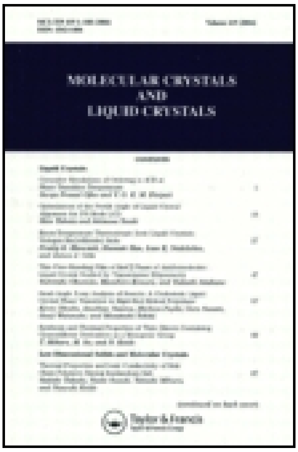

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LaSrCuGaO$_5$: A New Brownmillerite-Related Mixed-Metal Copper Oxide

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$LaSrCuGaO_5$: A New Brownmillerite-Related Mixed-Metal Copper Oxide.

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Abstract A new compound, $La_{1-x}Sr_{1+x}CuGaO_5$ ($0.10<x<0.15$), has been synthesized and characterized by magnetic susceptibility, X-ray diffraction, and resistivity. The powder patterns can be completely indexed on a cell of a=16.557(1), b=5.346(1) and c=5.523(1). Single crystals of the compound were grown from a CuO flux and a preliminary structure determination indicates that the compound is closely related to that of brownmillerite, Ca_2FeAlO_5.

INTRODUCTION

In recent years there has been a large amount of research in the area of mixed metal copper oxides due to the discovery of superconductivity in the La-Ba-Cu-O system by Bednorz and Müller[1]. Without the benefits of a comprehensive theory to predict new superconductors or an established list of properties that superconducting copper oxides should possess, most early work concentrated on the preparation of compounds which were closely related to the K_2NiF_4 structure, a perovskite-rocksalt intergrowth. Since the initial discovery, new superconducting compounds have been discovered in the Y-Ba-Cu-O[2], Bi-Ca-Sr-Cu-O[3], Tl-Ba-Ca-Cu-O[4], and the Pb-Sr-Ln-Cu-O[5] systems. As a group they possess common features such as copper-oxygen planes, a relationship to the perovskite structure, and mixed valency. In addition, some of the compounds, such as $YBa_2Cu_3O_{7-x}$ and $La_{2-x}Sr_xCuO_{4-x/2+\delta}$, exhibit oxygen-nonstoichiometry.

In this paper we describe the synthesis and properties of the new compound $La_{1-x}Sr_{1+x}CuGaO_5$ ($0.10<x<0.15$). The structure of this compound is closely related to that of Ca_2FeAlO_5[6], and incorporates features commonly seen in superconducting copper oxides, such as a close relationship to the perovskite structure, copper-oxygen planes, and mixed valency.

EXPERIMENTAL

Polycrystalline samples of $La_{1-x}Sr_{1+x}CuGaO_5$ where x=0.0, 0.05, 0.10, 0.15, 0.20, 0.25, 0.30, 0.35, and 0.40 were prepared by a solid state reaction of stoichiometric amounts of Aldrich copper oxide (99.999%), lanthanum oxide (99.999%), Johnson Matthey strontium carbonate (99.999%), and gallium oxide (99.999%). Powders were ground with a mortar and pestle and calcined in air at 980°C for 5 days with daily grindings. The compounds are dark black.

Thermogravimetric studies were carried out with a Du Pont Thermal Analysis System in a hydrogen atmosphere to determine the oxygen stoichiometry. Magnetic susceptibility measurements were done on an SHE Corporation VTS-50 susceptometer from 4K to 350K. Resistivity measurements were done on disc-shaped specimens of $La_{0.90}Sr_{1.10}CuGaO_5$ and $La_{0.85}Sr_{1.15}CuGaO_5$, 1.25 cm in diameter and 1.5 mm thick. The pellets were pressed at 15000 psi at room temperature. The disks were cut into rectangular specimens approximately 1.5mm x 3 mm^2 and four leads were attached with silver paint for four probe resistivity measurements from 4K to 300K with an excitation current of 1mA.

X-Ray diffraction (XRD) experiments were carried out on polycrystalline samples. The XRD powder patterns were recorded on a Rigaku diffractometer with nickel filtered Cu Kα radiation . An internal reference of NBS silicon was used in all patterns. Predicted d-spacings were calculated by the program POLSQ[7] based on a least squares fit of the powder pattern peak positions calibrated with the internal Si standard. The experimental peak positions were determined by the program Xray-Fit[8], a routine to least squares fit peaks to a pseudo-Voigt function independently varying the height, width and position of the peak.

Single crystals of the compound were grown from a CuO flux, with the composition $LaSr_4Cu_{10}GaO_x$. Single crystal structure analysis is in progress. Preliminary results indicate that the cell is orthorhombic; a=16.378(1)Å; b=5.330(1)Å; c=5.533(1)Å. The unit cell dimensions, compared to perovskite, are $a = 4\ a_p$, $b = \sqrt{2}a_p$, $c = \sqrt{2}a_p$. These relationships indicate the structure is more closely related to brownmillerite in terms of the ordering of the oxygen vacancies than to $LaSrCuAlO_5$[9]. A comparison of the oxygen vacancy ordering in perovskite, $LaSrCuAlO_5$, and $LaSrCuGaO_5$ is shown in Figure I.

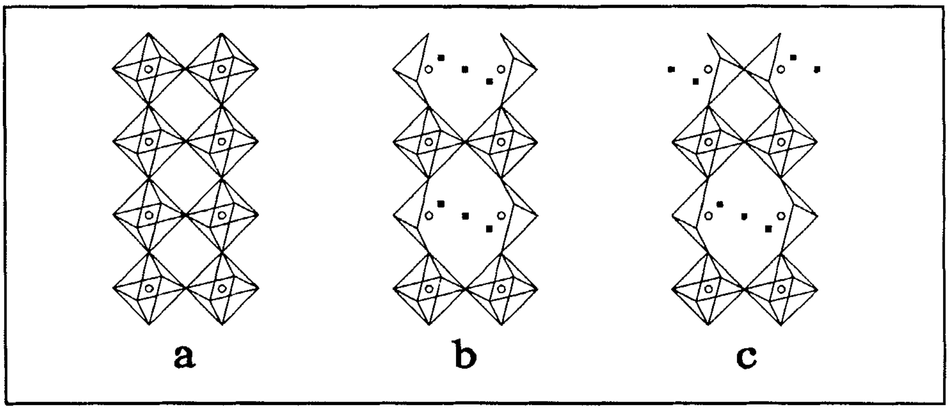

Figure I Idealized polyhedral representation of: a) perovskite, b) $LaSrCuAlO_5$, and c)$LaSrCuGaO_5$.

RESULTS AND DISCUSSION

In a continuation of our study of metallic and semi-conducting copper oxides with covalent metal-oxygen-copper bonds (that started with the synthesis and characterization of $LaSrCuAlO_5$[9]), we have synthesized the new compound $La_{1-x}Sr_{1+x}CuGaO_5$ $(0.10<x<0.15)$. As shown in Figure I, $LaSrCuAlO_5$, a compound structurally related to brownmillerite, exhibits a new arrangement of ordered oxygen vacancies compared to other known systems. The compound is a semiconductor, with a room temperature resistivity of .065Ω-cm.

In contrast, the gallium analogue of that compound, $LaSrCuGaO_5$, cannot be made as a single phase powder of that composition. However when the La/Sr ratio is approximately 0.90/1.10, i.e. $La_{0.90}Sr_{1.10}CuGaO_5$, the compound appears to be a single phase material by powder x-ray diffraction. The range of the solid solution was found to extend to $La_{0.85}Sr_{1.15}CuGaO_5$. The indexed x-ray powder diffraction pattern for $La_{0.90}Sr_{1.10}CuGaO_5$ is shown in table I. The c-lattice constant determined from the single crystals(16.378Å) and from polycrystalline samples (16.557Å) are significantly different. It was found that in Sr-rich mixtures $(x>0.15)$ outside the solid solution range, new phases appear, possibly including $Sr_3Ga_2O_6$,[10] in addition to the phase under study. When the composition was La-rich $(x<0.10)$, outside the solid solution range of the compound, one of the major impurities appears to be $LaSr_2GaO_5$[11].

Table I Indexed powder pattern of $La_{0.90}Sr_{1.10}CuGaO_5$

Orthorhombic Unit Cell: a=16.557Å; b= 5.346Å; c= 5.523Å.

hkl	d_{obs}	d_{calc}	hkl	d_{obs}	d_{calc}
200	8.296	8.278	213	1.702	1.703
101	5.245	5.239	231	1.664	1.662
400	4.137	4.139	802	1.656	1.656
301	3.903	3.903	413	1.606	1.605
011	3.844	3.841	431	1.571	1.569
211	3.486	3.485	1011	1.521	1.520
411	2.814	2.816	232	1.473	1.473
002	2.761	2.762	323	1.464	1.462
020	2.674	2.673	332	1.446	1.445
112	2.428	2.427	1002	1.419	1.420
402	2.296	2.297	822	1.407	1.407
420	2.241	2.245	004	1.379	1.380
321	2.206	2.206	204	1.361	1.362
800	2.068	2.069	040	1.336	1.336
512	1.971	1.971	340	1.298	1.299
602	1.952	1.952	1022	1.254	1.254
222	1.872	1.871	124	1.224	1.223
230	1.744	1.742			

A series of X-ray powder patterns ($28<2\theta<36$) above ($x=0.0$), within ($x=0.10$), and below ($x=0.25$) the solid solution range are shown in Figure II.

Thermogravimetric analysis was done on polycrystalline samples of the compound. The weight loss for $La_{0.85}Sr_{1.15}CuGaO_5$ was 4.03% experimental versus the 4.00% calculated; this corresponds to an oxygen stoichiometry of 5.01(1). The result supports the existence of mixed oxidation states for the copper in this compound.

The resistivity of pressed polycrystalline samples at each end of

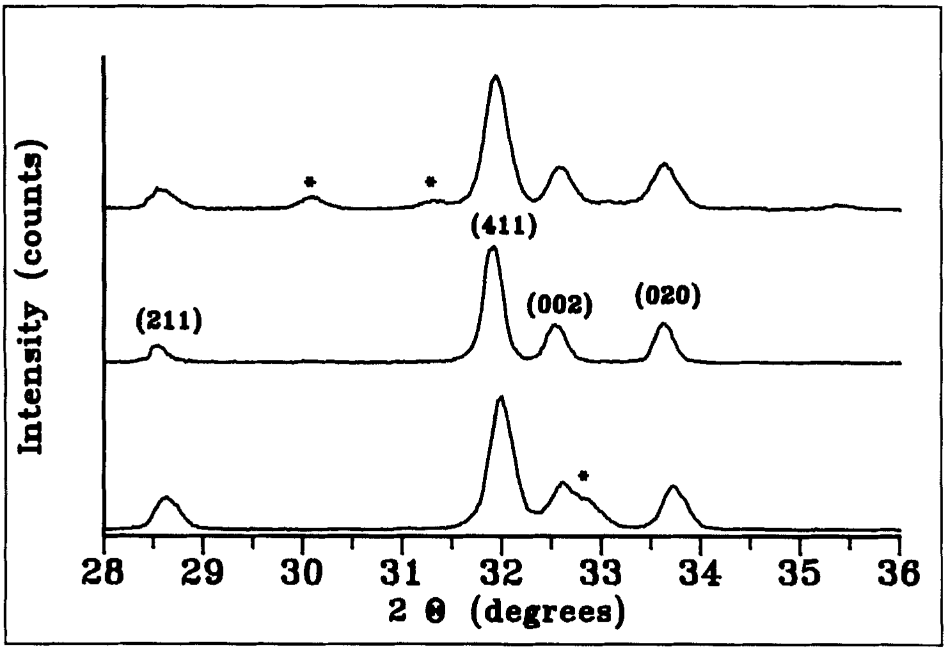

Figure II X-ray powder diffraction patterns of $La_{1-x}Sr_{1+x}CuGaO_5$ for a) x=0.0, b) x=0.10 and c) x=0.25. * = impurity (see text)

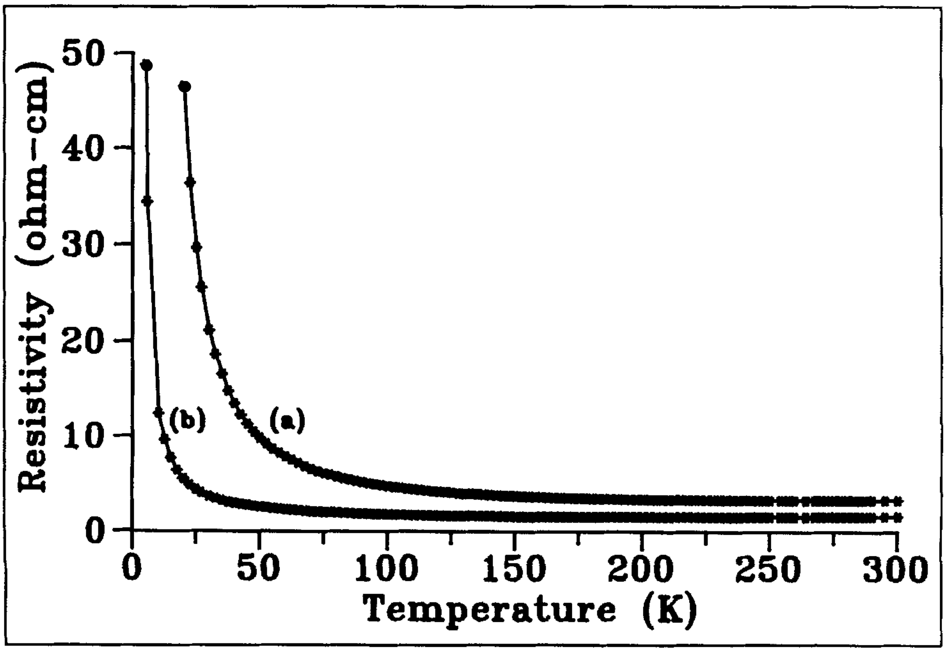

Figure III Resistivity of pressed polycrystalline samples of a) $La_{0.90}Sr_{1.10}CuGaO_5$ and b) $La_{0.85}Sr_{1.05}CuGaO_5$.

the solid solution support the mixed valency of the copper (Figure III). The room temperature resistivities for the two samples $La_{0.90}Sr_{1.10}CuGaO_5$ and $La_{0.85}Sr_{1.15}CuGaO_5$ are 3.23Ω-cm and 1.486Ω-cm respectively. The temperature dependance of the resistivity could be well represented by the form $R = R_0 \exp(T_0/T)^{1/2}$; we will loosely refer to it as an activation energy. This formula has been used to describe the behavior of the resistivity of granular metals, such as nickel embedded in silica[12]. Other models, including Mott's variable range hopping model, where $R \propto \exp(T_0/T)^{1/4}$, did not provide as good a fit to the experimental data. The experimentally determined activation energies were 28 meV and 7 meV, respectively.

The susceptibility of the two compositions ($x=0.10, 0.15$) is shown in Figure IV plotted as χ(emu/g) versus temperature(K). The data can be fit to a Curie-Weiss type law and are summarized in table II. From the table it is evident that the compositions at each end of the solid solution have very similar temperature dependant susceptibilities, and very different temperature independent susceptibilities. The positive values of the temperature independent component of the susceptibility, χ_0,

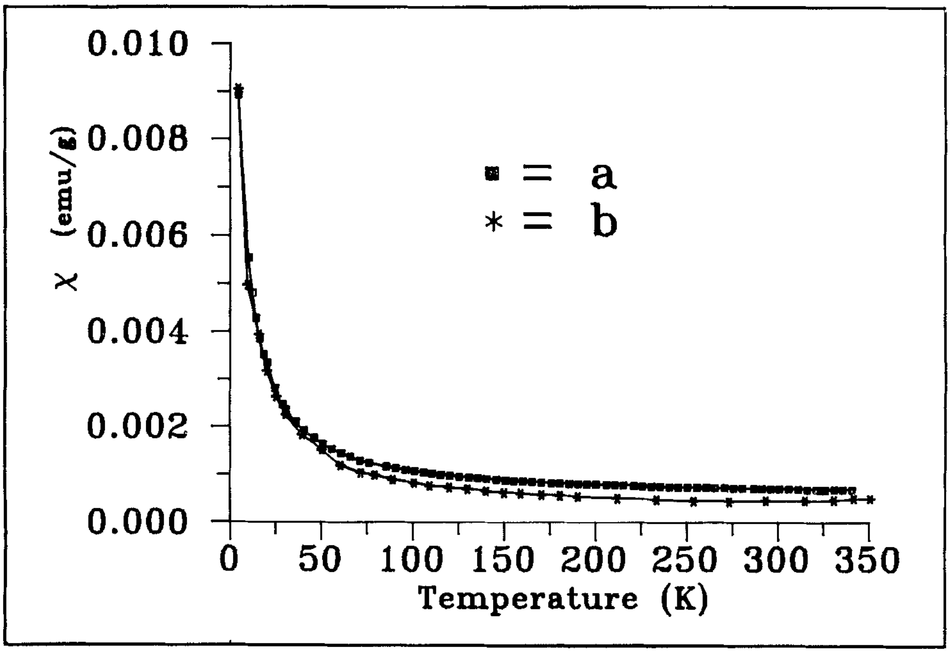

Figure IV Susceptibility of a)$La_{0.90}Sr_{1.10}CuGaO_5$ and b)$La_{0.85}Sr_{1.15}CuGaO_5$.

indicate a dominance of the Pauli paramagnetism (the Van Vleck diamagnetic contribution having a negative sign); the Pauli contribution is proportional to the density of states. In copper oxide systems with copper-oxygen planes the top of the conduction band is an admixture of Cu 3d and O 2p orbitals[13]. Removal of electrons from the Cu 3d - O 2p orbitals by oxidation would result in a decrease in χ_0, as is observed. However, the compounds are not superconducting and remain paramagnetic down to 4K.

TABLE II Magnetic Susceptibility Data for $La_{1-x}Sr_{1+x}CuGaO_5$

	Fit to Eqn: $\chi = \chi_0 + C_0/(T-\theta)$		
x	χ_0 (emu/g)	θ (K)	C_0 (emu-K/g)
0.10	0.000445	-3.17	.06498
0.15	0.000213	-2.84	.06440

CONCLUSIONS

The new solid solution $La_{1-x}Sr_{1+x}CuGaO_5$ (0.10<x<0.15) has been synthesized; The system is related to the compound brownmillerite in the ordering of its oxygen vacancies. The compounds are semiconducting oxides that remain paramagnetic down to 4K. In comparison to known superconducting copper oxides, the compound exhibits the common features of copper-oxygen planes, mixed valency, and a close relationship to the perovskite lattice.

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