Introduction

Since the discovery of superconductivity in La$_2$-Ba$_x$CuO$_y$ in 1986,1 intense exploratory research has yielded a large number of materials containing CuO$_2$ planes interleaved by spacer layers, insulating blocks, and charge reservoirs. This wealth of compounds is an essential aid in determining how the structure and defect chemistry of materials affect their high-temperature superconducting behavior. Notwithstanding this history of preparatory success, novel compounds continue to be synthesized, and many opportunities to prepare layered cuprates (as well as other transition-metal oxides) with interesting compositions, structures, and physical properties remain. In particular, the potential for new materials can be demonstrated in the system of perovskite-like oxides containing copper and titanium; however, the chemical factors which control the layering are only partially understood.

Owing to the size similarities between Cu$^{2+}$ (Jahn–Teller radius $\approx 0.60$ Å) and Ti$^{4+}$ (0.605 Å), BO$_{6/2}$ (B = Cu or Ti) nets derived from either of these cations exhibit similar lattice dimensions. Thus these nets (or 2-D planes) can be incorporated into materials with either a complete segregation of both B-cations to separate layers (having minimal mismatch between such layers), or with a statistical distribution of the two B-cations within a single layer. The former arrangement leads to materials with the structural requirements for high-$T_c$ superconductivity, and this structural motif is exhibited in the quadruple perovskites, Ln$^+$Ln$^-$Ba$_2$CuTiO$_{6.5}$ (Ln = lanthanide, Y),4–10 which contain double sheets of corner-sharing copper–oxygen square pyramids that are separated by double sheets of corner-sharing titanium–oxygen octahedra. The difference between the coordination environments of copper and titanium in the quadruple perovskites is the driving force behind the cation order. Similarly, Gd$_2$CaBa$_2$Cu$_2$Ti$_2$O$_{12}$ is composed of double CuO$_2$ pyramidal sheets interleaved by two TiO$_6$ octahedral block layers and an additional (Gd,Ca)O rock salt layer.11 Also, the structures of Gd$_2$$_{3.33}$$Ca$_0.67$Ba$_2$Cu$_2$Ti$_2$O$_{11}$, and Gd$_2$Ca$_{6.6}$Ba$_2$Cu$_2$Ti$_3$O$_{10}$ are proposed to contain double layers of CuO$_2$ square pyramids separated by multiple TiO$_6$ octahedra layers and (Gd,Ce)O fluorite layers.12 Despite the occurrence of distinct CuO$_{4x-2}$ layers in the aforementioned compounds, doping studies have not yet realized superconductivity in these materials. Examples where copper and titanium do not order into individual layers include La$_2$CuTiO$_{6.5}$13–16 and La$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11.17}$ In these materials, a variety of chemical

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1 Abstract published in AdvanceACS Abstracts, September 1, 1996.
3 The Cu$^{2+}$ ionic radius value corresponds to the equatorial radius for a distorted Jahn–Teller copper ion. This value was estimated from a survey of bond lengths given for several layered cuprates. The value differs from that given by Shannon because the equatorial bonds tend to be smaller than the apical bonds; therefore the average value does not reflect the anisotropic nature of this cation.
can be derived from the former $\text{Sr}_3\text{Ti}_2\text{O}_7$ structure by replacing only half of the $\text{Ti}^{4+}$ with $\text{Cu}^{2+}$ and choosing $\text{A}$-cations such that a nominal oxygen content of 6.5 is achieved (by consideration of charge neutrality). Because of the preference of $\text{Ti}^{4+}$ for octahedral coordination and the stability of $\text{Cu}^{2+}$ in square-pyramidal coordination, the oxygen vacancies may order to allow distinct layers of copper pyramids and titanium octahedra as shown in Figure 1b. One example of a material with the proper stoichiometry to potentially achieve this structure is $\text{LaSr}_2\text{CuTiO}_6$, of which the synthesis and structure are reported in the present investigation.

Experimental Section

Synthesis. $\text{LaSr}_2\text{CuTiO}_6.5$ was synthesized by a solid-state reaction technique. Stoichiometric amounts of high-purity ($\geq 99.99\%$) $\text{La}_2\text{O}_3$, $\text{SrCO}_3$, $\text{CuO}$, and $\text{TiO}_2$ were used as starting materials. The $\text{La}_2\text{O}_3$ was heated at 600 °C for 1 h prior to convert any hydroxide back into the oxide, and $\text{SrCO}_3$ was annealed in $\text{CO}_2$ at 800 °C to remove hydroxide and nitrate impurities. The starting materials were ball-milled for 25 min, placed in an alumina boat, and fired for 14 days at 975 °C with several intermediate regrindings.

X-ray Diffraction. Powder X-ray diffraction data were collected on a Rigaku diffractometer with Ni filtered Cu Kα radiation from 10 to 90° 2θ with a step size of 0.05° and a counting time of 20 s. Silicon was used as an internal standard. The lattice parameters and structure of $\text{LaSr}_2\text{CuTiO}_6.5$ were refined using Rietveld analysis. Profiles of diffraction patterns based on ordered and disordered models of the $\text{B}$-cations were also calculated using the program LAZY to calculate the effects of cation ordering on the relative intensities of the diffraction peaks.

Transmission and High-Resolution Electron Microscopy. Transmission electron microscopy (TEM) samples were prepared by crushing $\text{LaSr}_2\text{CuTiO}_6.5$ powdered samples in anhydrous methanol and subsequently dispersing them onto clean 1000 mesh copper grids. High-resolution electron microscopy (HREM) images and electron diffraction patterns (EDPs) were taken using a Hitachi H9000 microscope operated at 300 kV. HREM images and EDPs were digitized to 8 bits using an Optronics P1000 microdensitometer and analyzed with Semper 6 software. That the local stoichiometry (of the grains from which the HREM images and EDPs were taken) corresponded to the overall nominal stoichiometry was confirmed with X-ray energy dispersive spectroscopy (system from EDAX) using a Philips CM 30 operated at 300 kV.

Thermogravimetric Analysis. Hydrogen reduction thermogravimetry was performed using a Dupont Instruments 951 thermogravimetric analyzer. Approximately 50 mg powder samples of $\text{LaSr}_2\text{CuTiO}_{6.5}$ were heated to 800 °C in a 7% H$_2$/93% N$_2$ atmosphere until an equilibrium weight was established. The reduction products were identified by an X-ray diffraction trace, and the measured weight loss was used to calculate the overall oxygen content.

Results

Single-phase material was obtained after the preparation described above, and the powder X-ray diffraction

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(22) Wiles, D. B.; Sakhthivel, A.; Young, R. Rietveld Analysis Program, Version DBWS-9006, School of Physics, Georgia Institute of Technology, 1990.

To understand how cation and oxygen ordering affects the intensities of diffracted peaks in the LaSr$_2$CuTiO$_{6.5}$ system, the powder diffraction patterns of structures based on the I4/mmm and P4/mmm symmetries were first calculated using the program LAZY*22 and the atomic positions for Sr$_3$Ti$_2$O$_7$. In the I4/mmm model, the copper, titanium, and oxygen vacancies were completely mixed over their respective sites, while in the P4/mmm model the B cations and oxygen vacancies were ordered in distinct layers. A complete mixture of the lanthanum and strontium over the A-cation sites was employed in both models as this produced calculated patterns that most closely resembled the pattern obtained experimentally. The resulting patterns are depicted in Figure 2. The observance of $h + k + l = 2n + 1$ reflections would provide evidence for ordering; however, as seen in the P4/mmm pattern of Figure 2c, these reflections are extremely weak owing to the similar scattering capabilities of copper and titanium and the weak scattering ability of oxygen. These odd reflections are not observed in the experimental data but would be difficult to discern owing to their weak intensities which are on the order of signal-to-noise detectability. Moreover, Rietveld refinements of the structure in both the I4/mmm and the P4/mmm space group yielded similar values for the goodness of fit, indicating that X-ray diffraction was ineffective at determining the cation ordering unambiguously. Therefore, electron microscopy was implemented to determine the proper space group and cation arrangement.

Figure 3 shows the electron diffraction patterns along the [001] (a) and [100] (b) directions of the LaSr$_2$CuTiO$_{6.5}$ structure. All of the observed reflections could be indexed using the 3.88 × 3.88 × 20.3 Å tetragonal cell found from the X-ray diffraction data. Reflections indicative of an expanded unit cell (i.e., a superstructure resulting from possible complex ordering patterns of the cations and/or oxygen vacancies) were not observed, and only reflections satisfying an $h + k + l = 2n$ condition were present. This extinction condition is consistent with a body-centered structure of 14/mmm symmetry. None of the EDPs or HREM images collected on different grains provided evidence that copper and titanium were locally ordering, and the sample appeared homogeneous by these electron diffraction investigations. In addition, compositional analysis using EDS on multiple grains evidenced that the local cation stoichiometry was that of the nominal stoichiometry (within the experimental error of several atomic percent), further supporting the mixed B-cation arrangement. Figure 4 is the corresponding HREM images to the EDPs in Figure 3 along both the [001] (a) and the [100] (b) directions. A centered unit cell (corresponding to an n = 2 Ruddlesden–Popper structure) is apparent in the HREM image along the [100] direction as shown in Figure 4b.

The structure of LaSr$_2$CuTiO$_{6.5}$ was thus refined by Rietveld analysis in I4/mmm symmetry using the atomic positions of Sr$_3$Ti$_2$O$_7$ as a starting model. Copper and titanium were disordered over the 4e B-cation site, while the occupancies of lanthanum and strontium were refined over the two A-cation sites. The total occupancy of the A cations was constrained to maintain a 1:2 ratio of La: Sr. In the initial refinements, the oxygen vacancies were constrained to the O(1) site, which is between the adjacent B–O planes, and the O(2) and O(3) sites

The oxygen content was determined to be 6.5 ± 0.1, which is consistent with divalent copper and that 1/14 (or 0.5/7) of the total oxygen sites are vacant.

The reflections of the X-ray diffraction pattern of the polycrystalline LaSr$_2$CuTiO$_{6.5}$ sample, shown in Figure 2a, could be indexed on a tetragonal cell with the dimensions 3.88 × 3.88 × 20.3 Å. A few weak peaks (those near 41, 58.5, 59.3, and 38.3 2θ) could not be indexed on this cell or any related cells and are attributed to a small fraction of impurity phases that cannot be ascertained from these data. The diffraction pattern was similar to that of the Ruddlesden–Popper phase Sr$_3$Ti$_2$O$_7$ (I4/mmm symmetry) with only the $h + k + l = 2n$ reflections appearing. In Sr$_3$Ti$_2$O$_7$, the Ti cations occupy a six-coordinate site and the oxygen sites are fully occupied. However, in LaSr$_2$CuTiO$_{6.5}$ the oxygen stoichiometry is not sufficient to provide octahedral coordination about all of the B sites. The oxygen vacancy is expected in the coordination sphere of copper, as Cu$^{2+}$ can adopt coordination numbers less than six while the highly charged Ti$^{4+}$ strongly prefers an octahedral coordination environment. If CuO$_5$ square pyramids and TiO$_6$ octahedra were disordered over the single B site, then the I4/mmm symmetry would be retained, as observed in the PXD data. However, if the B–O polyhedra were ordered in the layered fashion illustrated in Figure 1b, the body-centering translation would be removed and the symmetry would be reduced to P4/mmm (neglecting further structural distortions; for examples, see Elcombe et al.), and the reflections $h + k + l = 2n + 1$ would appear.
were fully occupied. To maintain the correct overall oxygen stoichiometry, the O(1) site was only half-occupied. Using this model, a good fit was achieved between the calculated and observed intensities, and reasonable values were obtained for all crystallographic parameters except the thermal parameters of the oxygen.

The above-described model resulted in a negative thermal parameter for the O(1) site, indicating that this site has a larger occupancy than 50%. Therefore a variety of models with different vacancy distributions were tested, all of which had little effect on any of the crystallographic parameters except the thermal parameters and occupancies of the oxygen sites. As expected, owing to the weak X-ray scattering capability of oxygen, the various oxygen vacancy models were indistinguishable based on the refinement statistics, and correlations between the occupancies and thermal parameters hindered an unambiguous determination of the location of the oxygen vacancies. After testing a variety of models, however, it became evident that, while there is a distribution of the vacancies over the oxygen sites in this structure, the vacancies are heavily concentrated on the O(1) site. Because of the inability of X-ray powder diffraction to resolve the distribution of oxygen vacancies, a vacancy model (described below) which yielded reasonable thermal parameters and occupancies of the oxygen sites and was consistent with known crystal chemical principles (see Discussion), was selected. Neutron diffraction experiments are currently

Figure 3. Electron diffraction patterns of LaSr₂CuTiO₆.₅ taken along the (a) [001] and (b) [100] directions. The diagonal series of reflections in (b) result from diffraction along the [100] of a neighboring grain.

Figure 4. Experimental high-resolution electron microscopy images of LaSr₂CuTiO₆.₅ taken along the (a) [001] and (b) [100] directions. A centered cell is outlined in Figure 4b.
being conducted to more accurately determine the distribution of oxygen vacancies in this structure.

The oxygen vacancies in the final model were constrained within the perovskite blocks, which are the O(1) and O(2) sites. For these two sites, the thermal parameters were fixed to stable values found during the initial stages of the refinement, and the occupancies were allowed to vary such that the overall stoichiometry was maintained at 6.5. The occupancy of the O(3) site was constrained to be fully occupied while the thermal parameter was refined. This model led to reasonable and stable values for all parameters. Figure 5 illustrates the final profile fit and the difference pattern from the Rietveld analysis. The lattice parameters of LaSr$_2$CuTiO$_{6.5}$ were refined to $a = 3.8816(1)$ Å and $c = 20.296(2)$ Å. Crystallographic data and bond lengths and angles are given in Tables 1 and 2, respectively, and the structure is illustrated in Figure 6.

**Table 1. Refined Structural Parameters for LaSr$_2$CuTiO$_{6.5}$ (Space Group No. 139, I4 mm, $a = 3.8816(1)$ Å, $c = 20.296(2)$ Å)***

<table>
<thead>
<tr>
<th>atom</th>
<th>site</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>$\beta$ (Å$^2$)</th>
<th>occup</th>
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<td>2b</td>
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<td>0.5</td>
<td>0</td>
<td>0.70(2)</td>
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<tr>
<td>A2</td>
<td>4e</td>
<td>0.5</td>
<td>0.5</td>
<td>0</td>
<td>0.1816(1)</td>
<td>0.25(13) La/0.75(3) Sr</td>
</tr>
<tr>
<td>B</td>
<td>4e</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0959(3)</td>
<td>0.15(13) Cu/0.85 Ti</td>
</tr>
<tr>
<td>O(1)</td>
<td>2a</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0.0906(9)</td>
<td>1</td>
</tr>
<tr>
<td>O(2)</td>
<td>8g</td>
<td>0.5</td>
<td>0</td>
<td>0</td>
<td>0.0906(9)</td>
<td>1</td>
</tr>
<tr>
<td>O(3)</td>
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<td>0</td>
<td>0</td>
<td>0.1995(12)</td>
<td>2.02(58)</td>
</tr>
</tbody>
</table>

$a R_p = 5.98$, $R_{wp} = 7.69$ where $R_p = 100\Sigma|Y_{obs} - Y_{calc}|/\Sigma Y_{obs}$; $R_{wp} = 100\Sigma W(Y_{obs} - Y_{calc})^2/\Sigma WY_{obs}^2$, where $W = 1/Y_{obs}$, $Y_{obs}$ and $Y_{calc}$ are the observed and calculated profile intensities at a given 2 $\theta$ angle.

**Table 2. Bond Lengths (Å) and Angles (deg) for LaSr$_2$CuTiO$_{6.5}$***

<table>
<thead>
<tr>
<th>atoms</th>
<th>bond lengths</th>
<th>atoms</th>
<th>bond lengths</th>
</tr>
</thead>
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<tr>
<td>A1−O(1)</td>
<td>4 × 2.75</td>
<td>A2−O(2)</td>
<td>4 × 2.77</td>
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<tr>
<td>A1−O(2)</td>
<td>8 × 2.67</td>
<td>A2−O(3)</td>
<td>1 × 2.41</td>
</tr>
<tr>
<td>A2−O(3)</td>
<td>4 × 2.68</td>
<td>B−O(1)</td>
<td>1 × 1.95</td>
</tr>
<tr>
<td>B−O(1)</td>
<td>1 × 1.94</td>
<td>B−O(2)</td>
<td>1 × 2.10</td>
</tr>
<tr>
<td>B−O(2)</td>
<td>4 × 1.94</td>
<td>B−O(3)</td>
<td>2.10 Å</td>
</tr>
</tbody>
</table>

**Discussion**

The structure of LaSr$_2$CuTiO$_{6.5}$ has been determined from powder X-ray diffraction and electron microscopy and can be described as an oxygen-deficient member of the $n = 2$ Ruddlesden–Popper series. The most striking chemical feature is that copper and titanium are disordered over a single crystallographic site, despite the large number of oxygen vacancies in the coordination sphere of copper. In the known oxygen-deficient perovskite compounds containing copper and titanium, as well as the intergrowths of these phases with rock salt and fluorite blocks, long-range order is generally observed for copper and titanium. This ordering occurs to preserve the octahedral environment of Ti$^{4+}$, while Cu$^{2+}$ adopts a Jahn–Teller distorted square-pyramidal environment. However, mixing of these polyhedra within layers has been observed in La$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$ as determined by X-ray, neutron, and electron diffraction.$^7,8,17$ Short-range order in La$_2$Ba$_2$Cu$_2$Ti$_2$O$_{11}$ was evidenced by electron diffraction owing to the observation of intensity peaks corresponding to the layered quadruple perovskite structure in the EDPs.$^7$ In the present investigation, however, no evidence of either long- or short-range order was observed, and copper and titanium are distributed randomly over a single site in LaSr$_2$CuTiO$_{6.5}$. In contrast to the other known oxygen-deficient mixed copper–titanates, mentioned above, the occurrence of oxygen vacancies in combination with different coordination preferences of the multiple B-cations does not result in a layered structure for LaSr$_2$CuTiO$_{6.5}$.

The statistical distribution of copper and titanium in LaSr$_2$CuTiO$_{6.5}$ resembles that of La$_2$CuTiO$_{6}$, an oxygen stoichiometric perovskite which has no driving force for the segregation of copper and titanium to distinct...
over both sites in the structure. In LaSr$_2$CuTiO$_{6.5}$, the fully occupied 2b and 4e sites are approximately 38% and 31% occupied by La, respectively, where a 33% occupation factor on both sites would describe perfect disorder of the lanthanum and strontium. This distribution is similar to that observed in related materials, and also has implications on both the oxygen vacancy and B-cation order. While mixing occurs for lanthanum and strontium in the known Ruddlesden–Popper phases based on copper, preferential site occupancy (8 coordinate, 2b site) has been observed for calcium and yttrium cations. The site selectivity and preference for 8-fold coordination of yttrium and calcium may lead to concerted oxygen vacancy and B-cation order in substituted derivatives of LaSr$_2$CuTiO$_{6.5}$.

The oxygen-deficient Ruddlesden–Popper cuprate materials are known to have variable oxygen contents dependent on the size of the A-cation separating the copper–oxygen planes. The stoichiometry of the La$_2$-$\delta$Sr$_{1-x}$Cu$_2$O$_{6.0}$, intercalate oxygen when annealed in oxidizing environments, resulting in an increase in the distance separating CuO$_{4/2}$ planes as $\delta$ increases and the ability to exceed an oxygen content of 6.0, 29,36,42 However, when calcium occupies the site between the copper–oxygen planes, as in La$_2$CaCu$_2$O$_{6.3}$, an oxygen content of 6.0 cannot be exceeded, and the c axis (perpendicular to the CuO$_{4/2}$ planes) does not vary within detectable limits over the range of accessible $\delta$ values, suggesting that oxygen does not intercalate into the vacant oxygen sites between the CuO$_{4/2}$ sheets. 29,36,43 Moreover, Ruddlesden–Popper phases with more complex defect structures are known to occur among oxygen nonstoichiometric materials, such as NdSr$_2$Cu$_2$O$_{6.76}$, in which the high oxygen vacancy concentration is limited to sites similar to the O(1) and O(2) sites in LaSr$_2$CuTiO$_{6.5}$. Extending these ideas to a multiple B-site material, oxygen intercalation between CuO$_{4/2}$ nets creates a driving force for mixing of the two B cations. A-site cations, such as lanthanum and strontium, which allow for such disorder on the oxygen sublattice therefore can stabilize a random distribution of both B cations, as in LaSr$_2$CuTiO$_{6.5}$.

Transitions in the arrangements of the B cations and oxygen vacancies have been observed in perovskite-like materials as a function of A-cation composition. For example, the aforementioned quadruple perovskite LaBa$_2$Cu$_2$Ti$_2$O$_{11}$ contains a disordered arrangement of the B cations, whereas in the related compounds

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LaLnBa$_2$Cu$_2$Ti$_2$O$_{11}$ (Ln = Y, Er, Tm) the B-cations order into individual CuO$_{4/2}$ and TiO$_{4/2}$ planes to create an 8-coordinate A site which is preferentially occupied by the smaller Ln cation. The layered, ordered quadruple perovskite structure is destabilized when the largest lanthanide, La, is required to occupy the lower 8-coordinate site between the CuO$_2$ sheets. Thus, the ordering of the B-O framework polyhedra can be influenced by the coordination needs of the supporting A cations. Yttrium selectively occupies the 8-coordinate site in LaYSrCu$_2$O$_6$, an oxygen-deficient Ruddlesden–Popper phase, which suggests that A-cation substitutions in LaSr$_2$CuTiO$_{6.5}$ will yield new mixed-copper titanates. Studies are currently underway to investigate how smaller lanthanide substitutions for lanthanum and calcium substitution for strontium will influence cation and oxygen vacancy ordering.

**Conclusions**

The potential for the synthesis of novel copper titanates has been demonstrated in LaSr$_2$CuTiO$_{6.5}$, an oxygen-deficient n = 2 Ruddlesden–Popper phase. The synthesis was motivated by an interest in preparing an intergrowth structure of Sr$_3$Ti$_2$O$_7$ and La$_2$SrCu$_2$O$_6$, in which copper and titanium order over distinct BO$_{4/2}$ nets. The copper and titanium of LaSr$_2$CuTiO$_{6.5}$ were found to be disordered over a single site by both X-ray diffraction and electron microscopy. Owing to the similarity of the crystal chemistry and internal architecture between LaSr$_2$CuTiO$_{6.5}$ and known layered cuprates, alterations of the A-cation composition has great potential to result in an ordering of both the B cations and oxygen vacancies.

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