

Preparation and Characterization of Members of the System $\text{La}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_{6\pm y}$ where $\text{A} = \text{Ca}, \text{Sr}$

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Members of the system $\text{La}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_{6\pm y}$, where $\text{A} = \text{Ca}, \text{Sr}$, were prepared by decomposition of the nitrates. The tolerance of these compounds for oxygen uptake, as well as the ease of substitution for the A-site ions, is shown to be closely related to the distribution of the alkaline-earth ions on the 8- and 9-coordinated A-sites. © 1989 Academic Press, Inc.

Introduction

In 1978 Shaplygin *et al.* reported on the synthesis of compounds with the composition $(\text{La}, \text{Sr})_2\text{CuO}_4$ (1). Raveau *et al.* in a series of papers (2-4) has reported on the preparation and characterization of the series of compounds with the composition $\text{La}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_{6-x/2+\delta}$, where $\text{A} = \text{Ca}, \text{Sr}$. These compounds represent oxygen defect intergrowths of compounds crystallizing with the $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure. The studies showed that the oxygen content is different for the strontium and corresponding calcium compounds after postpreparation oxygen anneals. It was reported that the values of δ are much higher in the strontium oxides than in the corresponding calcium oxides. These results are correlated with changes in the cell parameters. However, there was no report concerning A-site ion substitutions for lanthanum, strontium, or calcium in these materials. It was the pur-

pose of this study to investigate such substitutions and to correlate oxygen uptake with structural changes.

Experimental

Sample Preparation

The samples were prepared by dissolving stoichiometric amounts of the starting materials in 30 ml of 1:1 nitric acid. The starting materials were copper metal (5-9's, Aesar Chemical Co.), La_2O_3 (4-9's, Aesar Chemical Co.), CaCO_3 and SrCO_3 (reagent grade), Y_2O_3 (4-9's Gallard-Schlesinger) and Nd_2O_3 (Research Chemicals, 99%). The solution was evaporated on a hot plate to dryness, and then placed in a furnace and heated to 500°C for 2 hr in order to decompose the nitrates. The sample was ground and heated to 950°C for 24 hr. Sintered pellets of both $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{6\pm y}$ and $\text{La}_2\text{SrCu}_2\text{O}_{6\pm y}$ were prepared at 1000° and 1050°C, respectively, and air quenched to room temperature. Samples were annealed under

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600 psi O_2 at 500°C for 12 hr. A Cahn thermal balance was used to determine the oxygen content of the samples by reduction with argon : hydrogen (85 : 15) at 1000°C . At this temperature constant weight was achieved and the reduction products were determined by X-ray analysis to be copper metal and a mixture of rare-earth and alkaline-earth oxides.

Characterization of Samples

Powder diffraction patterns were obtained with a Philips diffractometer using monochromatic high intensity $\text{CuK}\alpha_1$ radiation ($\lambda = 1.5405 \text{ \AA}$). For qualitative phase identification, patterns were taken with a scan rate of $1^\circ 2\theta/\text{min}$, while cell parameters were determined from scans taken at $0.25^\circ 2\theta/\text{min}$. Diffraction patterns were obtained over the range $12^\circ < 2\theta < 72^\circ$, and the lattice parameters were determined by a least-squares refinement of the data using a computer program which corrected for the systematic errors in the measurements.

Magnetic susceptibility measurements were made using a Faraday balance (5) from 77 to 300 K with a field strength of 10.4 kOe. At both 77 and 300 K, the field dependence was determined from 6.22 to 10.4 kOe. The van der Pauw method was used to measure the electrical resistivity. Contacts were made by ultrasonically soldering indium directly onto sintered pellets and their ohmic behavior was established by measuring the current-voltage characteristics.

Results and Discussion

Polycrystalline samples of the compound $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{5.97}$ were prepared by decomposition of the nitrates. This phase crystallizes with a tetragonal cell ($a = 3.825(2) \text{ \AA}$ and $c = 19.40(1) \text{ \AA}$). The compound $\text{La}_2\text{CaCu}_2\text{O}_6$ could not be made as a single phase, which is consistent with Raveau's work (2, 3). The oxygen content of the phase was

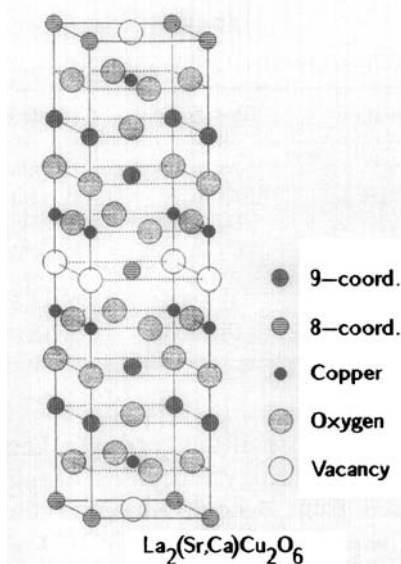


FIG. 1. Structure of $\text{La}_2(\text{Sr,Ca})\text{Cu}_2\text{O}_6$ showing the Cu-O planes surrounding a plane of 8-coordinated sites, and the 9-coordinated sites.

determined by thermogravimetric analysis to be $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{5.97}$. The oxygen defect structure adopted by this compound is shown in Fig. 1. There are copper-oxygen planes separated by 8-coordinated cations and the copper atoms occupy square pyramidal sites. The lanthanum and calcium can occupy two crystallographically different sites. One site is 8-coordinated and lies between the copper-oxygen planes, and the other is 9-coordinated and lies above or below these copper-oxygen planes. In this structure there are twice as many 9-coordinated sites as 8-coordinated sites. According to Raveau (2), the calcium atoms primarily occupy the 8-coordinated sites and the lanthanum atoms primarily occupy the 9-coordinated sites.

The compounds $\text{La}_2\text{SrCu}_2\text{O}_{6+y}$ and $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6+y}$ were prepared by decomposition of the nitrates. Both strontium compositions adopted a tetragonal unit cell with cell parameters of $a = 3.867(2) \text{ \AA}$, $c = 19.91(1) \text{ \AA}$. Hence, the cell parameters of the strontium compounds are significantly

TABLE I
OXYGEN CONTENT OF $\text{La}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_{6\pm y}$

Compound	Preparation	Reference
$\text{La}_2\text{SrCu}_2\text{O}_{6.0}$	As made	Raveau (2)
$\text{La}_2\text{SrCu}_2\text{O}_{6.08}$	As made	Present work
$\text{La}_2\text{SrCu}_2\text{O}_{6.20}$	O ₂ anneal	Raveau (2)
$\text{La}_2\text{SrCu}_2\text{O}_{6.22}$	O ₂ anneal	Present work
$\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{5.97}$	As made	Raveau (2)
$\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6.08}$	As made	Present work
$\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6.21}$	O ₂ anneal	Present work

larger than those of the corresponding calcium phase. The oxygen content of samples prepared from decomposition of the nitrates was found to be $\text{La}_2\text{SrCu}_2\text{O}_{6.08}$ and $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6.08}$ (Table I). Raveau (3) reports the composition of the same strontium phases which were prepared by ceramic techniques, to be $\text{La}_2\text{SrCu}_2\text{O}_{6.0}$ and $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{5.97}$. These compositions correspond to almost all of the copper being in a formal oxidation state of (II). Such results are consistent with the expectation that preparation by decomposition of the nitrates may lead to more oxidized samples than preparation by ceramic methods.

The occupancy of the sites is quite different in the lanthanum strontium system. The 8-coordinated sites are equally occupied by strontium and lanthanum, and the 9-coordinated sites are $\frac{2}{3}$ lanthanum and $\frac{1}{3}$ strontium (2). In this structure, there are vacant anion sites located between the copper-oxygen planes. If additional oxygen did occupy these vacancies, the copper then would occupy octahedral sites instead of square-pyramidal sites. Furthermore, the occupancy of these anion sites would result in 9-coordinated A-site strontium or lanthanum atoms.

The compound $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{5.97}$ was annealed at 500°C under 600 psi O₂ for 24 hr. The oxygen content rose slightly to $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{6.0}$. Therefore, the lanthanum calcium system was only able to stabilize a

small amount of copper(III). In the lanthanum calcium system, the calcium ions prefer to be 8-coordinated. Occupancy of oxygen vacancies would force the calcium to be 9-coordinated. Since the calcium prefers eightfold coordination, it is not surprising that the structure does not incorporate excess oxygen after annealing.

The compounds $\text{La}_2\text{SrCu}_2\text{O}_{6.08}$ and $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6.08}$ were also annealed at 500°C under 600 psi O₂ for 12 hr. There was a significant increase in the oxygen content from $y = 0.08$ to $y = 0.21$ for $\text{La}_{1.9}\text{Sr}_{1.1}\text{Cu}_2\text{O}_{6+y}$. The compound $\text{La}_2\text{SrCu}_2\text{O}_{6+y}$ showed a similar increase in the oxygen content after annealing. Both lanthanum and strontium are known to occupy 8- and 9-coordinated sites (2); hence, it is favorable for this system to incorporate excess oxygen. The incorporation of additional anions results in a corresponding change of Cu(II) to Cu(III).

In an attempt to stabilize larger amounts of copper(III) in the lanthanum calcium system, strontium was substituted for calcium up to the composition $\text{La}_{1.9}\text{Ca}_{0.9}\text{Sr}_{0.2}\text{Cu}_2\text{O}_{6.0}$. The TGA results indicate no detectable change in the oxygen content before and after oxygen anneal. This is not surprising since at these compositions, the calcium still occupies most of the 8-coordinated sites and therefore limits the amount of excess oxygen that can be introduced into the structure.

Substitutions into $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{5.97}$ were made both for lanthanum and calcium. Yttrium and neodymium could be substituted for lanthanum, and barium and strontium were substituted for calcium. There were small changes observed in the cell parameters for the above substitutions (Table II). Neodymium and yttrium are slightly smaller than lanthanum, which is consistent with the decrease in the *c* parameter. Strontium and barium are larger than calcium, and the X-ray data indicate an increase in both *a* and *c* parameters. The lanthanum

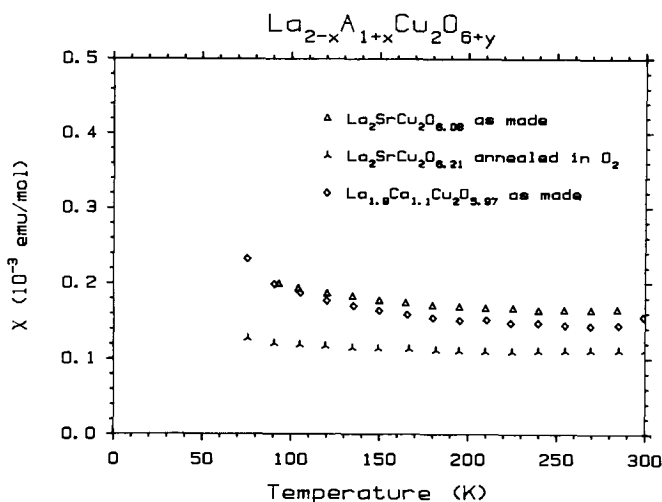


FIG. 2. Temperature dependence of the magnetic susceptibilities of $\text{La}_2\text{SrCu}_2\text{O}_{6+y}$ as made and as annealed in O_2 and of $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{5.97}$.

calcium system is primarily ordered with calcium atoms on the 8-coordinated sites and lanthanum atoms on the 9-coordinated sites (2). The planes of oxygen and 9-coordinated cations consist primarily of La–O–La bonds which appear to allow substitutions to be readily made for lanthanum. In this system it is also possible to substitute strontium and barium for calcium.

When substitutions for lanthanum or strontium are attempted in $\text{La}_2\text{SrCu}_2\text{O}_{6+y}$, the materials are no longer single-phase by X-ray analysis. Additional phases such as La_2CuO_4 are observed to be present in the products. In the lanthanum strontium sys-

tem, both lanthanum and strontium occupy the 8- and 9-coordinated sites. Since strontium is more basic than lanthanum, the La–O–Sr bonds are relatively strong. The

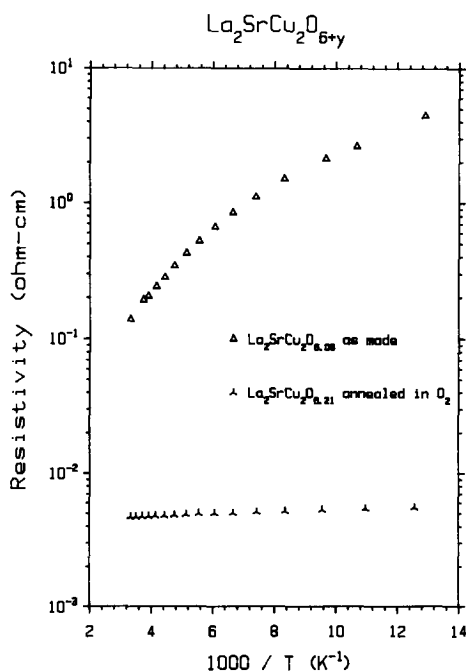


FIG. 3. Temperature dependence of the resistivities of $\text{La}_2\text{SrCu}_2\text{O}_{6+y}$ as made and as annealed in O_2 .

TABLE II

CELL CONSTANTS OF $\text{Ln}_{2-x}\text{A}_{1+x}\text{Cu}_2\text{O}_{6\pm y}$

Sample	a (± 0.002)	c (± 0.01)
$\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{5.97}$	3.825 Å	19.40 Å
$\text{La}_{1.6}\text{Nd}_{0.3}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{6-y}$	3.826 Å	19.36 Å
$\text{La}_{1.7}\text{Y}_{0.2}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{6-y}$	3.826 Å	19.36 Å
$\text{La}_{1.9}\text{Ca}_{1.03}\text{Ba}_{0.07}\text{Cu}_2\text{O}_{6-y}$	3.830 Å	19.48 Å
$\text{La}_{1.9}\text{Ca}_{0.9}\text{Sr}_{0.2}\text{Cu}_2\text{O}_{6-y}$	3.832 Å	19.52 Å

Note. Ln indicates La, Nd, Y. A indicates Ca, Ba, Sr.

strength of this bonding may be an important factor affecting substitutions into this system. All the ions that might be substituted for lanthanum or strontium are less basic and can not form bonds as strong as La-O-Sr bonds. On the other hand, in the lanthanum calcium system there are primarily La-O-La bonds because of the ordering of the lanthanum and calcium atoms. These La-O-La bonds are believed to be weaker than La-O-Sr bonds. Therefore, substitutions can be made more easily in the lanthanum calcium system.

The magnetic susceptibility data are shown in Fig. 2. There are relatively small differences in the magnetic susceptibility among the samples that are shown, with all of them indicating Pauli paramagnetic behavior. The resistivity results of two lanthanum strontium system samples are shown in Fig. 3. There is a significant decrease in the resistivity after annealing at 500°C under 600 psi oxygen. This behavior

is consistent with the formation of additional holes in the π^* band, i.e., increase in concentrations of Cu(III).

Acknowledgments

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