PREPARATION AND CHARACTERIZATION OF MEMBERS OF THE SYSTEM

\[ \text{La}_{2-x}A_{1+x}\text{Cu}_{2}O_{4+y} \] Where A = Ca, Sr

by

K. Doverspike, J-H. Liu, K. Dwight and A. Wold

Prepared for Publication in

JOURNAL OF SOLID STATE CHEMISTRY

May 12, 1989

Brown University
Department of Chemistry
Providence, RI 02912

Reproduction in whole or in part is permitted for
any purpose of the United States Government

This document has been approved for public release and sale;
its distribution is unlimited
Members of the system La$_{2-x}$A$_x$Cu$_{2-y}$O$_6$ where $A = $Ca,Sr were prepared by decomposition of the nitrates. The tolerance of these compounds for oxygen uptake, as well as the substitution for the A-site ions, is shown to be closely related to the distribution of the alkali earth ions on the 8- and 9-coordinated A-sites.
PREPARATION AND CHARACTERIZATION OF MEMBERS OF THE SYSTEM

$La_{2-x}A_{1+x}Cu_2O_{6+y}$ where $A = Ca, Sr$

K. Doverspike, J-H. Liu, K. Dwight and A. Wold+

Department of Chemistry

Brown University, Providence, RI 02912

+Address all correspondence
ABSTRACT

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

In 1978 Shaplygin et al. reported on the synthesis of compounds with the composition (La, Sr)$_2$CuO$_4$ (1). Raveau, in a series of papers (2-4) has reported on the preparation and characterization of the series of compounds with the composition La$_{2-x}$A$_x$Cu$_2$O$_{6-x/2}$ where $A =$ Ca, Sr. These compounds represent oxygen defect intergrowths of compounds crystallizing with the Sr$_3$Ti$_2$O$_7$ structure. The studies showed that the oxygen content is different for the strontium and corresponding calcium compounds after post-preparation oxygen anneals. It was reported that the values of $x$ are much higher in the strontium oxides than for 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 purpose 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 (99.9% Aesar Chemical Co.), La$_2$O$_3$ (4-9% Aesar Chemical Co.), CaCO$_3$ and SrCO$_3$ (reagent grade), Y$_2$O$_3$ (4-9% Gallard & Schlesinger) and Nd$_2$O$_3$ (Research Chemicals 99%). The solution was evaporated on a hot plate to dryness, then placed in a furnace and heated to 500°C for 2 hours in order to decompose the nitrates. The sample was ground and heated to 950°C for 24 hours. Sintered pellets of both La$_{1.9}$Ca$_{1.1}$Cu$_2$O$_{6.2}$ and La$_2$SrCu$_2$O$_{6.2}$ were prepared at 1000°C and 1050°C, respectively, and air quenched to room temperature. Samples were annealed under 600 psi $O_2$ at 500°C for 12 hours. 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 CuKa\(_1\) radiation (\(\lambda = 1.5405\)\(\text{\AA}\)). For qualitative phase identification, patterns were taken with a scan rate of 1°2θ/min, while cell parameters were determined from scans taken at 0.25°2θ/min. Diffraction patterns were obtained over the range 12° < 2θ < 72°, 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 with their ohmic behavior being 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 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 La$_2$SrCu$_2$O$_{6+y}$ and La$_{1.9}$Sr$_{1.1}$Cu$_2$O$_{6+y}$ were prepared by decomposition of the nitrates. Both strontium compositions adopted a tetragonal unit cell with cell parameters of $a = 3.867(2)$Å, $c = 19.91$Å. Hence, the cell parameters of the strontium compounds are significantly larger than those of the corresponding calcium phase. The oxygen content of samples prepared from decomposition of the nitrates was found to be La$_2$SrCu$_2$O$_{6.08}$ and La$_{1.9}$Sr$_{1.1}$Cu$_2$O$_{6.08}$ (Table I). Raveau (3) reports the composition of the same strontium phases, which were prepared by ceramic techniques, to be La$_2$SrCu$_2$O$_{6.0}$ and La$_{1.9}$Sr$_{1.1}$Cu$_2$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 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 $3/4$ lanthanum and $1/4$ 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 now 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 La$_{1.9}$Ca$_{1.1}$Cu$_2$O$_{5.97}$ was annealed at 500°C under 600 psi O$_2$ for 24 hours. The oxygen content rose slightly to La$_{1.9}$Ca$_{1.1}$Cu$_2$O$_{6.0}$. Therefore, the lanthanum calcium system is 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 8-fold coordination, it is not
surprising that the structure does not incorporate excess oxygen after
annealing.

The compounds La$_2$SrCu$_2$O$_{6+y}$ and La$_{1.9}$Sr$_{1.1}$Cu$_2$O$_{6+0.8}$ were also annealed
at 500°C under 600 psi O$_2$ for 12 hours. There was a significant increase in
the oxygen content from $y = 0.08$ to $y = 0.21$ for La$_{1.9}$Sr$_{1.1}$Cu$_2$O$_{6+y}$. The
compound La$_2$SrCu$_2$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
La$_{1.9}$Ca$_{0.9}$Sr$_{2}$Cu$_2$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 La$_{1.9}$Ca$_{1.1}$Cu$_2$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 of both the a and c parameters. The
lanthanum calcium system is primarily ordered with the calcium atoms on the 8-
coordinated sites and lanthanum 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 $\text{La}_2\text{CuO}_4$ are observed to be present in the products. In the lanthanum strontium system, 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 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 samples systems 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 $n^*$ band, i.e., increase in concentrations of Cu(III).

Acknowledgements

This research was supported in part by the Office of Naval Research and by the Eastman Kodak Co. of Rochester, New York.
References


TABLE I
OXGEN CONTENT OF La_{2-x}Sr_{1+x}Cu_{2}O_{6+y}

<table>
<thead>
<tr>
<th>Compound</th>
<th>Preparation</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>La_{2}SrCu_{2}O_{6.0}</td>
<td>as made</td>
<td>Raveau (2)</td>
</tr>
<tr>
<td>La_{2}SrCu_{2}O_{6.08}</td>
<td>as made</td>
<td>present work</td>
</tr>
<tr>
<td>La_{2}SrCu_{2}O_{6.20}</td>
<td>O_2 anneal</td>
<td>Raveau (2)</td>
</tr>
<tr>
<td>La_{2}SrCu_{2}O_{6.22}</td>
<td>O_2 anneal</td>
<td>present work</td>
</tr>
<tr>
<td>La_{1.9}Sr_{1.1}Cu_{2}O_{5.97}</td>
<td>as made</td>
<td>Raveau (2)</td>
</tr>
<tr>
<td>La_{1.9}Sr_{1.1}Cu_{2}O_{6.08}</td>
<td>as made</td>
<td>present work</td>
</tr>
<tr>
<td>La_{1.9}Sr_{1.1}Cu_{2}O_{6.21}</td>
<td>O_2 anneal</td>
<td>present work</td>
</tr>
</tbody>
</table>
TABLE II

CELL CONSTANTS OF Ln$_{2-x}A_1+x$Cu$_2$O$_{6+y}$
Where Ln = La, Nd, Y and A = Ca, Ba, Sr

<table>
<thead>
<tr>
<th>Sample</th>
<th>a (+ .002)</th>
<th>c (+ .01)</th>
</tr>
</thead>
<tbody>
<tr>
<td>La$<em>{1.9}$Ca$</em>{1.1}$Cu$<em>2$O$</em>{5.97}$</td>
<td>3.825 Å</td>
<td>19.40 Å</td>
</tr>
<tr>
<td>La$<em>{1.6}$Nd$</em>{0.3}$Ca$_{1.1}$Cu$<em>2$O$</em>{6-y}$</td>
<td>3.826 Å</td>
<td>19.36 Å</td>
</tr>
<tr>
<td>La$<em>{1.7}$Y$</em>{0.2}$Ca$_{1.1}$Cu$<em>2$O$</em>{6-y}$</td>
<td>3.826 Å</td>
<td>19.36 Å</td>
</tr>
<tr>
<td>La$<em>{1.9}$Ca$</em>{1.03}$Ba$_{0.07}$Cu$<em>2$O$</em>{6-y}$</td>
<td>3.830 Å</td>
<td>19.48 Å</td>
</tr>
<tr>
<td>La$<em>{1.9}$Ca$</em>{0.9}$Sr$_{0.2}$Cu$<em>2$O$</em>{6-y}$</td>
<td>3.832 Å</td>
<td>19.52 Å</td>
</tr>
</tbody>
</table>
Figure Captions

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.

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 $\text{O}_2$ and of $\text{La}_{1.9}\text{Ca}_{1.1}\text{Cu}_2\text{O}_{5.97}$.

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