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# Synthesis and Study in 23 Metal–La–Cu–O Systems

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High-pressure, high-temperature synthesis of $LaCuO_3$, the substituted series $La_{1-x}M_xCuO_3$, where $M$ = Mg, Ca, Sr, Ba, Pb, Sc, Y, Pr, Nd, Tl, Sb, Bi, Ti, Zr, or Ce, and $LaCu_{1-x}M'_xO_3$, where $M'$ = Cr, Fe, Co, Ni, Zn, Ag, or Tl, was undertaken. The rhombohedrally distorted perovskite structure of $LaCuO_3$ was found to persist in the following systems, where the number in parentheses is the maximum $x$: Ag (1.0), Ba (0.8), Bi (0.6), Ca (0.8), Ce (0.4), Co (1.0), Cr (0.2), Fe (0.2), Mg (0.8), Nd (0.4), Ni (1.0), Pr (0.4), Sb (0.2), Sc (0.2), Sr (0.8), Ti (0.1), Zr (0.8). This structure was not found with Y, Pb, or Zn at any level of substitution, although Zn did permit formation of this structure when Ni was used instead of Cu. This structure was detected at the $x$ = 0.6 level with Tl, but not at $x$ = 0.4 or 0.8. Samples were tested for superconductivity effects by magnetic susceptibility, without positive results. The synthesis stability region of $P$–$T$ space for $LaCuO_3$ was found to be above 1200°C at pressures above 5 GPa. Stability of $LaCuO_3$ at ambient pressure was studied by differential thermal analysis, and an endothermic phase change to a tetragonal structure was noted around 400°C. The relationship of these results to the high-temperature superconducting copper oxide ceramics is discussed.

## Background

Demazeau *et al.* showed that high oxygen pressures, derived in a belt apparatus by thermal decomposition of $KClO_3$, could stabilize the trivalent state of copper and permit formation of black $LaCuO_3$ (*1*). They accomplished this by treating a stoichiometric mix of $La_2CuO_4$ and CuO, to which was added an excess of $KClO_3$, at 6.5 GPa and 900°C for 10 min. This procedure was unsuccessful in producing similar $LnCuO_3$ products from the other rare earths. $LaCuO_3$ has also been reported from a mixture of the oxides heated at 800°C for 40 hr under 400 atm of oxygen (*2*). The metallic $LaCuO_3$ product had a distorted perovskite rhombohedral structure analogous to $LaNiO_3$, with $a = 5.431 \pm 0.002$ Å and $\alpha = 60.85 \pm 0.02°$ (*1*). $LaCuO_3$ could not be produced by firing a mixture of the oxides in air (*3*), or by means of precipitation of mixed hydroxides (*4*), but was reported, with X-ray confirmation of a perovskite product, to be produced from a calcined mixture of acetates (5). Recent work at 900°C under oxygen pressures of 20–100 MPa gave three $LaCuO_{3-y}$ phases: tetragonal for $0 \leq y \leq 0.4$ at $40 \leq P_{O2} \leq 100$ MPa, monoclinic for $0.2 \leq y \leq 0.4$ at $P_{O2}$ = 20–40 MPa, and an orthorhombic form with $0.43 \leq y \leq 0.5$, obtained by heating the tetragonal form in $N_2$ to 700–800°C (*6*). An estimate of the free energy of formation of $LaCuO_3$ shows it to be stable to above 4500 K (*7*). Given the avid current interest in Cu-based ceramic oxides, arising

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from the existence of high $T_c$ superconductivity (*8*), we felt that further investigation of $LaCuO_3$ was warranted.

The basic $La_2CuO_4$ structure fundamental to that original high-$T_c$ material consists of single layers of perovskite units separated by NaCl-structured layers. Subsequent superconducting materials, e.g., $YBa_2Cu_3O_{6+y}$, consist of even larger assemblages of these basic building blocks, with more NaCl-type layers and varied stacking arrangements. $LaCuO_3$ is the simplest member of this series, lacking the NaCl-type layers. Because of the high degree of both chemical and structural similarity, it has a strong possibility of being a superconductor, but would be of interest in any case since it may provide material for better theoretical understanding of this fascinating class of materials.

## Experimental

### *A. High-Pressure Techniques*

The pressures necessary for this high-pressure, high-temperature (HPHT) study were obtained using a tetrahedral anvil apparatus equipped with anvil guides (*9*). Working pressures of 6.5 GPa were routinely obtained. Pressures were estimated using a calibration against known fixed-point resistance transitions (*10*). A pyrophyllite tetrahedral sample container with an internal graphite tube heater was used. Temperatures up to 2500°C were achieved by driving an ac current of approximately 850 A at low voltage (2–3 V) through the electrically isolated anvils to the internal graphite tube heater. Temperatures were estimated by use of a calibration of input power vs temperature for runs in which a thermocouple replaced the sample charge; they are accurate to within about ±3% (*11*). The sample charge was electrically isolated from the tube furnace by a BN capsule, and then further isolated chemically by a metal capsule, either Ta or Pt, within the BN. The powdered charge mixture was hand-tamped into the tube. Even with this protection, water, driven out of the pyrophyllite by the intense heat, can enter the reaction chamber. This has mixed consequences: favorable since water acts as a mineralizer, facilitating reactions, and unfavorable since $La(OH)_3$ is very stable under the operating conditions and indeed was found to form in many of the runs. Seeking to eliminate this water, runs were assembled with the graphite heater in a heavy-walled BN tube (of a thickness greater than the usual pyrophyllite reaction zone); these were also found to contain the $La(OH)_3$ impurity. Therefore this additional protective measure was not continued.

### *B. Materials*

$LaCuO_3$ was formed from the constituent oxides, $La_2O_3$ and CuO, with an excess of $KClO_3$ to maintain an oxidizing environment favorable to $Cu^{3+}$. Thermal decomposition of $KClO_3$ provided the requisite oxygen, and both residual reactant $KClO_3$ and product KCl could be readily washed out with water after the product was removed from the HPHT chamber. The presence of gas at 6.5 GPa in the molten sample, indicative of the presence of excess oxygen, was evidenced by spherical voids in a number of the recovered samples. The reaction sought was

$$3\,La_2O_3 + 6\,CuO + KClO_3 \rightarrow 6\,LaCuO_3 + KCl.$$

It should be noted that there was a possibility of inclusion of Cl in the product since a number of oxychlorides had been synthesized, including $Ba_2Cu_3O_4Cl_2$ (*12*), $Sr_2Cu_3O_4Cl_2$ (*13*), $Sr_2CuO_2Cl_2$ (*14*), $Ca_2CuO_2Cl_2$ (*15*). The existence of compounds of alkali cuprates, such as $KCuO_2$, further complicated the possible products (*16*).

Since the high-$T_c$ materials had substitutional impurities such as Ba and Sr, and subsequent materials either had favorable structures stabilized or the $T_c$ elevated by elements such as Pb, Tl, and Ca, the substitional series $La_{1-x}M_xCuO_3$ was also formulated with $M$ = Mg, Ca, Sr, Ba, Sc, Y, Ti, Zr, Ce, Pr, Nd, Tl, Pb, Sb, and Bi, using MgO, CaO, SrO or $La_{2-x}Sr_xCuO_4$, BaO, $Sc_2O_3$, $Y_2O_3$, Ti or $TiO_2$, $ZrO_2$, $CeO_2$, $Pr_6O_{11}$, $Nd_2O_3$, $Tl_2O_3$, $PbO_2$, $Sb_2O_3$, and $Bi_2O_3$, respectively. High-purity starting materials were weighed to the appropriate proportions, mixed, and ground in a mortar to give a uniform powder. These powders were then loaded into the sample container of BN, Ta, or Pt. Since these were survey studies only, a coarse composition grid ($x$ = 0.2, 0.4, 0.6, 0.8, 1.0) was chosen. It is recognized that such a coarse grid can readily miss a limited stability field, such as was recently reported in the system $La_{1-x}Sr_xCuO_{3-y}$, $0.20 \leq x \leq 0.25$ (*17*), but even a 10% grid (with double the effort required) could have missed such a limited field. Since a previous attempt at synthesis of $LnCuO_3$ (Ln = a rare earth other than La) failed (*1*), the series with $M$ = Ce, Pr, and Nd was also studied.

In addition to substitution of the La, replacement of the Cu was also investigated, viz, $LaCu_{1-x}M'_xO_3$, where $M'$ = Cr, Fe, Co, Ni, Zn, Ag, and Tl (using $Cr_2O_3$, $CrO_2$, or $CrO_3$; $Fe_2O_3$; $Co_3O_4$; NiO; ZnO; $Ag_2O$ or AgO; and $Tl_2O_3$, respectively), with preparation as noted above for the La substitution series. Synthesis was expected to be difficult since the related niccolates of Y, Sr, and Ba, generally seen as being more readily synthesized than the cuprates, required 400 atm oxygen pressure for synthesis (*18*).

### C. Analysis

The products were retrieved from the sample assembly and a small portion was broken from the slug and powdered for X-ray diffraction study by the Debye-Scherrer method for determination of the products present. Least-squares refinement of indexed lines gave the hexagonal lattice parameters which are reported throughout this paper; rhombohedral parameters were referenced to the equivalent hexagonal lattice for purposes of comparison with previously published work. The hexagonal cell parameters are given in Table I for those products which displayed the $LaCuO_3$ structure. The bulk of each sample, about 0.02 $cm^3$, was reserved for superconductivity tests. Although gross resistivity was checked, susceptibility measurements were favored for screening purposes, since a continuous path is not then necessary. It was estimated that if as little as 1% of the sample were to expel flux it would be detectable.

Some materials were investigated using differential scanning calorimetry (DSC) on a Perkin–Elmer 7 Series thermal analysis system. Samples of 3–25 mg were sealed in Al containers and heated to 600°C at a rate of 20°C/min.

## Results

### A. General

Early work involved the use of only the BN isolation tubes to separate the sample charge from the graphite heater. Adherence of the BN to the sample, occasional intermixing at the interface, and thus possible reaction prompted use of an additional Ta capsule within the BN to chemically isolate the sample. Both $La_2O_3$ and $KClO_3$ left the Ta container dark and brittle, however, which prompted the substitution of 0.051 mm thick Pt capsules. These proved suitable for the task. Except for one run in which the Pt was heated to melting on one end, the Pt was found to be readily freed from the product after HPHT treatment with no obvious evidence of reaction, contrary to a prior report of dissolution of Pt by $La_{2-x}Sr_xCuO_4$ (*19*).

Preliminary work included treatment of the individual reactants to the HPHT synthesis conditions. The product obtained by

## TABLE I

LATTICE PARAMETERS FOR PRODUCTS WITH $\mathrm{LaCuO_3}$ STRUCTURE

| Composition (kbar/°C) | a (Å) | ± | c (Å) | ± | Volume (Å$^3$) |
|---|---|---|---|---|---|
| $\mathrm{LaCuO_3}$ 65/1500[a] | 5.494 | 0.017 | 13.225 | 0.072 | 345.7 |
| $\mathrm{LaCuO_3}$ 50/1500[b] | 5.508 | 0.015 | 13.237 | 0.087 | 347.8 |
| $\mathrm{LaCuO_3}$ 50/1700 | 5.494 | 0.013 | 13.215 | 0.056 | 345.4 |
| $\mathrm{LaCuO_3}$ 55/1500 | 5.499 | 0.011 | 13.206 | 0.034 | 345.8 |
| $\mathrm{LaCuO_3}$ 59/1500 | 5.473 | 0.048 | 13.191 | 0.235 | 342.1 |
| $\mathrm{LaCuO_3}$ 60/1500 | 5.504 | 0.018 | 13.215 | 0.071 | 346.6 |
| $\mathrm{LaCuO_3}$ 65/1200 | 5.490 | 0.011 | 13.181 | 0.038 | 344.0 |
| $\mathrm{LaCuO_3}$ 65/1500 | 5.475 | 0.035 | 13.193 | 0.131 | 342.5 |
| $\mathrm{LaCuO_3}$ 65/1700 | 5.494 | 0.020 | 13.189 | 0.140 | 344.8 |
| $\mathrm{LaCuO_3}$ 1 min[c] | 5.501 | 0.017 | 13.199 | 0.068 | 345.9 |
| $\mathrm{LaCuO_3}$ 2 min | 5.492 | 0.007 | 13.214 | 0.047 | 345.2 |
| $\mathrm{LaCuO_3}$ 20 min | 5.500 | 0.012 | 13.211 | 0.070 | 346.0 |
| $\mathrm{LaCuO_3}$ $\mathrm{H_2O}$ cold[d] | 5.500 | 0.012 | 13.210 | 0.047 | 346.0 |
| $\mathrm{LaCuO_3}$ $\mathrm{H_2O}$ hot | 5.500 | 0.022 | 13.214 | 0.089 | 346.2 |
| $\mathrm{LaCuO_3}$ air 300°C[e] | 5.496 | 0.013 | 13.211 | 0.045 | 345.6 |
| $\mathrm{LaCuO_3}$ 300° 10mo[f] | 5.474 | 0.017 | 13.05 | 0.108 | 338.7 |
| $\mathrm{LaCuO_3}$ $\mathrm{O_2}$ 300°C[e] | 5.499 | 0.007 | 13.216 | 0.025 | 346.1 |
| $\mathrm{LaCuO_{2.9}}$[g] | 5.499 | 0.010 | 13.230 | 0.041 | 346.5 |
| $\mathrm{LaCuO_{3.0}}$ | 5.505 | 0.013 | 13.227 | 0.043 | 347.1 |
| $\mathrm{LaCu_{0.8}Cr_{0.2}O_3}$[h] | 5.467 | 0.036 | 13.386 | 0.274 | 346.5 |
| $\mathrm{LaCu_{0.8}Cr_{0.2}O_3}$ | 5.490 | 0.013 | 13.296 | 0.097 | 347.1 |
| $\mathrm{LaCu_{0.8}Fe_{0.2}O_3}$ | 5.519 | 0.007 | 13.255 | 0.028 | 349.7 |
| $\mathrm{LaCu_{0.8}Co_{0.2}O_3}$ | 5.493 | 0.007 | 13.188 | 0.028 | 344.6 |
| $\mathrm{LaCu_{0.6}Co_{0.4}O_3}$ | 5.494 | 0.007 | 13.167 | 0.024 | 344.1 |
| $\mathrm{LaCu_{0.4}Co_{0.6}O_3}$ | 5.482 | 0.007 | 13.152 | 0.025 | 342.3 |
| $\mathrm{LaCu_{0.2}Co_{0.8}O_3}$ | 5.459 | 0.004 | 13.110 | 0.017 | 338.3 |
| $\mathrm{LaCoO_3}$ | 5.441 | 0.006 | 13.085 | 0.021 | 335.5 |
| $\mathrm{LaCu_{0.8}Ni_{0.2}O_3}$ | 5.501 | 0.019 | 13.145 | 0.127 | 344.5 |
| $\mathrm{LaCu_{0.8}Ni_{0.2}O_3}$ | 5.505 | 0.014 | 13.206 | 0.052 | 346.6 |
| $\mathrm{LaCu_{0.6}Ni_{0.4}O_3}$ | 5.487 | 0.010 | 13.215 | 0.037 | 344.6 |
| $\mathrm{LaCu_{0.4}Ni_{0.6}O_3}$ | 5.463 | 0.009 | 13.171 | 0.038 | 340.3 |
| $\mathrm{LaCu_{0.2}Ni_{0.8}O_3}$ | 5.449 | 0.018 | 13.175 | 0.061 | 338.8 |
| $\mathrm{LaNiO_3}$ | 5.448 | 0.012 | 13.199 | 0.043 | 339.2 |
| $\mathrm{LaZn_{0.2}Ni_{0.8}O_3}$ | 5.444 | 0.009 | 13.095 | 0.042 | 336.1 |
| $\mathrm{LaZn_{0.4}Ni_{0.6}O_3}$ | 5.451 | 0.009 | 13.094 | 0.040 | 337.0 |
| $\mathrm{LaZn_{0.6}Ni_{0.4}O_3}$ | 5.451 | 0.013 | 13.127 | 0.061 | 337.9 |
| $\mathrm{LaZn_{0.8}Ni_{0.2}O_3}$ | 5.450 | 0.022 | 13.212 | 0.145 | 339.9 |
| $\mathrm{LaCu_{0.8}Ag_{0.2}O_3}$ | 5.491 | 0.020 | 13.208 | 0.083 | 344.8 |
| $\mathrm{LaCu_{0.6}Ag_{0.4}O_3}$ | 5.512 | 0.021 | 13.127 | 0.104 | 345.4 |
| $\mathrm{LaCu_{0.4}Ag_{0.6}O_3}$ | 5.513 | 0.035 | 13.165 | 0.206 | 346.5 |
| $\mathrm{LaCu_{0.2}Ag_{0.8}O_3}$ | 5.509 | 0.025 | 13.177 | 0.099 | 346.3 |
| $\mathrm{LaAgO_3}$ | 5.527 | 0.020 | 13.257 | 0.085 | 350.8 |
| $\mathrm{La_{0.8}Mg_{0.2}CuO_3}$ | 5.506 | 0.011 | 13.198 | 0.043 | 346.5 |
| $\mathrm{La_{0.6}Mg_{0.4}CuO_3}$ | 5.502 | 0.060 | 13.156 | 0.214 | 344.9 |
| $\mathrm{La_{0.4}Mg_{0.6}CuO_3}$ | 5.499 | 0.028 | 13.201 | 0.107 | 345.7 |
| $\mathrm{La_{0.2}Mg_{0.8}CuO_3}$ | 5.493 | 0.009 | 13.242 | 0.033 | 346.0 |
| $\mathrm{La_{0.9}Ca_{0.1}CuO_3}$ | 5.494 | 0.037 | 13.201 | 0.136 | 345.1 |
| $\mathrm{La_{0.8}Ca_{0.2}CuO_3}$ | 5.523 | 0.015 | 13.176 | 0.065 | 348.1 |
| $\mathrm{La_{0.8}Ca_{0.2}CuO_3}$ | 5.498 | 0.011 | 13.205 | 0.053 | 345.7 |
| $\mathrm{La_{0.6}Ca_{0.4}CuO_3}$ | 5.493 | 0.008 | 13.229 | 0.055 | 345.7 |
| $\mathrm{La_{0.4}Ca_{0.6}CuO_3}$ | 5.496 | 0.012 | 13.214 | 0.083 | 345.7 |
| $\mathrm{La_{0.2}Ca_{0.8}CuO_3}$ | 5.512 | 0.009 | 13.225 | 0.037 | 348.0 |
| $\mathrm{La_{0.9}Sr_{0.1}CuO_3}$ | 5.490 | 0.023 | 13.249 | 0.079 | 345.8 |
| $\mathrm{La_{0.8}Sr_{0.2}CuO_3}$ | 5.497 | 0.009 | 13.219 | 0.035 | 345.9 |
| $\mathrm{La_{0.6}Sr_{0.4}CuO_3}$ | 5.491 | 0.010 | 13.227 | 0.041 | 345.3 |
| $\mathrm{La_{0.4}Sr_{0.6}CuO_3}$ | 5.499 | 0.007 | 13.207 | 0.026 | 345.9 |
| $\mathrm{La_{0.2}Sr_{0.8}CuO_3}$ | 5.501 | 0.014 | 13.208 | 0.062 | 346.1 |
| $\mathrm{La_{0.8}Ba_{0.2}CuO_3}$ | 5.499 | 0.019 | 13.263 | 0.066 | 347.4 |
| $\mathrm{La_{0.6}Ba_{0.4}CuO_3}$ | 5.501 | 0.021 | 13.217 | 0.074 | 346.4 |
| $\mathrm{La_{0.4}Ba_{0.6}CuO_3}$ | 5.490 | 0.015 | 13.211 | 0.055 | 344.9 |
| $\mathrm{La_{0.2}Ba_{0.8}CuO_3}$ | 5.503 | 0.016 | 13.158 | 0.054 | 345.1 |
| $\mathrm{La_{0.8}Sc_{0.2}CuO_3}$ | 5.492 | 0.015 | 13.231 | 0.059 | 345.6 |
| $\mathrm{La_{0.8}Ce_{0.2}CuO_3}$ | 5.432 | 0.043 | 13.059 | 0.152 | 333.7 |
| $\mathrm{La_{0.6}Ce_{0.4}CuO_3}$ | 5.411 | 0.049 | 12.956 | 0.172 | 328.5 |
| $\mathrm{La_{0.8}Nd_{0.2}CuO_3}$ | 5.496 | 0.009 | 13.165 | 0.033 | 344.4 |
| $\mathrm{La_{0.8}Nd_{0.2}CuO_3}$ | 5.497 | 0.020 | 13.155 | 0.068 | 344.2 |
| $\mathrm{La_{0.6}Nd_{0.4}CuO_3}$ | 5.491 | 0.011 | 13.159 | 0.040 | 343.6 |
| $\mathrm{La_{0.8}Pr_{0.2}CuO_3}$ | 5.493 | 0.012 | 13.167 | 0.055 | 344.0 |
| $\mathrm{La_{0.6}Pr_{0.4}CuO_3}$ | 5.501 | 0.026 | 13.184 | 0.097 | 345.5 |
| $\mathrm{La_{0.8}Sb_{0.2}CuO_3}$ | 5.494 | 0.014 | 13.196 | 0.066 | 345.0 |
| $\mathrm{La_{0.9}Ti_{0.02}CuO_3}$ | 5.521 | 0.014 | 13.092 | 0.101 | 345.6 |
| $\mathrm{La_{0.9}Ti_{0.1}CuO_3}$ | 5.501 | 0.029 | 13.164 | 0.133 | 345.0 |
| $\mathrm{La_{0.9}Ti_{0.1}CuO_3}$ | 5.497 | 0.008 | 13.220 | 0.032 | 345.9 |
| $\mathrm{La_{0.8}Zr_{0.2}CuO_3}$ | 5.503 | 0.015 | 13.211 | 0.058 | 346.4 |
| $\mathrm{La_{0.6}Zr_{0.4}CuO_3}$ | 5.497 | 0.015 | 13.225 | 0.056 | 346.1 |
| $\mathrm{La_{0.4}Zr_{0.6}CuO_3}$ | 5.494 | 0.008 | 13.217 | 0.030 | 345.5 |
| $\mathrm{La_{0.2}Zr_{0.8}CuO_3}$ | 5.498 | 0.018 | 13.231 | 0.091 | 346.3 |
| $\mathrm{La_{0.4}Tl_{0.6}CuO_3}$ | 5.490 | 0.014 | 13.184 | 0.079 | 344.1 |
| $\mathrm{La_{0.8}Bi_{0.2}CuO_3}$ | 5.500 | 0.036 | 13.201 | 0.271 | 345.8 |
| $\mathrm{La_{0.6}Bi_{0.4}CuO_3}$ | 5.492 | 0.023 | 13.166 | 0.096 | 343.9 |
| $\mathrm{La_{0.4}Bi_{0.6}CuO_3}$ | 5.497 | 0.030 | 13.169 | 0.123 | 344.6 |

[a] Combined product from six runs at 65 kbar and 1500°C.
[b] Treatment at 50 kbar and 1500°C.
[c] Heating time varied from the usual 5 min.
[d] KCl washed out of product with water.
[e] Product was treated in air or $\mathrm{O_2}$ at 300°C.
[f] Stability check; re-X-rayed after 10 months.
[g] $\mathrm{KClO_3}$ limited to give indicated stoichiometry.
[h] La or Cu substituted by indicated element.

treatment of stock $\mathrm{La_2O_3}$ was principally $\mathrm{La(OH)_3}$, which also was the most persistent impurity in the reaction runs. Many moderately intense lines of the XRD pattern were not identified, however. Also the product had an X-ray density 0.3% less than that given by the Powder Diffraction File reference. This was confirmed by subsequent

XRD work on material not exposed to HPHT conditions, which found $a$ = 6.523 and $c$ = 3.851 Å for the untreated sample, and $a$ = 6.521 and $c$ = 3.842 Å for the HPHT sample, for cell volumes of 141.91 and 141.49 Å$^3$, respectively. The difference derives from an elongation of the $c$-axis in the HPHT product which exceeds the combined uncertainties. A wide reaction zone noted in the pyrophyllite after this HPHT treatment was probably due to increased dehydration caused by the uptake of water (the mineral of the container has both bound water and water of hydration) by the reactant, which then migrated through heater, BN and Pt tubes. It may be noted that intentional addition of water during synthesis of $La_{1.84}Sr_{0.16}CuO_4$ was reported to cause a significant decrease in the fraction of product which was superconducting (*20*). In the HPHT synthesis system therefore, the water may, through a similar mechanism, prohibit exhibition of superconductivity in the products. The CuO runs were of no particular note. Heated alone, a trace of $Cu_2O$ resulted; with the addition of oxidizer, KCl and a trace of $KClO_3$ were also found.

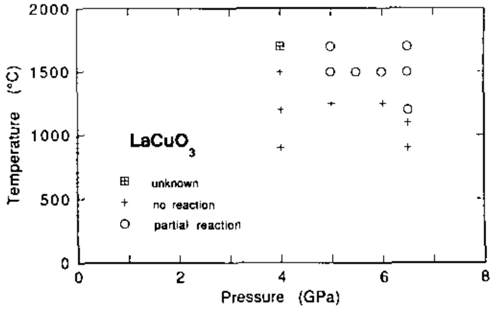

FIG. 1. Pressure temperature reaction product diagram. ○ indicates the presence of $LaCuO_3$, + the presence of reactant oxides, and □ the presence of unknown products.

### *B. Synthesis of* $LaCuO_3$

As noted above, the synthesis of $LaCuO_3$ in this study commenced from the constituent oxides rather than from $La_2CuO_4$ as had been published (*1*). To obtain the desired product it was found that somewhat higher temperatures, viz, 1500°C, were required (rather than the previously reported 900°C; *1*). The region of synthesis in pressure–temperature space is shown in Fig. 1. Synthesis was not achieved below 5 GPa, and the minimum required temperature decreased as the pressure increased, with a minimal temperature requirement of about 1200°C. Some CuO and $La(OH)_3$ were present in all samples retrieved; many also contained KCl. Survey samples were not routinely washed (washing did not change the amount of $La(OH)_3$ in a sample). It was difficult to fully assign all the lines observed in the X-ray diffraction pattern. Since some of the higher angle lines appeared only when $LaCuO_3$ was present (though lines in this region were not reported by Demazeau *et al.*; *1*) these lines were indexed by comparison with those calculated from the observed cell parameters and space group to give an intensity greater than 1% for the most intense line. The pattern derived after extracting the KCl with cold water is given in Table II with full indexing, along with the calculated $d$-values. Boiling water extraction led to similar results, indicating stability of $LaCuO_3$ to these more severe conditions. The $c$-cell parameter of $LaCuO_3$ increased slightly with increased processing temperature, while the $a$ parameter showed a shallow maximum at 1500°C. From these results a standard HPHT processing condition of 6.5 GPa and 5 min at 1500°C was selected for the subsequent substitution survey work.

An attempt to study the compressibility of $LaCuO_3$ in a diamond-anvil cell gave serendipitous information on stability in water. Well-crystallized $La(OH)_3$ resulted from hydrolysis by the water contained in the hydrostatic fluid when the sample was subjected to a pressure above about 0.5 GPa.

Runs with $LaCuO_3$ were made at nonstandard (other than 5 min) heating periods, seeking an optimum run time. Those made

## TABLE II

X-RAY DIFFRACTION PATTERN FOR $LaCuO_3$ EXTRACTED WITH COLD WATER

| $d_{obs}$ (Å) | $I/I_o$ | h | k | l | $d_{calc}$ (Å) | Δ d (Å) |
|---|---|---|---|---|---|---|
| 3.83 | 3 | 0 | 1 | 2 | 3.863 | -0.033 |
| 3.241 | 2 | | | | $La(OH)_3$ | |
| 3.167 | 7 | | | | $La(OH)_3$ | |
| 2.732 | 60 | 1 | 1 | 0 | 2.750 | -0.018 |
| 2.687 | 60 | 1 | 0 | 4 | 2.714 | -0.027 |
| 2.509 | 5 | | | | CuO | |
| 2.312 | 10 | | | | CuO | |
| 2.278 | 15 | | | | $La(OH)_3$ | |
| 2.232 | 5 | 2 | 0 | 2 | 2.240 | -0.008 |
| 2.200 | 2 | 0 | 0 | 6 | 2.202 | -0.002 |
| 2.146 | 2 | | | | $La(OH)_3$ | |
| 2.052 | 1 | | | | ?? | |
| 1.920 | 100 | 0 | 2 | 4 | 1.932 | -0.012 |
| 1.876 | 10 | | | | $La(OH)_3$ | |
| 1.859 | 25 | | | | CuO ? | |
| 1.727 | 2 | 1 | 2 | 2 | 1.737 | -0.010 |
| 1.709 | 3 | 1 | 1 | 6 | 1.719 | -0.010 |
| 1.658 | 2 | | | | ?? | |
| 1.635 | 1 | | | | ?? | |
| 1.576 | 70 | 0 | 3 | 0 | 1.588 | -0.012 |
| 1.576 | | 2 | 1 | 4 | 1.581 | -0.005 |
| 1.554 | 20 | 0 | 1 | 8 | 1.560 | -0.006 |
| 1.499 | 2 | | | | ?? | |
| 1.449 | 2 | | | | $La(OH)_3$ | |
| 1.410 | 2 | | | | $La(OH)_3$ | |
| 1.370 | 2 | 2 | 2 | 0 | 1.375 | -0.005 |
| 1.355 | 30 | 2 | 0 | 8 | 1.357 | -0.002 |
| 1.288 | 2 | 0 | 3 | 6 | 1.288 | 0.000 |
| 1.223 | 40 | 1 | 3 | 4 | 1.227 | -0.004 |
| 1.214 | 40 | 1 | 2 | 8 | 1.217 | -0.003 |
| 1.167 | 5 | 0 | 4 | 2 | 1.172 | -0.005 |
| 1.154 | 3 | 0 | 2 | 10 | 1.155 | -0.001 |
| 1.117 | 15 | 4 | 0 | 4 | 1.172 | -0.055 |
| 1.103 | 15 | 0 | 0 | 12 | 1.101 | 0.002 |
| 1.088 | 3 | | | | ?? | |
| 1.076 | 5 | 2 | 3 | 2 | 1.078 | -0.002 |
| 1.063 | 5 | 2 | 1 | 10 | 1.065 | -0.002 |
| 1.038 | 70 | 4 | 1 | 0 | 1.039 | -0.001 |
| | | 3 | 2 | 4 | 1.037 | 0.001 |
| 1.032 | 35 | 3 | 1 | 8 | 1.032 | 0.000 |
| 1.022 | 35 | 1 | 1 | 12 | 1.022 | 0.000 |
| 0.9813 | 2 | | | | ?? | |
| 0.9657 | 35 | 0 | 4 | 8 | 0.9658 | -0.0001 |
| 0.9403 | 5 | 4 | 1 | 6 | 0.9398 | 0.0005 |
| 0.9162 | 40 | 3 | 3 | 0 | 0.9166 | -0.0004 |
| | | 0 | 5 | 4 | 0.9152 | 0.0010 |
| 0.9110 | 50 | 2 | 3 | 8 | 0.9112 | -0.0002 |
| 0.9117 | 25 | 2 | 3 | 8 | 0.9112 | 0.0005 |
| 0.9047 | 60 | 3 | 0 | 12 | 0.9046 | 0.0001 |
| 0.9049 | 30 | 3 | 0 | 12 | 0.9046 | 0.0003 |
| 0.8681 | 60 | 2 | 4 | 4 | 0.8684 | -0.0003 |
| 0.8686 | 30 | 2 | 4 | 4 | 0.8684 | 0.0002 |
| 0.8594 | 80 | 2 | 2 | 12 | 0.8593 | 0.0001 |
| 0.8601 | 40 | 2 | 2 | 12 | 0.8593 | 0.0008 |
| 0.8474 | 3 | 1 | 5 | 2 | 0.8483 | -0.0009 |
| | | 3 | 3 | 6 | 0.8462 | 0.0012 |
| 0.8410 | 3 | 3 | 2 | 10 | 0.8419 | -0.0009 |
| 0.8360 | 2 | 1 | 2 | 14 | 0.8357 | 0.0003 |
| 0.8290 | 40 | 5 | 1 | 4 | 0.8281 | 0.0009 |
| 0.8287 | 20 | 5 | 1 | 4 | 0.8281 | 0.0006 |
| 0.8266 | 30 | 5 | 0 | 8 | 0.8251 | 0.0015 |
| 0.8260 | 15 | 5 | 0 | 8 | 0.8251 | 0.0009 |
| 0.8133 | 30 | 1 | 0 | 16 | 0.8135 | -0.0002 |
| 0.8036 | 15 | | | | ?? | |
| 0.7942 | 15 | 0 | 6 | 0 | 0.7938 | 0.0004 |
| 0.7941 | 10 | 0 | 6 | 0 | 0.7938 | 0.0003 |
| 0.7905 | 50 | 4 | 2 | 8 | 0.7903 | 0.0002 |
| 0.7908 | 25 | 4 | 2 | 8 | 0.7903 | 0.0005 |
| 0.7800 | 45 | 0 | 2 | 16 | 0.7801 | -0.0001 |
| 0.7800 | 25 | 0 | 2 | 16 | 0.7801 | -0.0001 |

at 2 and 20 min both showed additional lines at low diffraction angles, but the high angles were well defined and sharp, implying better crystallinity. The 20-min run also showed fewer weak, additional lines at the high angles, implying better purity of the product. Runs at 1 min and at 30 sec gave lesser yields of $LaCuO_3$. Runs at 40 min, 1, and 2 hr failed to produce the $LaCuO_3$ structure; their compositions, from the XRD patterns, did not show the same major components. The 2-hr run particularly was notably heterogeneous and well segregated. No particular variance of the lattice parameters was noted as a function of heating time.

Averaging of the lattice parameters derived from least-squares fits to X-ray powder diffraction film data on 25 different runs gave the hexagonal cell parameters $a$ = 5.496 ± 0.010 Å, $c$ = 13.228 ± 0.092 Å, which corresponds to the rhombohedral parameters $a$ = 5.432 ± 0.028 Å, $\alpha$ = 60.78 ± 0.23°. Data collected on a rotating anode X-ray diffractometer gave cell parameters of $a$ = 5.5019 ± 0.0003, $c$ = 13.2121 ± 0.0005 Å, or the equivalent rhombohedral values $a$ = 5.4301 ± 0.0002 Å, $\alpha$ = 60.877 ± 0.001°. These latter compare very favorably with those reported by Demazeau *et al.*; $a$ = 5.431 Å, $\alpha$ = 60.85° (*1*). However, whereas those authors reported an $R$ factor of 7%, we were unable, even with the introduction of an occupancy factor for the oxygen ions, to obtain an $R$ factor less than 17% for the 34 measured reflections, assuming the space group $R\overline{3}c$. Our final refined positions were essentially the same as those which Demazeau *et al.* found with 100% occupancy. Using only the eight lowest angles and strongest reflections from our data brought a reduction in the $R$ factor to 7%. An $R$ factor of 17% could also be achieved for a fit in the $R32$ space group. It is possible that contamination of the intensity data by impurity constituents complicates our interpretations. A pure, single phase sample is needed for further work, but such was not found during this study.

A series of samples was formulated with limited oxygen availability, i.e., $LaCuO_y$, $y$ = 2.5, 2.6, 2.7, 2.8, 2.9, 3.0, using appropriate stoichiometric amounts of $KClO_3$ rather than the excess normally employed. The $LaCuO_3$ structure was only found for $y$ = 2.9 and 3.0; the $c$-cell parameters observed were slightly larger than the $LaCuO_3$ average value. The samples for $x < 2.9$ all contained the usual CuO and $La(OH)_3$ as well as small amounts of an unidentified pattern.

The $LaCuO_3$ product persisted in both atmospheric oxygen and in flowing pure oxygen at 300°C. At 400°C in either environment the $LaCuO_3$ transformed, giving an X-ray pattern that was indexed in the tetragonal system (*21*), with parameters summarized in Table III. A growth of 0.4% in the $c$-axis was observed which suggests that, like the $La_2CuO_4$ family of materials, oxygen deficiencies may be inherent in this purely perovskite structure. When $LaCuO_3$ was heated to 600°C in the DSC study, the residual product exhibited this same tetragonal structure. Recent work by Bringley *et al.* found an oxygen-deficient series $LaCuO_{3-y}$ (*6*). The X-ray diffraction powder pattern for the tetragonal structure obtained in the current study by heating rhombohedral La $CuO_3$, compared with the graphical data given in their paper, shows strong resemblances, particularly to their monoclinic form, as well as several notable differences. This is in marked contrast to their comparison, which noted "no obvious similarities." Their tetragonal form is closely related to the above tetragonal form by $a_W \approx \sqrt{2}\, a_B$, and $c_W \approx 2c_B$.

TABLE III

PARAMETERS OF $LaCuO_3$ WITH TETRAGONAL STRUCTURE

| Composition | $a$ (Å) | $c$ (Å) | Standard deviation | Volume (Å$^3$) |
|---|---|---|---|---|
| $LaCuO_3$ air | 5.415 | 7.785 | 0.0060 | 228.27 |
| $LaCuO_3$ $O_2$ | 5.417 | 7.817 | 0.0059 | 229.38 |
| $LaCuO_3$ DSC | 5.415 | 7.927 | 0.0434 | 232.44 |

### *C. Copper-Substituted $LaCuO_3$*

The effect of substituting metals which should replace the Cu in the $LaCuO_3$ was studied using Cr, Fe, Co, Ni, Zn, Ag, and Tl. Previously $LaNiO_3$ had been reported at ambient pressures (*22*); Demazeau *et al.* (*23*) also formed it under HPHT conditions. A pseudocubic product was reported for $x$ = 0.50 and 0.75 (*4*). The replacement of Cu by Ni in $La_{2-x}Sr_xNiO_4$ did not destroy superconductivity, implying that Cu is not unique to this phenomenon, and that Ni maintains the same conditions favoring it (*24*). The current study found the $LaCuO_3$ structure to exist at all mixtures of Cu and Ni. Figure 2 shows that there is a discontinuity in lattice parameters around $x$ = 0.5, suggesting perhaps two solid solution series or maybe the presence of a second-order transition. Further study is needed to better understand this system.

The next element to the left of Ni in the periodic table is Co; $LaCoO_3$ has been synthesized using conventional high-tempera-

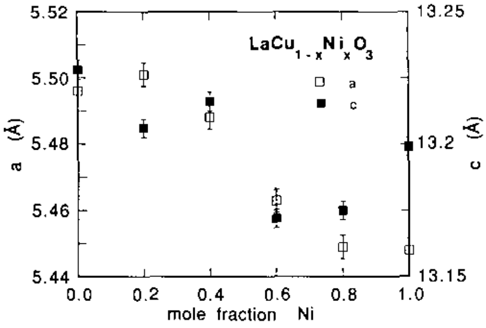

FIG. 2. Effect of composition on the hexagonal lattice parameters of the $LaCu_{1-x}Ni_xO_3$ series.

ture techniques (*25*). Oxygen deficiency has been reported without change to the rhombohedrally distorted perovskite structure (*26*). This study found the rhombohedral $LaCuO_3$ structure to persist at all values of $x$. The substitution of Co also was found to suppress the CuO and $La(OH)_3$ impurities at the $x = 0.4$ and 0.2 levels, respectively, suggesting that reaction is more favorable in this system than in that of $LaCuO_3$.

Moving away from Cu yet further, the series with Fe provided the $LaCuO_3$ structure only for $x = 0.2$, with both $a$ and $c$ somewhat larger than in $LaCuO_3$. For higher Fe contents the orthorhombic $LaFeO_3$ structure was obtained, with the volume increasing linearly by about 3% for the maximum Fe content. Results are given for this structure in Table IV.

An extended paper by Goodenough differentiated several groups for the series of $LaMO_3$ compounds where $M$ was a transition metal of the first row (*27*). In progressing from $M$ = Ti to Ni, three types of behavior were noted: from collective $d$ electrons (Ti), to only the $t_{2g}$ electrons localized (V, Cr, Co, Ni), to fully localized $d$ electrons (Mn, Fe, Co). Note that Co is on the boundary. In this scheme $LaCuO_3$ should also have intermediate character. Since Cr shares this character, it was thought possible that the series Cu–Cr would be of interest. Three sources of Cr, varying in oxidation state, were available, viz, $Cr_2O_3$, $CrO_2$, and $CrO_3$. Mixtures utilizing each of these Cr sources for $x = 0.2$ were reacted at 6.5 GPa and 1500°C for 5 min. The sample with $CrO_3$ did not produce the $LaCuO_3$ structure, while both the lower oxides did. Since $CrO_2$ had the highest yield, an additional study of the series with $x$ = 0.1, 0.3, 0.4, and 0.5 was undertaken. The $LaCuO_3$ structure was not found in any of these subsequent products. The lines for CuO, $La(OH)_3$, and KCl, along with a number of weak, unidentified lines, were found for $x = 0.1$. An unidentified structure occurred over the range $x = 0.3$–$0.5$, which was also found in the $x = 0.2$ product derived from $CrO_3$. A small quantity of $LaCrO_3$ may have been formed for $x \geq 0.3$. the orthorhombic perovskite form previously reported over the range $0.5 \leq x \leq 1.0$ was not observed, nor was the predicted Mott transition around $x = 0.23$ (*28*).

The series with Ag replacing Cu exhibited the $LaCuO_3$ structure for all values of $x$. Calculation of the Goldschmidt tolerance factor for each of the compositions (*29*) gave the ranges, for $Ag^{1+}$, 0.887–0.674, and, for $Ag^{2+}$, 0.887–0.735. Since the perovskite structure is restricted to the Goldschmidt range of 0.75–1.0, this suggests that Ag is divalent in the $LaCuO_3$ structure. The $a$ unit cell parameter increased with $x$, while the $c$

TABLE IV

PARAMETERS FOR PRODUCTS WITH ORTHORHOMBIC $LaFeO_3$ STRUCTURE

| Composition | $a$ (Å) | $b$ (Å) | $c$ (Å) | Standard deviation |
|---|---|---|---|---|
| $LaCu_{0.6}Fe_{0.4}O_3$ | 5.501 | 5.493 | 7.772 | 0.0013 |
| $LaCu_{0.4}Fe_{0.6}O_3$ | 5.514 | 5.523 | 7.801 | 0.0018 |
| $LaCu_{0.2}Fe_{0.8}O_3$ | 5.548 | 5.534 | 7.829 | 0.0013 |
| $LaFeO_3$ | 5.559 | 5.551 | 7.853 | 0.0009 |
| $La_{0.4}Nd_{0.6}CuO_3$ | 5.432 | 5.445 | 7.691 | 0.0035 |

parameter had a minimum around $x = 0.5$; the parameters found for $x = 0.6$ were anomalously large.

Treatment of reactants to form $LaCu_{1-x}Zn_xO_3$ did not lead to the $LaCuO_3$ structure, even for the $x = 0.2$ sample. The reported existence of perovskite-structured oxides of the formula $La_2TiMO_6$, $M$ = Zn, Cu, Ni, or Co (*30*), further emphasizes the lack of a perovskite product in the current study. This complete lack of $LaCuO_3$ structure in the Zn-substituted series coupled with its ubiquitous presence in the Ni series prompted study of the $LaNi_{1-x}Zn_xO_3$ series. The $LaCuO_3$ structure was found in the latter for all values of $x$ except $x = 1.0$, in sharp contrast to the Cu–Zn series. Clearly there are major differences between Cu and Zn which are effective in this structure.

Thallium substitution was investigated, as a replacement for Cu as well as for La. The ionic radius of $Tl^{3+}$ (0.95 Å) indicates it might substitute for the somewhat smaller $Cu^{2+}$ (0.69 Å), whereas $Tl^{1+}$ (1.40 Å) may replace the smaller $La^{3+}$ (1.15 Å); note that $Ba^{2+}$ (1.35 Å) is close to the size of monovalent Tl, whereas the trivalent radius is close to that of $Ca^{2+}$.

For the Tl substitution of Cu in this study only the lower values of $x = 0.2$ and 0.4 were attempted. The products contained $La(OH)_3$, CuO, and small amounts of the high-pressure form of $Tl_2O_3$ (*31*), suggesting that reaction could not take place under these conditions.

### *D. Lanthanum-Substituted $LaCuO_3$*

*1. Divalent cations.* Small to moderate amounts of the La have been substituted in the $La_2CuO_4$ series with divalent cations, without change to the structure and with enhancement of the superconducting critical temperature $T_c$. The effect of such addition was varied in the system $La_{2-x}M_xCuO_4$. The amount of Cu raised to trivalency was approximately equal to $x$ for Sr and Ba (after correcting for increases in oxygen vacancies). For Ca, however, the concentration $[Cu^{3+}]$ was far below $x$, and actually decreased with increasing $x$ for $x > 0.1$. The oxygen defects were also reported to have increased (*32*). These differences may arise from structural strains derived from the different ionic radii of the substituents. Thus formation of $Cu^{3+}$ from the divalent species may not result from such substitution, and the materials of the current study may also reflect such complex interplay of defect concentration and ion size. Where $M$ = Ca, Sr, Ba, or Pb the product showed improved conductivity, but its character remained unchanged; viz, it remained metallic and orthorhombic for La and semiconducting and tetragonal if Nd, Sm, or Gd were used instead of La (*33*). An indication of possible substituent size restrictions may be inferred from work on this same system. The tetragonal $K_2NiF_4$ structure persisted for Ca, Sr, or Ba for $x < 0.3$ (*34*), or to $x < 0.3$ for Ba and $x < 0.5$ for Sr (*35*). For Ca the product remained orthorhombic for $x \leq 0.05$, becoming tetragonal for higher Ca contents (*36*). In the current study substitution with Mg up through $x = 0.8$ produced the $LaCuO_3$ structure, as well as unreacted oxides. The $a$ lattice parameter generally decreased slightly, while the $c$ parameter showed a sharp minimum at $x = 0.4$. The series with Ca found strong persistence of the $LaCuO_3$ structure to at least $x = 0.8$, with a slight increase in both the cell parameters, $a$ and $c$, at the higher values of $x$. The $LaCuO_3$ structure is thus more accepting of these substituents than the $K_2NiF_4$ structure.

An orthorhombic single phase with a perovskite structure was recently reported as superconducting by Khan for $La_{1-x}Sr_xCuO_3$, when $0.05 < x < 0.3$ (*37*). An oxygen-deficient tetragonal product with a composition limited to $0.20 \leq x \leq 0.25$ was reported by Murayama *et al.* (*17*). Subsequent work, however, found no superconductivity down to 10 K (*38*). Neutron diffraction investigation of tetragonal $La_{0.8}Sr_{0.2}CuO_{2.48}$

found random distribution of La and Sr over the same sites (*39*). Other possible products of La and Sr which have been reported include orthorhombic $Sr_2CuO_3$ (*40*) and $La_4 SrCu_5O_y$ (*41*), although no pattern was available to check for the latter. This study found that substitution of Sr for La gave the $LaCuO_3$ structure through $x = 0.8$, with a slight increase in $a$ and a more marked decrease in $c$ as $x$ increased to 0.6, then essentially constant thereafter. The system $La_{2-x}Sr_x CuO_{4-y}$ reportedly maintains the perovskite-related $K_2NiF_4$ structure for Sr contents to maximum values of 1.34 (*42, 43*), 1.2 (*44*), or 1.0 (*41*). One study reported single phase product only for $x < 0.2$ (*45*) and a published phase diagram gave an upper value of 0.90. Another report indicated that this series was orthorhombic for $0 \leq x \leq 0.20$, and tetragonal from this point up to the maximum Sr content (*41*). The $K_2NiF_4$ structure is therefore apparently about as tolerant of Sr substitution as is the $LaCuO_3$ structure under study here.

$BaCuO_{2.5}$ has been prepared starting with $BaO_2$, and from $BaCuO_2$ fired under 400 atm of oxygen (*2*). Structures were not reported, although X-ray patterns were. This study found the $LaCuO_3$ structure to persist for replacement of La with Ba to $x = 0.8$. The $a$ lattice parameter remained unchanged, while the $c$ parameter decreased markedly with increasing $x$. The product with $x = 0.8$ included lines resembling the pattern of $BaNiO_3$ (*46*).

2. *Trivalent cations.* One of the advances in the high-$T_c$ superconductors was the substitution of Y for La, effectively placing the structure under pressure due to the presence of the smaller $Y^{3+}$ ion (*47*). $YCuO_3$ has been synthesized from the oxides at 800°C under 400 atm of oxygen (*2*). The series with Y substituting for La in $LaCuO_3$ was therefore studied. The $LaCuO_3$ structure was not found even for $x = 0.2$, however. Reaction apparently did not occur at 6.5 GPa and 1500°C, however, since CuO and $La(OH)_3$ persisted. The absence of either $Y(OH)_3$ or $Y_2O_3$ suggests the possible substitution of Y into the La compound structure. Additional lines were found for $x \gtrsim 0.6$ which were not identified.

Even though $Sc^{3+}$ is smaller than $Y^{3+}$ (0.745 vs 0.90 Å; *48*), the $LaCuO_3$ structure was found for $x = 0.2$ with lattice parameters essentially the same as the unsubstituted material. A new, unidentified pattern was noted for $x \geq 0.6$, which only had lines with $d$ values < 2.81 Å.

3. *Lanthanides.* Substitution of other lanthanides for La was prompted by various reports that the pure end members were not obtainable, and by recent work with the electron-carrier $Ln_{2-x}Ce_xCuO_{4-y}$ (Ln = Pr, Nd, Sm) superconducting compounds (*49, 50*). Studies in the system $Ln_2CuO_4$ found an orthorhombic, metallic product for Ln = La, and a tetragonal, semiconducting one for Ln = Pr–Gd. No similar product was formed for Ln = Tb–Lu (*32*). Clearly, there is a difference between La and the following lanthanides. Work with the niccolates had found ready replacement of La by Sm with no structural change up to $x = 0.30$, a new phase for $0.50 \leq x \leq 0.85$, and no compound formation from the oxides for higher values of $x$ (*22*). As will be seen in the following, unlike the $YBa_2Cu_3O_{7+y}$ structure where replacement of Y with a wide variety of Ln ions had little effect on either structure or superconductivity (*20*), the $LaCuO_3$ structure is quite sensitive to such substitution.

Previous attempts at synthesis of $CeCuO_3$ (*1*), $CeNiO_3$ (*23*), and $CeCoO_3$ proved unsuccessful. $Ce_{1-x}Sr_xCoO_3$ could not be formed from mixed acetates; the stability of $CeO_2$ prevailing instead (*51*). This prompted inclusion of the $La_{1-x}Ce_xCuO_3$ series in this study. The $LaCuO_3$ structure was found to persist up through $x = 0.4$, with a marked reduction in cell size for $x = 0.4$. No reaction occurred at the standard HPHT conditions for higher values of $x$.

HPHT has been reported to be ineffective for synthesis of $PrCuO_3$ (*1*) or $PrNiO_3$ (*23*). As with the Ce study, substitution of La by Pr in this study resulted in the $LaCuO_3$ structure up through $x = 0.4$. The lattice parameters had sharp minima at $x = 0.2$. For $x > 0.4$ only the constituent oxides were detected, with the possibility of La substitution in the $PrO_2$.

Although $NdNiO_3$ has been reported (*23*), $NdCuO_3$ did not result from HPHT synthesis conditions (*1*). Our survey of this system found persistence of the $LaCuO_3$ structure through $x = 0.4$, with a decrease in the $a$ lattice parameter, and to a lesser degree, in the $c$ parameter. For $x \geq 0.6$, lines assignable to neither CuO nor $La(OH)_3$ could be fitted reasonably well to the cubic cell reported for $NdCoO_3$ by reference to JCPDS card #25-1064, or to an orthorhombic cell, with a constant cell volume as a function of $x$. For $x = 0.6$ the cubic parameter was $a = 7.683 \pm 0.007$ Å, and the orthorhombic parameters $a = 5.432$, $b = 5.445$, and $c = 7.691$ Å (each ±0.003 Å).

*4. Tetravalent cations.* Preliminary calculations (*52*) suggested that an excess of electrons rather than the deficit provided by the divalent ions might be beneficial, and that a better match to the ionic radius of the $La^{3+}$ would be obtained with Zr or Hf. Deng-Ping previously proposed the possibility of electron-carrier tetravalent doping in the system $La_{2-x}M_xCuO_4$, with $M$ = Zr, Ce, Hf, or Sn; these systems were considered important by the theorists, in terms either of understanding electron-pairing mechanisms or of explaining negative results (*53*). Consequently series with Ti and Zr were studied. Previous work on $LaTi_{0.5}CuO_3$, synthesized from the oxides in air at 1000°C, found divalent Cu in the cubic products (cell edges twice those of the primitive perovskite cells) (*28*). For Ti preliminary synthesis runs were attempted with either Ti metal powder or $TiO_2$ as the Ti source. With the metal and $x = 0.02$, the $LaCuO_3$ structure was strongly present. Using $TiO_2$ with $x = 0.1$ gave a product whose XRD pattern was nearly a pure $LaCuO_3$ structure, with expansion of the $a$ and shortening of the $c$ cell dimensions. The Ti series (using $TiO_2$) did not yield the $LaCuO_3$ structure for any value of $x > 0.2$. A new, relatively simple, unidentified structure was generated for $x = 0.2$–$0.8$. Unreacted rutile, CuO, and KCl resulted from the $x = 1.0$ mix.

The $LaCuO_3$ structure was observed in moderate amounts for the Zr series, with $ZrO_2$ as the Zr source, decreasing through $x = 0.8$. Monoclinic zirconia and CuO were found in all runs and were the only observed products with $x = 1.0$. There was a slight decrease in the $a$ lattice parameter, and a larger increase in the $c$ parameter, going from $x = 0.2$ to $x = 0.8$. Residual KCl was also noted in all these runs.

*5. p-Electron substituents.* As noted above in the section on Cu substitution, an attempt was made to substitute Tl for either the Cu or the La. In the latter case the products ($La(OH)_3$ and CuO, along with KCl) indicated that no reaction took place. In the $x = 0.6$ sample there was apparently a small amount of the $LaCuO_3$ structure found, indicated by the presence of four of the stronger lines of that latter structure which were free of interference from lines of the other products.

Studies of the system $La_{2-x}Pb_xCuO_4$ treated Pb as divalent (*33, 34*). The tetragonal $K_2NiF_4$ structure was found to persist only for $x \leq 0.1$, while the substitution increasingly activated the semiconductivity up to $x \leq 0.3$, but produced no superconductivity (*34*). Replacement of La with Pb was also undertaken in this study with the same coarse survey grid series. Due to interest sparked by the susceptibility and resistivity results for these samples, however, additional compositions were formed in the higher Pb-content regions, with $x = 0.75$, 0.85, 0.90, and 0.95. None of the Pb runs exhibited the $LaCuO_3$ structure. The products always contained $PbO_2$, whose orthorhombic cell dimensions were unaffected by the varied starting compositions.

Antimony produced the $LaCuO_3$ structure for $x = 0.2$, with similar cell size to that produced with the same content of Bi. The oxides were noted for higher values of $x$; viz, $Sb_2O_3$ for $x \geq 0.6$ and $\beta$-$Sb_2O_4$ for $x = 1.0$.

Unlike the Pb results, the Bi replacement series gave the $LaCuO_3$ structure for $x \leq 0.6$, though the yield diminished markedly with increasing Bi content. Tentatively $Bi_2Cu_2O_5$ was identified for $0.4 \leq x\ 0.8$, and an additional, unknown pattern was found for $x \geq 0.4$. Although the $a$ cell parameter remained near the unsubstituted $LaCuO_3$ value, the $c$ parameter was markedly depressed for $x \geq 0.4$.

Electron microscopy of samples from the Ca, Ba, Ti, and Zr series found a common anisotropic matrix and twinning of perhaps 50% of the grains. Particles were typically 5–10 μm in size. Some grains showed interpenetration by another component, and some grain boundaries contained a small amount of another phase.

It should perhaps be noted that many of the La-substituted products had lattice parameters close to the average found for $LaCuO_3$, viz, in the ranges $a = 5.496 \pm 0.013$, $c = 13.23 \pm 0.03$. The Ti- and Ce-substituted products fell outside this range, while the Cu-substituted products were rather markedly outside this range. This may indicate somewhat less structural sensitivity to substitution on the La positions than on those occupied by Cu in the $LaCuO_3$ structure.

### *E. Electrical Conductivity*

The multiphase product slugs resulting from our HPHT synthesis were generally found to be insulators using a two-probe rapid survey system. The $La_{1-x}Pb_xCuO_3$ samples with $x > 0.75$, on the other hand, were relatively good conductors. Details of these results are given elsewhere (*54*). It may be that, as with $La_2CuO_4$ (*53, 55*), slight variations in oxygen content are possible, and that these do occur between the various synthesis methods, giving rise to either hole or electron conduction in the resultant defective products.

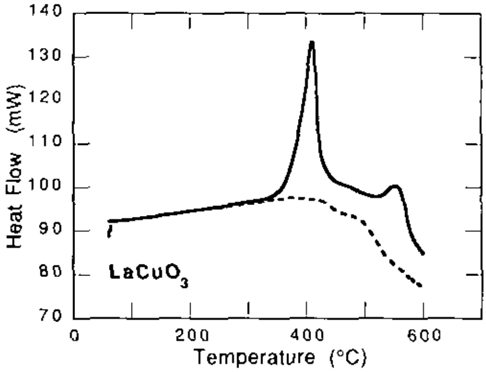

FIG. 3. DSC traces for $LaCuO_3$ after washing to remove KCl. Solid line is from initial heating to 600°C, showing endothermic peaks at 411°C and 559°C. Dotted line is from the second heating, showing permanent change in the material.

### *F. Magnetic Susceptibility*

Magnetic susceptibility was measured by several techniques during the progress of this study due to changing equipment availabilities. Most of these results have been reported elsewhere (*54*). Since that publication the series $La_{1-x}Tl_xO_3$, $LaCu_{1-x}Co_xO_3$, and $LaCu_{1-x}Tl_xO_3$ were prepared as detailed above, and were found, like the earlier samples, to show no sign of superconductivity to a sensitivity of at least 1% of the sample volume.

### *G. Thermal Analysis*

A number of samples were studied using DSC. The starting materials, $LaCuO_3$, $La_{1-x}Ca_xCuO_3$ ($x = 0.05$, $0.1$), and $La_{0.9}Sr_{0.1}CuO_3$ were investigated. The $LaCuO_3$ and the Ca-substituted $LaCuO_3$ showed endothermic peaks. Figure 3 shows the DSC traces for $LaCuO_3$ for first and second heatings to 600°C. The endothermic

TABLE V

DSC RESULTS

| Material | Peak (°C) | Enthalpy (J/g) |
|---|---|---|
| $LaCuO_3$ | 411 | 587 |
| | 559 | 138 |
| $La_{0.95}Ca_{0.05}CuO_3$ | 392 | 484 |
| | 526 | 306 |
| $La_{0.90}Ca_{0.10}CuO_3$ | 401 | 197 |
| | 526 | 133 |
| $La_{0.90}Sr_{0.10}CuO_3$ | none | |

peaks noted on the first heating were absent in the subsequent reheating. The temperatures for these peaks are given in Table V, along with the enthalpy changes. For the related compound $LaCoO_3$ an endothermic transition has been reported at 937°C which was evidently electronic in nature since there was no structure change; other activity was noted at 125–375°C and around 650°C (*27*). The structure was reported stable for the Co compound to around 1000°C (*50*). For $LaMnO_3$ similar endothermic peaks were observed around 900°C that were associated with a metal–insulator transition which occurred without structural change; substitution of 20% Ca, however, suppressed all changes in the differential thermal analysis (*56*). For $LaCuO_3$ the thermal instability noted in this study resulted in a structure change as noted below. Figure 4 shows DSC traces for $La_{0.90}Ca_{0.10}CuO_3$ and $La_{0.90}Sr_{0.10}CuO_3$. The Ca-substituted product showed a similar loss of peaks after the first heating, while the Sr-substituted material gave no peaks on either the initial heating, nor any change in a second heating. X-ray diffraction has shown the $LaCuO_3$ structure to be present in both the Ca- and Sr-substituted materials. This implies that Sr stabilized the $LaCuO_3$ structure (as did Ca in $LaMnO_3$; *56*) to at least 600°C at ambient pressure, and that the peaks reflected a transformation process in the other samples. Recent TGA studies support this. They reported that $La_{1-x}Sr_xCuO_{3-y}$ showed no appreciable weight change up to 1000°C (*38*). However, these same workers reported that heating these compounds to 860°C and above resulted in decomposition into a series of phases richer in La and/or Cu. No explanation of this discrepancy was given. It might be noted here that $LaNiO_3$ and $NdNiO_3$ have both been found to decompose to $Ln_2NiO_4$ and NiO at around 800°C (*23*). The cuprates are thus somewhat less stable than the corresponding niccolates, cobaltates, or manganites.

The $LaCuO_3$ product which was retrieved after the second heating excursion to 600°C was examined by X-ray diffraction. A new, simpler pattern was found, which has been indexed on a tetragonal cell as noted above (*21*). This gave a calculated density of 7.20 g/cm$^3$, for a 0.3% decrease in density in going from the rhombohedral HPHT phase to this new, thermally generated tetragonal phase.

## Discussion

The Goldschmidt tolerance factor *t* has a somewhat higher limit for perovskite-de-

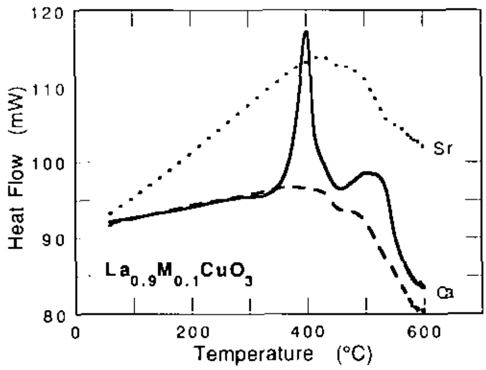

FIG. 4. DSC traces for $La_{0.90}Ca_{0.10}CuO_3$—initial heating, solid line; second heating, dashed line—and $La_{0.90}Sr_{0.1}CuO_3$—initial heating, dotted line—which show the absence of thermally induced transformation. There is a difference in the base-line correction for the two compounds.

rived structures which are hexagonal than for those which are cubic (*57*). The largest tolerance factor observed in this work for the $LaCuO_3$ rhombohedral structure is that for $La_{0.2}Ba_{0.8}CuO_3$, where $t = 0.98$. The lower limit for the tolerance factor is 0.75 (*27*). Among those systems showing the $LaCuO_3$ structure in this study the lowest values observed were 0.735 for $LaCu_{0.2}Ag_{0.8}O_3$, and 0.796 for $La_{0.2}Zr_{0.8}CuO_3$ and $La_{0.2}Mg_{0.8}CuO_3$. The Ag products with $x = 0.8$ and 1.0 give values below the lower limit. These limits are derived geometrically, and this suggests that the effective radius of Ag, at the HPHT conditions of synthesis, varies from those published for ambient conditions.

None of the conditions or compositions presented herein have yielded superconductivity above the minimum test temperatures, which varied from 5–50 K. This does not fully rule out the possibility, and there are many other combinations of composition, temperature, treatment procedure, time, pressure, flux, etc., which could be tried. It was thought for some time that the $La_2CuO_4$ system was totally insulating, requiring doping to become superconducting (*53*). Subsequently an involved heat treatment with slow cooling in pure oxygen was found to yield a superconducting product (*55*). A common theme in the study of these copper oxide ceramics has been the critical nature of the processing procedures chosen. Although the additional restraints of working at HPHT restricts some processing options, a number of combinations are still possible. Within the limits chosen for this study, however, the tentative conclusion must be that the $LaCuO_3$ structure does not contain all the criteria requisite for superconductivity.

The environment of the Cu–O linkage does, it should be noted, differ markedly between $La_2CuO_4$ and $LaCuO_3$, as was noted elsewhere (*54*). In both cases the Cu is octahedrally surrounded by O. In the first case it forms a two-dimensional structure with no linkages along the *c*-axis due to the insertion of an NaCl-structured layer of La–O. In $LaCuO_3$, however, the Cu–O forms a three-dimensional structure of corner-linked octahedra. The –Cu–O–Cu–O– chains are not linear in this structure, which may itself disrupt potential superconductivity. Conversely, the increased dimensionality (three vs two in $La_2CuO_4$) may be the impediment, as proposed recently by the calculations of Randeria *et al.* (*58*). The current work may, therefore, provide an important clue to the origin of superconductivity in the copper oxide ceramic materials.

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## References

*1.* G. Demazeau, C. Parent, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **7,** 913 (1972).

*2.* M. Arjomand and D. J. Machin, *J. Chem. Soc. Dalton Trans.* **1975,** 1061.

*3.* P. K. Gallagher, D. W. Johnson, Jr., and E. M. Vogel, *J. Am Ceram. Soc.* **60,** 28 (1977).

*4.* K. Vidyasagar, J. Gopalakrishnan, and C. N. R. Rao, *J. Solid State Chem.* **58,** 29 (1985).

*5.* H. Arai, T. Yamada, K. Eguchi, and T. Seiyama, *App. Catal.* **26,** 265 (1986).

*6.* J. F. Bringley, B. A. Scott, S. J. La Placa, R. F. Boehme, T. M. Shaw, M. W. McElfresh, S. S. Trail, and D. E. Cox, *Nature* **347,** 263 (1990).

*7.* O. M. Sreedharan, C. Mallika, and K. Swaminathan, *J. Mater. Sci.* **23,** 2735 (1988).

*8.* J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64,** 189 (1986).

*9.* H. T. Hall, *Rev. Sci. Instrum.* **29,** 267 (1958); **33,** 1278 (1962).

*10.* A. W. Webb, *J. Phys. Chem. Solids* **34,** 501 (1973).

*11.* A. W. Webb, T. L. Francavilla, R. A. Meussner, and R. M. Waterstrat, in "High-Pressure Science and Technology" (K. D. Timmerhaus and M. S. Barber, Eds.), Vol. 1, pp. 297–308, Plenum, New York (1979).

*12.* Hk. Müller-Buschbaum, *Angew. Chem. Int. Ed. Engl.* **16,** 674 (1977).

13. B. Grande and Hk. Müller-Buschbaum, *Z. Naturforsch. B* **31,** 405 (1976).
14. B. Grande and Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **417,** 68 (1975).
15. B. Grande and Hk. Müller-Buschbaum, *A. Anorg. Allg. Chem.* **429,** 88 (1977).
16. W. Klemm, G. Wehrmeyer, and H. Bade, *Z. Elektrochem.* (*Ber. Bunsenges. Phys. Chem.*) **63,** 56 (1959).
17. N. Murayama, S. Sakaguchi, F. Wakai, E. Sudo, A. Tsuzuki, and Y. Torii, *Jpn. J. Appl. Phys.* **27,** L55 (1988).
18. M. Arjomand and D. J. Machin, *J. Chem. Soc. Dalton Trans.* **1975,** 1055.
19. C. Chen, B. E. Watts, B. M. Wanklyn, P. A. Thomas, and P. W. Haycock, *J. Crystal Growth* **91,** 659 (1988).
20. K. Fueki, K. Kitazawa, K. Kishio, T. Hasegawa, S-i. Uchida, H. Takagi, and S. Tanaka, *in* "Chemistry of High-Temperature Superconductivity" (D. L. Nelson, M. S. Whittingham, and T. F. George, Eds.), pp. 38–48 (and references therein), Chemical Society, Washington, DC (1987).
21. A. W. Webb, E. F. Skelton, S. B. Qadri, E. R. Carpenter, Jr., M. S. Osofsky, R. J. Soulen, and V. LeTourneau, *Phys. Lett.* **137,** 205 (1989).
22. A. Wold, B. Post, and E. Banks, *J. Am. Chem. Soc.* **79,** 4911 (1957).
23. G. Demazeau, A. Marbeuf, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.* **3,** 582 (1971); G. Demazeau, A. Marbeuf, M. Pouchard, P. Hagenmuller, and J. B. Goodenough, *C.R. Acad. Sci. Paris* **272,** 2163 (1971).
24. Z. Kakol, J. Spalek, and J. M. Honig, *J. Solid State Chem.* **79,** 288 (1989).
25. F. Askham, I. Fankuchen, and R. Ward, *J. Am. Chem. Soc.* **72,** 3799 (1950).
26. G. H. Jonker and J. H. Van Santen, *Physica* **19,** 120 (1953).
27. J. B. Goodenough, *Czech. J. Phys. B* **17,** 304 (1967).
28. Y. Hirai and K. Kubota, *J. Appl. Phys.* **64,** 3051 (1988).
29. O. Fukunaga and T. Fujita, *J. Solid State Chem.* **8,** 331 (1973).
30. N. Ramadass, J. Gopalakrishnan, and M. V. C. Sastri, *J. Inorg. Nucl. Chem.* **40,** 1453 (1978).
31. C. Prewitt, *Inorg. Chem.* **8,** 1985 (1969).
32. K. Oh-ishi, M. Kikuchi, Y. Syono, N. Kobayashi, T. Sasaoka, T. Matsuhira, Y. Muto, and H. Yamauchi, *Jpn. J. Appl. Phys.* **27,** L1449 (1988).
33. I. S. Shaplygin, B. G. Kakhan, and V. B. Lazarev, *Zh. Neorgan. Khimii* **24,** 1478 (1979) [*Russ. J. Inorg. Chem.* **24,** 820 (1979)].
34. D. U. Gubser, R. A. Hein, S. H. Lawrence, M. S. Osofsky, D. J. Schrodt, L. E. Toth, and S. A. Wolf, *Phys. Rev. B* **35,** 5350 (1987).
35. K. Oh-ishi, M. Kikuchi, Y. Syono, K. Hiraga, and Y. Morioka, *Jpn. J. Appl. Phys.* **26,** L484 (1987).
36. K. Kojima, K. Ohbayashi, M. Udagawa, and T. Hihara, *Jpn. J. Appl. Phys.* **27,** L852 (1988).
37. Y. Khan, *J. Mater. Sci. Lett.* **6,** 1387 (1987).
38. N. Murayama and Y. Torii, *Mater. Sci. Eng. A* **109,** 307 (1989).
39. L. Er-Rakho, C. Michel, and B. Raveau, *J. Solid State Chem.* **73,** 514 (1988).
40. C. L. Teske and Hk. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **371,** 325 (1969).
41. H. Kitaguchi, M. Ohno, M. Kaichi, J. Takada, A. Osaka, Y. Miura, Y. Ikeda, M. Takano, Y. Bando, Y. Takeda, R. Kanno, and O. Yamamoto, *Nippon Seramnikkusu Kyokai Gakujutsu Ronbunshi* **96,** 397 (1988) [*J. Ceram. Soc. Jpn. Inter. Ed.* **96,** 388 (1988)]; *Chem. Abs.* **109,** 42413m (1988).
42. N. Nguyen, J. Choisnet, M. Hervieu, and B. Raveau, *J. Solid State Chem.* **39,** 120 (1981).
43. C. Michel and B. Raveau, *Rev. Chim. Miner.* **21,** 407 (1984).
44. C. Chauvin, C. Michel, D. E. Williams, and B. C. Tofield, *Mater. Chem. Phys.* **13,** 197 (1985).
45. Y. Khan, *J. Mater. Sci. Lett.* **6,** 1221 (1987).
46. J. J. Lander, *Acta Crystallogr.* **4,** 148 (1951).
47. M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, *Phys. Rev. Lett.* **58,** 908 (1987).
48. R. D. Shannon, *Acta Crystallogr. A* **32,** 751 (1976).
49. Y. Tokura, H. Takagi, and S. Uchida, *Nature* (*London*) **337,** 345 (1989).
50. G. Demazeau, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.* **9,** 202 (1974).
51. H. Ohbayashi, T. Kudo, and T. Gejo, *Jpn. J. Appl. Phys.* **13,** 1 (1974).
52. W. E. Pickett, private communication.
53. X. Deng-Ping, *J. Phys. C.* **21,** L31 (1988).
54. A. W. Webb, E. F. Skelton, S. B. Qadri, V. Browning, and E. R. Carpenter, Jr., *Phys. Rev. B* **45,** 2480 (1992).
55. P. M. Grant, S. S. P. Parkin, V. Y. Lee, E. M. Engler, M. L. Ramirez, J. E. Vazquez, G. Lim, R. D. Jacowitz, and R. L. Greene, *Phys. Rev. Lett.* **58,** 2482 (1987).
56. H. Taguchi and M. Shimada, *J. Solid State Chem.* **63,** 290 (1986).
57. Y. Syono, S. Akimoto, and K. Kohn, *J. Phys. Soc. Jpn.* **26,** 993 (1969).
58. M. Randeria, J.-M. Duan, and L.-Y. Shieh, *Phys. Rev. B* **41,** 327 (1990).