hellwege, Ed.), Group 3, Vol. 4a, p. 126, Springer-Verlag, New York/Berlin (1970).
20. L. M. Lopato, *Ceramurgia Int.* **2,** 18 (1976).
21. A. R. Schulze and H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **471,** 59 (1980).
22. Chr. L. Teske and H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **371,** 325 (1969).
23. Chr. L. Teske and H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **379,** 234 (1970).
24. Chr. L. Teske and H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **379,** 113 (1970).
25. D. M. de Leeuw, C. A. H. A. Mutsaers, C. Langereis, H. C. A. Smoorenburg, and P. J. Rommers, *Physica C* **152,** 39 (1988).
26. H. Haas and E. Kordes, *Z. Kristallogr.* **129,** 259 (1969).
27. J. M. Longo and P. M. Racah, *J. Solid State Chem.* **6,** 526 (1973).
28. B. Grande, H. Müller-Buschbaum, and M. Swazer, *Z. Anorg. Allg. Chem.* **428,** 120 (1977).
29. G. Demazeau, C. Parent, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **7,** 913 (1972).
30. C. Michel, L. Er-Rakho, and B. Raveau, *Mater. Res. Bull.* **20,** 667 (1985).
31. C. Michel, L. Er-Rakho, and B. Raveau, *J. Phys. Chem. Solids* **49,** 451 (1988).
32. N. Nguyen, L. Er-Rakho, C. Michel, J. Choisnet, and B. Raveau, *Mater. Res. Bull.* **15,** 891 (1980).
33. R. A. Steeman *et al.*, submitted for publication.
34. N. Nguyen, J. Choisnet, M. Hervieu, and B. Raveau, *J. Solid State Chem.* **39,** 120 (1981).
35. J. B. Torrance, Y. Tokura, A. I. Nazzal, A. Bezinge, T. C. Huang, and S. S. P. Parkin, *Phys. Rev. Lett.* **61,** 1127 (1988).
36. J. B. Goodenough, G. Demazeau, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.* **8,** 325 (1973).
37. R. Moret, J. P. Pouget, and G. Collin, *Europhys. Lett.* **4,** 365 (1987).
38. R. M. Fleming, B. Batlogg, R. J. Cava, and E. A. Rietman, *Phys. Rev. B* **35,** 7191 (1987).
39. D. M. de Leeuw, *J. Less Com. Metals,* in press.