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$LaSrCuAlO_5$: A New Oxygen-Deficient Perovskite Structure[1]

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DEDICATED TO PROFESSOR J. M. HONIG ON THE OCCASION OF HIS 65TH BIRTHDAY

A new oxygen-deficient perovskite, $LaSrCuAlO_5$, has been prepared. The compound crystallizes in the orthorhombic crystal system with the space group *Pbcm*. The unit cell dimensions ($Z = 4$) are $a = 7.9219(6)$, $b = 11.020(1)$, and $c = 5.4235(4)$ Å. The compound is a layered copper oxide with a structure related to that of the mineral brownmillerite. Important structural features include buckled copper oxygen planes and nonmagnetic, insulating aluminum–oxygen chains that alternate with the copper oxygen planes along the 7.9-Å axis. Resistivity measurements show that $LaSrCuAlO_5$ is a semiconductor ($\rho_{300\,K} = 0.065\ \Omega$ cm) and magnetic susceptibility measurements demonstrate that the compound is paramagnetic down to 4 K. © 1990 Academic Press, Inc.

Introduction

The oxygen-deficient perovskite-related compounds, $La_{2-x}Sr_xCuO_{4-x/2+\delta}$ ($0 \leq x \leq 1.33$) (*1*), $La_{2-x}Sr_{1+x}Cu_2O_{6-x/2+\delta}$ ($0 \leq x \leq 0.14$) (*2*) and $La_{2-x}Sr_xCu_2O_{5-\delta}$ ($0.32 \leq x \leq 0.48$) (*3, 4*) have been studied extensively over the last several years. Interest in these compounds has stemmed from their structural and redox chemistry, with more recent investigations concentrating on the property of superconductivity found in $La_{2-x}Sr_xCuO_{4-x/2+\delta}$ (*5*). Several studies involving the introduction of a fourth cation, either a transition metal or a large electropositive cation, have been carried out (*6–13*). These substitutional studies have the immediate goal of modifying the properties of the parent compound. In contrast we have found that in the case of aluminum the new oxygen-deficient perovskite-related $LaSrCuAlO_5$ can be prepared. This paper describes the preparation, single crystal X-ray structure determination, and electron diffraction-HRTEM study of this compound.

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[1] See NAPS Document No. 04791 for 5 pages of supplementary materials from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, New York 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid.

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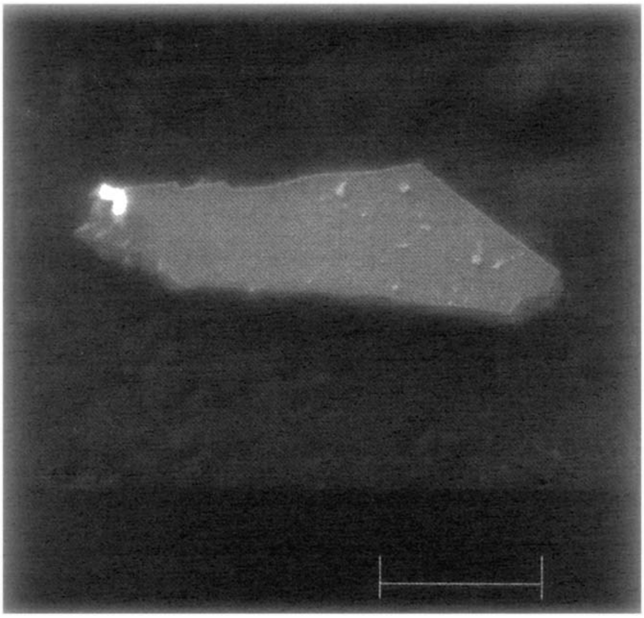

FIG. 1. Scanning electron micrograph of $LaSrCuAlO_5$ single crystal. Magnification, ×260, bar = 0.086 mm.

Experimental

Sample Preparation

Crystal growth. Single crystals of $LaSrCuAlO_5$ were grown from an copper oxide flux. Lanthanum oxide (99.999%, Aldrich), strontium carbonate (99.999%, Aldrich), and cupric oxide (99.999%, Aldrich) in the molar ratio 1 : 2 : 8 (La : Sr : Cu) were mixed thoroughly and placed in an alumina boat (Coors). This mixture was heated in air in a tube furnace at 1000°C for 24 hr, cooled to 930°C at 1°C/hr, and finally cooled to room temperature (ca. 50°C/hr). Isolation of the crystals from the solid flux required that the boat and its contents be broken into smaller pieces. The $LaSrCuAlO_5$ crystals grew as black plates (Fig. 1). The crystals were always found as a minor component when the alumina boat was used as the source of alumina. The greater luster of the CuO could be used to distinguish the $LaSrCuAlO_5$ crystals from the CuO matrix. The major products were CuO and $SrCu_2O_3$. The introduction of Al_2O_3 directly into the melt (La : Sr : Cu : Al molar ratios of 1 : 1 : 1 : 1, 1 : 2 : 4 : 1, 1 : 2 : 8 : 1, and 1 : 2 : 10 : 1) produced, in addition to CuO and $SrCu_2O_3$, the spinel phase $SrAl_2O_4$. The stability range of $SrAl_2O_4$ in the La–Sr–Cu–Al–O system is presently under study.

Crystallographic studies. Crystallographic data are summarized in Table I. Diffraction studies were performed on an Enraf–Nonius CAD4 diffractometer with Mo$K\alpha$ radiation (λ = 0.71069 Å). Lattice parameters, initially established by oscillation and zero-level Weissenberg photographs, were verified by a least-squares technique applied to the setting angle of 25 reflections. Systematic absences of the type: $0kl$: $k = 2n + 1$ and $h0l$: $l = 2n + 1$ indicated the orthorhombic space groups: $Pbc2_1$ (No. 29) and $Pbcm$ (No. 57). The latter was shown to be correct on the basis of the successful structure solution and re-

TABLE I

Summary of Crystallographic Data

Formula	$LaSrCuAlO_5$
Molecular weight	397.05
Crystal size (mm)	0.2 × 0.2 × 0.08
Crystal system	orthorhombic
Space group	*Pbcm* (No. 57)
Lattice parameters (Å)	
a	7.9219(6)
b	11.020(1)
c	5.4235(4)
Volume ($Å^3$)	473.5(1)
Z	4
Calculated density (g/cm^3)	5.57
$\mu(MoK\alpha)$ (cm^{-1})	352.96
Radiation	graphite-monochromated $MoK\alpha$ ($\lambda = 0.71069$ Å)
Temperature (°C)	−20.0
Scan type	$2\theta/\theta$
2θ range (°)	4–60
No. of unique data	864
No. of unique data with $I > 3\sigma(I)$	651
No. of parameters	56
R	0.029
R_w	0.043
Goodness of fit	1.02
Largest peak in final difference map	1.66

finement. The intensities of three standard reflections were measured every 3 hr of X-ray exposure and showed no significant variations. Data were corrected for Lorentz and polarization effects and empirical absorption corrections, obtained from psi scans of seven Bragg reflections, were applied. Subsequently, data were further corrected for absorption by means of the DIFABS program (*14*).

All calculations were carried out on a VAX 11/730 computer with the use of TEXSAN crystallographic software (*15*). The structure was solved by direct methods (*16*). Refinement was performed by a full-matrix least-squares calculation that included in addition to anisotropic thermal parameters a thorough site population analysis. The final values of the discrepancy factors were $R = 0.029$ ($R = [(\Sigma\, ||F_o| - |F_c||)/(\Sigma\, |F_o|)]$) and $R_w = 0.043$ ($R_w = [(\Sigma\, w(|F_o| - ||F_c|)^2)/(\Sigma\, w|F_o|^2)]$, $w = 1/\sigma^2(F)$). The goodness-of-fit was 1.02 and the highest peak in the final difference map (1.7 $e/Å^3$) was not associated with any of the atoms of the structure. The atomic scattering factors were those tabulated by Cromer and Waber (*17*) and corrections for anomalous dispersion were from Cromer and Ibers (*18*).

Polycrystalline samples. Lanthanum oxide (99.999%), strontium carbonate (99.999%), cupric oxide (99.999%), and boehmite ($Al_2O_3 \cdot xH_2O$, $x = 0.54$ as determined from thermogravimetric analysis) were used in the synthesis of polycrystalline samples. Samples were thoroughly mixed, pressed into pellets, and calcined in air at 1000°C for 4 to 6 days with frequent grindings.

Scanning electron microscopy (*SEM*)

and energy dispersive X-ray analysis (*EDAX*). A Hitachi S-570 SEM was used to image crystals. This instrument was equipped with a Tracor Northern energy dispersive X-ray spectrometer. EDAX initially established the presence of the four cations, La, Sr, Cu, and Al, in the single crystals. The Tracor Northern computer program SQ was used without standards to analyze the X-ray emission spectra. Though this program provides appropriate values for ZAF corrections, to obtain a reasonable analysis, it is still necessary to determine the angle between the plane of the sample and the emitted X-ray photons that reach the detector. This angle can be obtained from geometric considerations if the face of the crystal under analysis lies parallel to the plane of the sample holder. The determination of this angle becomes difficult, however, when the crystal is irregularly shaped or cannot be easily mounted in the desired orientation. The take-off angle was varied until the atomic percentage of strontium calculated from the *K* and *L* emission lines of strontium were equivalent. Based on this method, approximate cation ratio (La : Sr : Cu : Al) was found to be 1.0 : 1.0 : 1.0 : 1.2. The large correction for absorption in the ZAF calculation for energies less than 1 keV still limits; however, the accuracy of the aluminum determination where the corrections applied varied from only ~0.2% for the strontium *K* line to ~200% for the aluminum *K* line.

High resolution transmission electron microscope (HRTEM) images and selected area electron diffraction patterns (SADP)

TABLE II

REFINED POSITIONAL AND THERMAL PARAMETERS FOR $LaSrCuAlO_5$

Atom	Site	Population	x	y	z
La(1)	4*d*	0.57(1)	0.19497(5)	0.13578(3)	0.2500
Sr(2)	4*d*	0.61(1)	−0.25266(6)	0.09786(4)	0.2500
La(2)	4*d*	0.39(1)	−0.25266(6)	0.09786(4)	0.2500
Sr(1)	4*d*	0.43(1)	0.19497(5)	0.13578(3)	0.2500
Cu	4*d*	1.0	−0.0234(1)	0.12623(6)	−0.2500
Al	4*d*	1.0	0.5014(3)	0.1573(2)	−0.2500
O(1)	4*a*	1.0	0.0000	0.0000	0.0000
O(2)	4*c*	1.0	−0.0429(5)	0.2500	0.5000
O(3)	4*d*	1.0	0.2823(6)	0.1375(4)	−0.2500
O(4)	4*c*	1.0	−0.454(6)	0.2500	0.5000
O(5)	4*d*	1.0	0.372(1)	−0.0317(6)	0.2500

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
La(1)	0.0088(3)	0.0085(3)	0.0081(3)	0.0003(1)	0	0
Sr(2)	0.0136(4)	0.0126(3)	0.0140(3)	0.0040(2)	0	0
La(2)	0.0136(4)	0.0126(3)	0.0140(3)	0.0040(2)	0	0
Sr(1)	0.0088(3)	0.0085(3)	0.0081(3)	0.0003(1)	0	0
Cu	0.0107(5)	0.0080(4)	0.0051(3)	0.0007(2)	0	0
Al	0.0049(7)	0.0109(8)	0.0078(8)	0.0009(6)	0	0
O(1)	0.014(2)	0.010(2)	0.010(2)	0.005(1)	−0.001(2)	0.001(1)
O(2)	0.017(2)	0.013(2)	0.009(2)	0	0	0.004(1)
O(3)	0.011(2)	0.015(2)	0.020(3)	0.001(2)	0	0
O(4)	0.015(2)	0.022(2)	0.011(2)	0	0	0.008(1)
O(5)	0.043(4)	0.028(3)	0.067(5)	0.022(3)	0	0

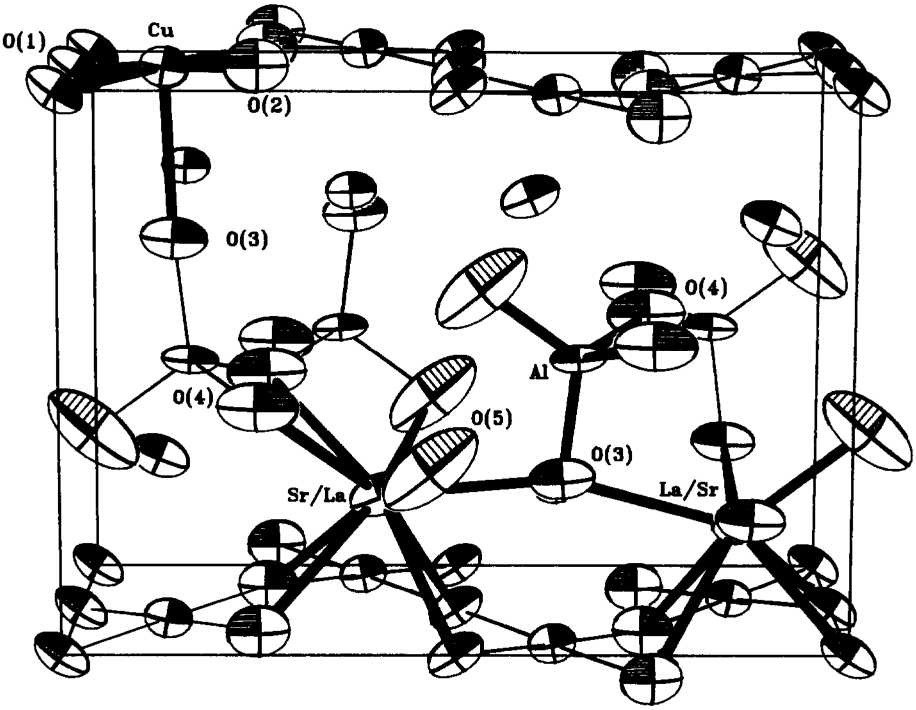

FIG. 2. Structure of $LaSrCuAlO_5$.

were obtained from the polycrystalline sample using a JEOL 200 CX. The microscope was fitted with a high-resolution top-entry goniometer stage (C_s = 1.2 mm) and operated at 200 kV. Samples were prepared by the usual method of crushing a small quantity of the material in an agate mortar under ethanol and placing the suspension onto a holey carbon-covered grid. Additionally, gold-sputtered grids were used in order to obtain diffraction patterns calibrated by using the gold (111) and (200) diffraction rings.

Results

The final positional and thermal parameters are listed in Table II. Selected interatomic bond distances and bond angles are shown in Table III. The structure of LaSr $CuAlO_5$ is shown in Fig. 2.

$LaSrCuAlO_5$ has a perovskite-related structure. If this compound were a true perovskite, ABO_3 ($\equiv A_2B_2O_6$), $BO_{6/2}$ octahedra of copper and aluminum would corner-share to form alternating copper oxygen and aluminum oxygen planes parallel to the *b,c*-plane. The lower oxygen content ($A_2B_2O_5$), however, results in significant structural changes relative to $A_2B_2O_6$. The greatest differences are seen in the Al–O layer. Here the absence of rows of oxygens along the [001] completely disrupts the planarity of this layer and leads to tetrahedrally coordinated aluminum in pyroxene-like aluminum oxygen chains. The Al–O tetrahedra are slightly distorted with bond distances and angles (Table III) comparable to those reported for aluminum in analogous environments (*19*). Compared with bond distances predicted from the effective ionic radii of Shannon (*20*), the combination of tetrahedral aluminum (0.39 Å) and O^{2-} in either

TABLE III

SOME INTERATOMIC DISTANCES AND BOND ANGLES

Interatomic distances (Å)			
$A(1)^a$–O(1)(×2)	2.5422(4)	$A(2)^a$–O(1)(×2)	2.6472(4)
A(1)–O(2)(×2)	2.641(3)	A(2)–O(2)(×2)	2.722(3)
A(1)–O(3a)(×1)	2.592(4)	A(2)–O(3)(×1)	2.604(4)
A(1)–O(3b)(×2)	2.799(1)	A(2)–O(4)(×2)	2.642(3)
A(1)–O(5)(×1)	2.320(6)	A(2)–O(5)(×2)	2.964(3)
Cu–O(1)(×2)	1.9513(5)	Al–O(3)(×1)	1.749(5)
Cu–O(2)(×2)	1.9294(6)	Al–O(4)(×2)	1.749(2)
Cu–O(3)(×2)	2.425(5)	Al–O(5)(×1)	1.708(6)
Cu–O(5)(×1)	2.954(8)		
Cu–Cu	3.8465(9)	Al–Al	3.395(2)
	3.903(1)		3.570(5)

Selected bond angles (°)	
O(1*a*)–Cu–O(1*b*)	88.03(3)
O(2*a*)–Cu–O(2*b*)	89.29(3)
O(1*a*)–Cu–O(2*a*)	91.33(1)
O(1)–Cu–O(3)	86.68(8)
O(2)–Cu–O(3)	92.5(1)
O(3)–Cu–O(5)	162.3(2)
Cu–O(3)–Al	175.8(2)
O(3)–Al–O(4)	108.2(2)
O(3)–Al–O(5)	118.7(3)
O(4)–Al–O(4)	101.7(1)
O(4)–Al–O(5)	109.4(2)

[a] A(1) is the lanthanum-rich site and A(2) is the strontium-rich site.

fourfold (1.38 Å) or sixfold coordination (1.40 Å) predicts slightly longer bond distances than are found in this compound.

The copper environment is also different from that found in the perovskite structure. Instead of octahedra, the Cu–O polyhedra are best described as square pyramids. In the square plane the copper–oxygen bonds average 1.94 Å, while the apical O(3) oxygen distance is elongated in a Jahn–Teller fashion characteristic of d^9 copper, e.g., Cu–O(3) : 2.425(5) Å. The next nearest oxygen (O(5)), the oxygen that would complete a Cu–O octahedron, is 2.954(8) Å away and is considered beyond the coordination sphere of copper. The Cu–O bond distances of the square pyramid are similar to those reported for other mixed metal copper oxides (e.g., $YBa_2Cu_3O_7$) (*21*). The copper itself does not deviate out of the Cu–O square plane. The Cu–O planes, formed by the corner-shared square pyramids, are buckled along the [010] after every other square planar unit. The angle formed by O(1)–O(2)–O(1) is 166.0(1)°.

The Al–O tetrahedra are connected to the Cu–O square pyramids through the apical oxygen O(3). The extended structure contains chains of corner-shared AlO_4 tetrahedra parallel to the *c*-axis which follow the depressions created by the buckling of the Cu–O planes.

The *A*-cations, lanthanum and strontium, are nonstatistically distributed over two sites. Ordinarily the coordination of the *A*-cation is 12 and is designated 4 + 4 + 4. The middle number corresponds to the four bonds from the $AO_{4/4}$ layer and the first and last numbers represent the other eight bonds from the $BO_{4/2}$ layers above and below the $AO_{4/4}$ layer. One site, *A*(1), is eight coordinate (1 + 3 + 4) similar to a square antiprism. The other site, *A*(2), is nine coordinate (2 + 3 + 4) and relatively distorted. Bond distances to oxygen are listed in Table III. The larger strontium

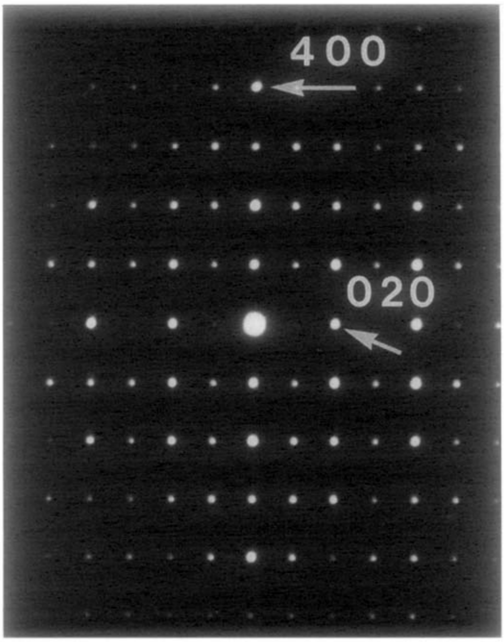

FIG. 3A.

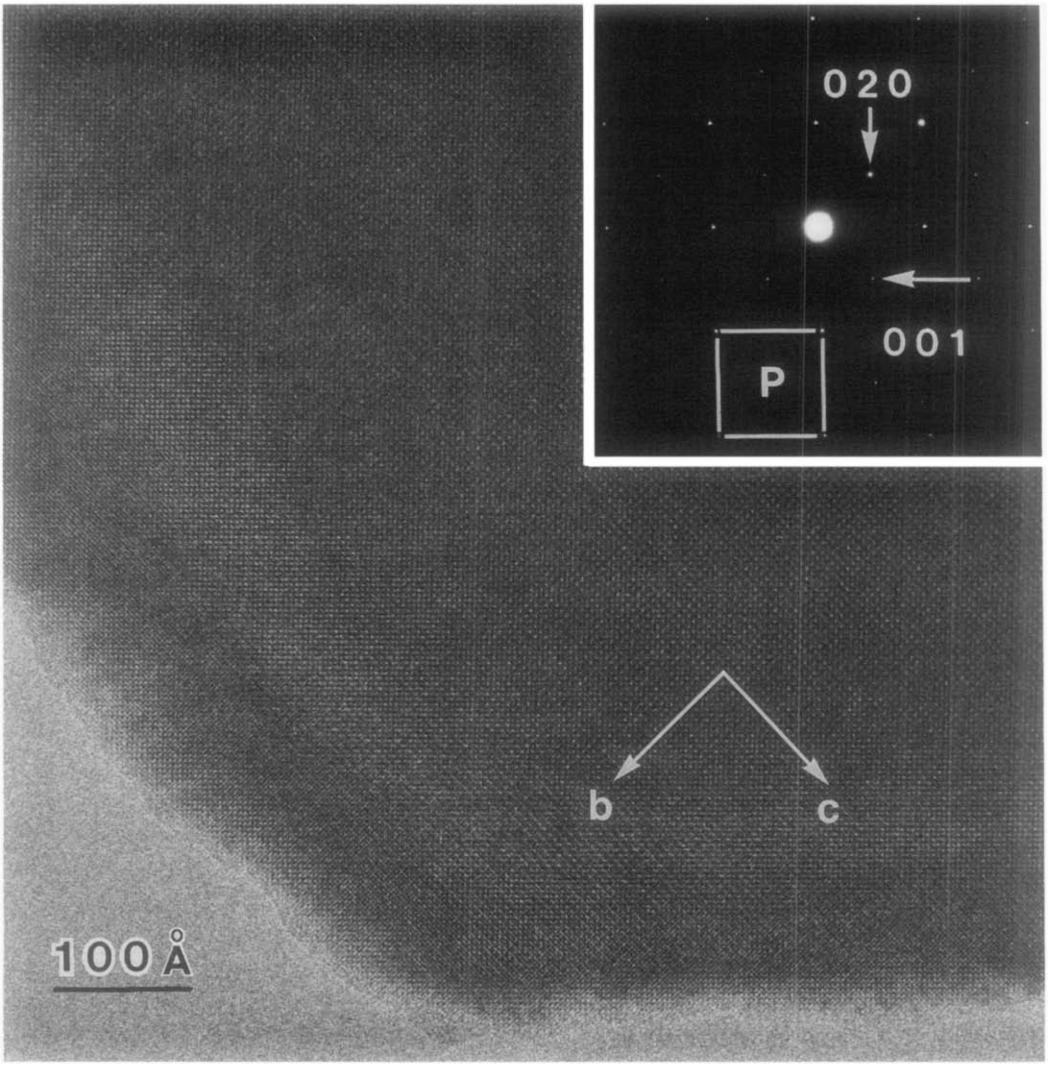

FIG. 3. (a) Selected area electron diffraction pattern of the [001] zone of $LaSrCuAlO_5$. The intensity distribution of the reflections indicate possible twinning and/or cation A-site ordering. (b) High resolution electron micrograph and corresponding electron diffraction pattern of the [100] zone of $LaSrCuAlO_5$ illustrating perfect ordering in this zone.

(*20*) has a preference for the more highly coordinated site. The refined population ratios of lanthanum to strontium (La : Sr) are 57(1) : 43(1) for the $A(1)$ site and 39(1) : 61(1) for the $A(2)$ site. The values are consistent with an overall La : Sr ratio of approximately 1 : 1. The La : Sr ratio and the ordering of La^{3+} and Sr^{2+} on the two sites as a function of composition and preparation temperature would have considerable influence on the properties of $La_{1-x}Sr_{1+x}CuAlO_5$ and is under study.

The thermal parameters of all the oxygens are unexceptional except for O(5) (See Table II). Although it was unlikely that aluminum would be less than four

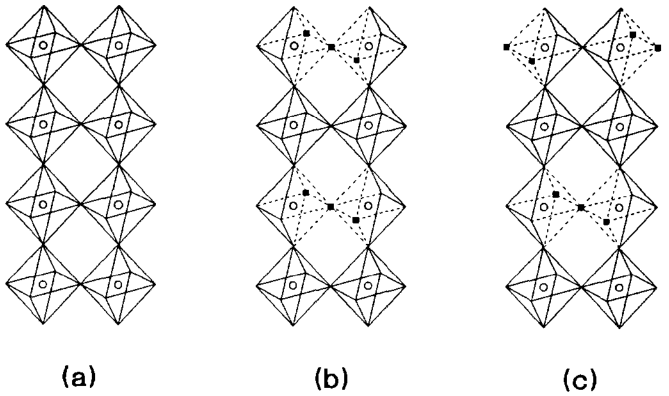

FIG. 4. Comparison of the defect structures of $LaSrCuAlO_5$ and $Ca_2Fe_2O_5$: (a) corner-shared octahedra of fully oxidized perovskite, (b) idealized polyhedral representation of $LaSrCuAlO_5$, and (c) idealized polyhedral representation of $Ca_2Fe_2O_5$. (A-cations not shown for clarity, B-cations represented by open circles, vacancies represented by filled squares, and oxygen lie at the vertices.) Vacancies in $LaSrCuAlO_5$ are aligned between every tetrahedral layer, while in $Ca_2Fe_2O_5$ they are staggered and repeat every other tetrahedral layer.

coordinate the occupation parameter of the O(5)site was made a variable in the refinement, but it remained at unity. The probable origin of the slightly larger thermal parameter of the O(5) site is its coordination. It forms only one bond to Al at 1.708(6) Å, another to A(1) at 2.320(6) Å, and two long bonds to A(2) at 2.964(3) Å. All other oxygen atoms form four or more metal–oxygen bonds shorter than 2.8 Å.

A HRTEM image and corresponding electron diffraction pattern for the [100] zone of $LaSrCuAlO_5$ is shown in Fig. 3. The crystals appear to have few structural defects and the same unit cell dimensions determined from X-ray diffraction were observed by electron diffraction from the [001] and [100] zones. Intensites of reflections from the [001] zone indicate possible twinning or cation ordering. This is under further study.

Discussion and Conclusions

The structure of $LaSrCuAlO_5$ is closely related to $Ca_2Fe_2O_5$ and Ca_2FeAlO_5 (brownmillerite) (*22—24*). Figure 4 compares the B–O polyhedra of $Ca_2Fe_2O_5$ with those of an idealized representation (i.e., Cu with octahedral coordination) of $LaSrCuAlO_5$. The ordering of oxygen vacancies can be clearly seen from this figure. In $Ca_2Fe_2O_5$, Fe is tetrahedrally coordinated in every other B–O layer. The rows of oxygen vacancies are staggered and repeat in every other tetrahedral layer. This leads to a quadrupling of the b-axis relative to that of an ideal cubic perovskite, a_c ($a_c \approx 4$ Å). In $LaSrCuAlO_5$, the rows of vacancies are aligned in every Al tetrahedral layer and therefore the a-axis is only doubled relative to a_c. Table IV compares the lattice parameters of both $Ca_2Fe_2O_5$ and $LaSrCuAlO_5$ to those of an ideal perovskite. In $Ca_2Fe_2O_5$, the A-cation is located on one site, not two as in $LaSrCuAlO_5$.

The planarity of the copper oxygen sheets in different perovskite-related compounds is varied. Often the planes are flat (Fig. 5a). This feature is found in Nd_2CuO_4 with its square planar copper (*25*) and in $Tl_2Ba_2Ca_nCu_{n+1}O_{6+2n}$ (n = 0, 1, 2) and $La_{2-x}Sr_xCuO_4$ where copper is octahedrally coordinated (*26*). In $YBa_2Cu_3O_{7-x}$, the planes are puck-

TABLE IV

COMPARISON OF $LaSrCuAlO_5$ AND $Ca_2Fe_2O_5$ LATTICE PARAMETERS

$LaSrCuAlO_5$	$Ca_2Fe_2O_5$
a_{Cu} = 7.9219(6) Å	a_{Fe} = 5.64 Å
$\simeq 2a_c$ ($\simeq b_{Fe}/2$)	$\simeq \sqrt{2}a_c$
b_{Cu} = 11.020(1) Å	$b_{Fe} \times$ 14.68 Å
$\simeq 2\sqrt{a_c}$	$\simeq 4a_c$
c_{Cu} = 5.4235(4) Å	c_{Fe} = 5.39 Å
$\simeq \sqrt{2}a_c$	$\simeq \sqrt{2}a_c$

ered with the square pyramidally coordinated copper sitting above the oxygen square plane (Fig. 5b) (*5*). One compound that contains buckled planes is La_2CuO_4 (*27*) which adopts the K_2NiF_4 structure. Corner-sharing of octahedra does not occur above and below the Cu–O plane. This allows a flexibility in the planes not generally available to ABO_3 perovskites and buckling occurs after every square planar unit (Fig. 5c).

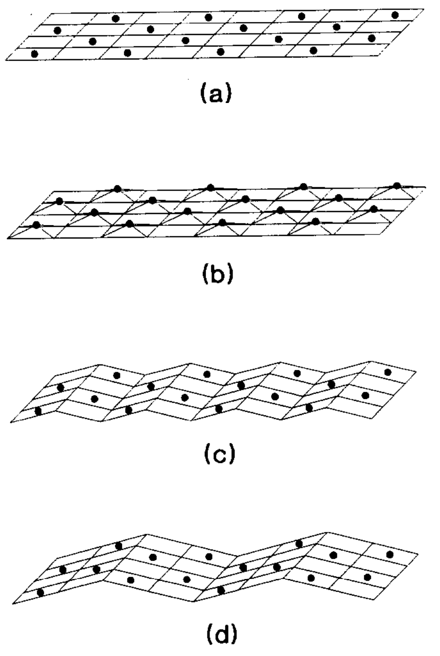

FIG. 5. Comparison of known copper oxide planes formed from corner-shared structural units: (a) flat planes of Nd_2CuO_4, $Tl_2Ba_2Ca_nCu_{n+1}O_{6+2n}$, and $La_{2-x}Sr_xCuO_4$, (b) puckered planes of $YBa_2Cu_3O_{7-x}$ with copper lying above the oxygen plane, (c) buckled planes found in La_2CuO_4, and (d) buckled planes in $LaSrCuAlO_5$.

Buckling also occurs in the Cu–O planes of $LaSrCuAlO_5$. Here directional changes are observed after every other square planar unit (Fig. 5d). It would appear that the combination of coordination environments prefered by Cu^{2+} and Al^{3+} is primarily responsible for this phenomenon. Consider the structure of brownmillerite (Ca_2FeAlO_5). The general preference of both Fe^{3+} and Al^{3+} for octahedral and tetrahedral coordination is also found in this compound. Octahedra and distorted tetrahedra corner-share (Fig. 4c) and as with normal perovskites, this extended corner sharing necessarily limits the flexibility of the B–O planes. The replacement of iron by a cation with a preference for square pyramidal coordination, such as copper, would in effect release one of the apical oxygens and allow the tetrahedra to form a more ideal configuration. Additionally, the removal of the extended connectivity enjoyed by the polyhedra would allow a deviation of the B–O planes from planarity. This appears to be the case in $LaSrCuAlO_5$. The presence of copper in square pyramidal coordination which leads to a buckling of the Cu–O planes allows aluminum to form a more ideal tetrahedron.

Recently the $YBa_2Cu_3O_7$ analog, $YSr_2Cu_{3-x}Al_xO_7$ ($0.4 \leq x \leq 1.0$), was reported (*28*). This compound is similar to $LaSrCuAlO_5$ in that it is a perovskite-related quinary oxide that contains aluminum. A comparison of the B–O frameworks of $LaSrCuAlO_5$ and the suggested structure for $YSr_2Cu_2AlO_7$ ($x = 1.0$) is shown in Fig. 6. In $YSr_2Cu_2AlO_7$ the aluminum is thought to occupy a distorted tetrahedron similar to that found in brownmillerite. Though it is expected that the large difference in the relative sizes of the Y^{3+} (1.16 Å) and Sr^{2+} (1.4 Å) cations favors the $YSr_2Cu_2AlO_7$ structure and the

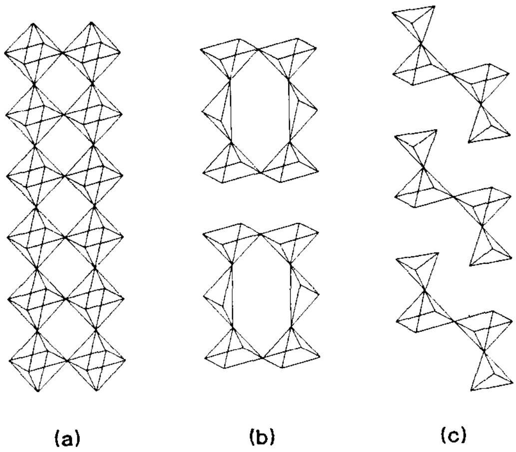

FIG. 6. Comparison of corner-shared polyhedra: (a) fully oxidized perovskite, (b) $YSr_2Cu_2AlO_7$, and (c) $LaSrCuAlO_5$. (Coppers occupy square pyramids and aluminums occupy tetrahedra.)

1 : 2 : 2 : 1 (A^{3+} : Sr : Cu : Al) composition, it may still be possible to form the lanthanum analog. The possibility that $LaSr_2Cu_2AlO_7$ or $La_{3+x}Sr_{2-x}Cu_{3-y}Al_yO_7$ is one of the impurities in the polycrystalline samples is presently under investigation.

The structural details of vacancy orderings are of great interest in the study of oxygen-deficient perovskites (ABO_{3-x}) (*29*). $LaSrCuAlO_5$ exemplifies an alternate approach to the study of oxygen-deficient perovskites. In ABO_{3-x} compounds, the oxygen deficiency is dependent on the variable oxidation state of the *B*-cation. Incorporation of a fixed-valent *B*-cation into the structure, either by itself or with a charge compensating *A*-cation, have made it possible to obtain oxygen-deficient perovskites that do not display a variable oxygen stoichiometry. Model compounds include $A_2BB'O_5$ or, as in the case of $LaSrCuAlO_5$, $AA'BB'O_5$.

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