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New phases induced by hydrogen reduction and by subsequent oxidation of L_2CuO_4 (L =La,Pr,Nd,Sm,Eu,Gd)

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We report the synthesis of new compounds $L_2CuO_{3.5}$ (L =Pr,Nd,Sm,Eu,Gd) and $La_2CuO_{3.67}$, obtained by heating conventionally prepared L_2CuO_4 powders in a 5 mol % H_2/He atmosphere at low temperatures ($\simeq 300\,^{\circ}C$). The structures of the La, Pr, and Nd compounds appear related to that of Sr_2CuO_3, whereas those of the Sm, Eu, and Gd compounds are different. A new Nd_2CuO_4-type (T') $La_2CuO_{4+\delta}$ system was synthesized by oxidation of $La_2CuO_{3.67}$ at 300–500 °C; the oxygen contents are exceptionally high, ranging from 4.10 to 4.42. Annealing $La_2CuO_{3.67}$ above 620 °C in oxygen converts it to the original K_2NiF_4-type (T-phase) structure, but with excess oxygen (up to 4.06) and with smaller orthorhombicity compared to the La_2CuO_4 starting material. Oxidation of the other $L_2CuO_{3.5}$ phases (L =Pr,Nd,Sm,Eu,Gd) above 300 °C leads to recovery of the original T' structures, with oxygen contents ranging from 3.98 (Eu,Gd) to 4.03 (Nd). Magnetization measurements in a field of 50 G did not reveal superconductivity in any of the samples above 5 K.

INTRODUCTION

The nature of the Cu-O networks in the high-T_c cuprate superconductors is intimately related to the doping and superconducting properties. Various configurations are found. For instance, the $La_{2-x}Sr_xCuO_4$ system[1] has the K_2NiF_4-type (T-phase) structure containing edge-shared CuO_6 octahetra arranged in a planar array, and $Nd_{2-x}Ce_xCuO_4$ (Ref. 2) has the Nd_2CuO_4-type (T'-phase) structure in which the apical oxygens in the T structure are shifted away from the Cu atoms so as to form lines of oxygen atoms along the c axis perpendicular to the CuO_2 planes. The structure of $YBa_2Cu_3O_7$ (Ref. 3) contains both CuO_2 plane and Cu-O chain elements. Nonsuperconducting[4] Sr_2CuO_3 (Ref. 5) (S-phase) has isolated CuO_3 chains running along the a axis of the orthorhombic structure. The T, T', and S structures are shown in Fig. 1. From Fig. 1, removing one-half of the oxygens in the CuO_2 plane transforms the T structure to the S structure, whereas translating the apical oxygens to positions on the faces of the unit cell converts the T phase to the T' phase. Transitions between the T', T, and S phases were found in the Nd_2CuO_4-Sr_2CuO_3 system.[4] Annealing T-phase La_2CuO_4, La_2NiO_4, and La_2CoO_4 in oxygen at various pressures induces formation of oxygen-rich phases, with two-phase regions between these phases and the stoichiometric La_2TO_4 (T=Cu,Ni,Co) compounds.[6,7] In the case of La_2CuO_4, oxygen-rich samples with overall stoichiometry $La_2CuO_{4.08}$ and $La_2CuO_{4.03}$ were obtained in which the oxygen-rich phase showed bulk superconductivity below $\simeq$40 K.

Herein, we report that exposing L_2CuO_4 (L=La,Pr,Nd,Sm,Eu,Gd) compounds to hydrogen at low ($\simeq 300^{\circ}$ C) temperatures leads to new $L_2CuO_{4-\delta}$ compounds, where $\delta=\frac{1}{3}$ for L =La and $\delta=\frac{1}{2}$ for L=Pr, Nd, Sm, Eu, and Gd. The La, Pr, and Nd compounds appear to have structures related to that of Sr_2CuO_3. Hydrogen-treating the T^*-type compounds[8–11] $La_{1.1}Dy_{0.9}CuO_4$ and $La_{1.3}Tb_{0.7}CuO_4$ similarly also leads to new compounds, where $\delta=0.39$ for the Dy compound. We further report the synthesis of the T-phase system $La_2CuO_{4+\delta}$ containing excess oxygen ($\delta \le 0.06$). Finally, we report the synthesis of a new T'-phase system $La_2CuO_{4+\delta}$ which has a high excess oxygen solubility ($0.10 \le \delta \le 0.42$). None of the above compounds exhibit superconductivity above 5 K as determined by magnetization measurements in a field of 50 G. The synthesis of new $La_{2-x}Sr_xCuO_{4\pm\delta}$ and $La_{2-x}Ca_xCuO_{4\pm\delta}$ compositions will be reported separately.[12] A brief summary of these results, along with magnetic susceptibility and resistivity measurements on some of the samples, was presented previously.[13]

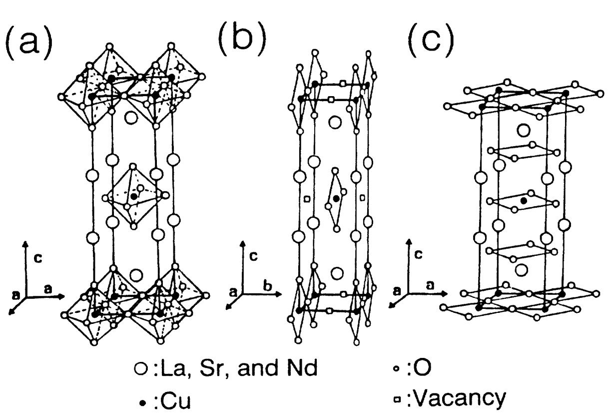


FIG. 1. Structures of (a) La_2CuO_4 (T phase), (b) Sr_2CuO_3 (S phase), and (c) Nd_2CuO_4 (T' phase), after Ref. 4.

EXPERIMENTAL

Powder samples of *T*-phase La_2CuO_4 and *T'*-phase L_2CuO_4 (L=Pr,Nd,Sm, Eu, Gd) were prepared from stoichiometric mixtures of CuO and predried L_2O_3. The ground powders were sintered in air for 12 h at 925 °C and 1 h at 1100 °C with several intermediate grindings. The final samples were air-quenched from 925 °C to room temperature and found to be single phase by powder x-ray diffraction. x-ray data were obtained using a Rigaku diffractometer. Lattice parameters were determined using Si powder as an internal standard. Oxygen contents were determined in 5 mol % H_2/He using a Perkin-Elmer TGA 7 thermogravimetric analyzer (TGA) with an accuracy of ±0.01. Magnetization data were obtained using a Quantum Design superconducting quantum interference device (SQUID) magnetometer.

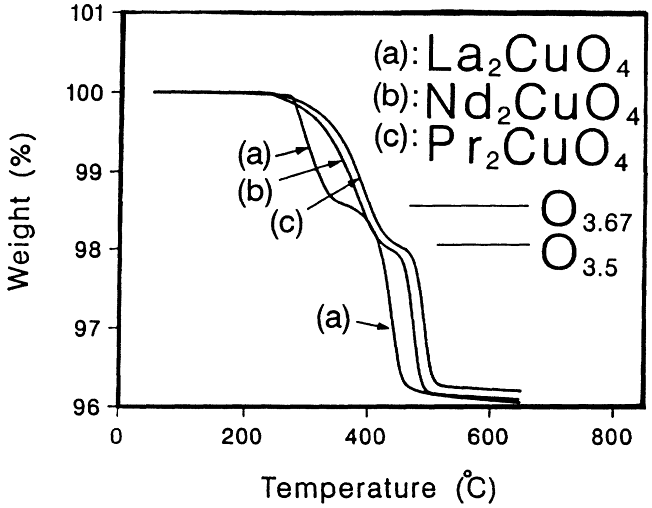
RESULTS

A. $L_2CuO_{4-\delta}$ compounds (L=La,Pr,Nd,Sm,Eu,Gd)

Weight versus temperature profiles obtained using the TGA in 5 mol % H_2/He at a temperature scan rate of 5 °C/min for the L_2CuO_4 starting materials are shown in Fig. 2. Inflection points in most of the curves are seen at $\simeq$350–450 °C, suggesting the formation of new reduced oxygen content phases. To check this possibility, isothermal reductions of the starting compounds in the same gas mixture were carried out at $\simeq$300 °C (below the inflection point temperatures). Figure 3 shows a typical isothermal TGA profile for La_2CuO_4 at 330 °C. The product after 1 h has a composition $La_2CuO_{3.67}$ and is very loose and fine grained compared with the starting material. The x-ray diffraction pattern of this product is shown in Fig. 4(a). It is very similar to that of *S*-phase Sr_2CuO_3 shown in Fig. 4(b), but with extra peaks as compared to Fig. 4(b). The small grain size, lattice disorder, and/or the material's metastable nature (see below) may be responsible for the broadened x-ray peaks. Using longer isothermal reduction times at 330 °C or the same time at higher temperatures usually decompose the samples into a mixture of Cu metal and La_2O_3. The same *S* phase, but with somewhat higher oxygen contents up to 3.76, was obtained at lower gas flow rates and showed different intensities for certain of the x-ray diffraction peaks compared with samples with oxygen content 3.67.

Isothermal hydrogen reductions of the L_2CuO_4 (L=Pr,Nd) starting materials similar to that of La_2CuO_4 above yielded products with oxygen stoichiometry 3.50 and x-ray patterns as shown in Figs. 4(c) and (d). The x-ray patterns of the $L_2CuO_{3.5}$ phases with L=Sm, Eu, and Gd are shown in Fig. 5. The major differences between the $L_2CuO_{3.5}$ and $La_2CuO_{3.67}$ phases are that the former do not show significant grain size reductions after treatment and need much longer times ($\gtrsim$ 10 h, depending on the L ion) at 300 °C to obtain single-phase products without the occurrence of decomposition.

We successfully indexed the x-ray patterns of $La_2CuO_{3.67}$ and of $L_2CuO_{3.5}$ with L=Pr and Nd, but not with L=Sm, Eu, or Gd, on the basis of the orthorhombic



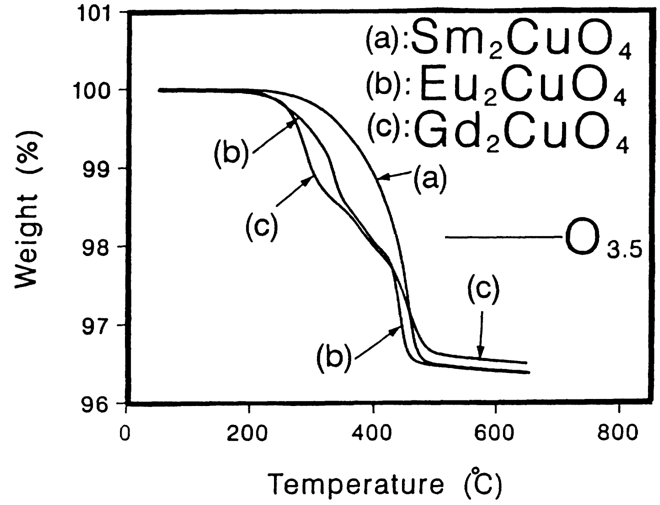


FIG. 2. Sample weight vs temperature in 5 mol % H_2/He upon increasing the temperature at a rate of 5 °C/min for L_2CuO_4 (L=La,Pr,Nd,Sm,Eu,Gd) compounds.

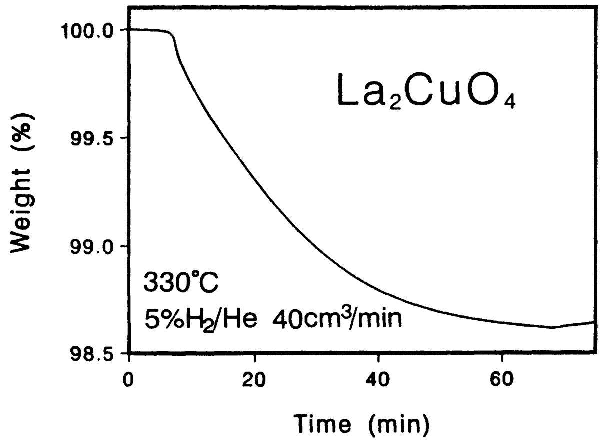


FIG. 3. Isothermal sample weight at 330 °C vs time for $\simeq$100 mg of La_2CuO_4 in a 5 mol % H_2/He atmosphere. The final oxygen content is $\simeq$3.67 and the product has a single-phase Sr_2CuO_3-type structure.

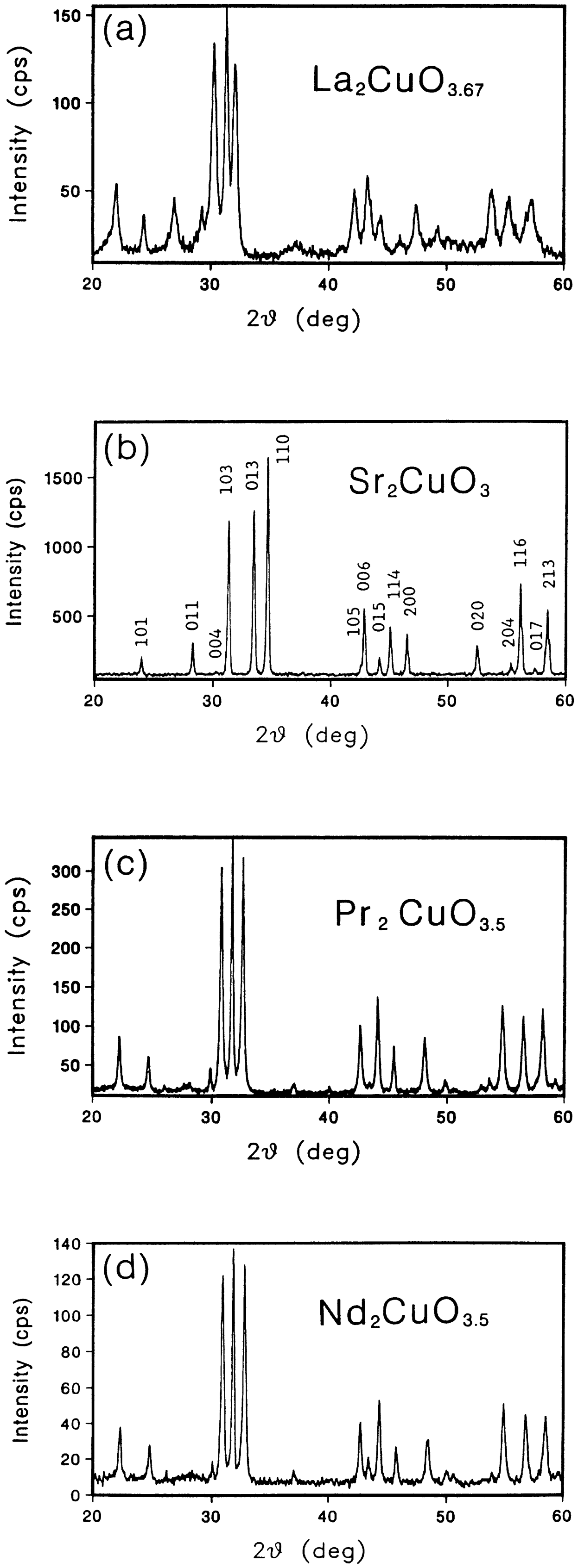


FIG. 4. Powder x-ray diffraction patterns of (a) $La_2CuO_{3.67}$, (b) Sr_2CuO_3, (c) $Pr_2CuO_{3.5}$, and (d) $Nd_2CuO_{3.5}$ using Cu $K\alpha$ radiation.

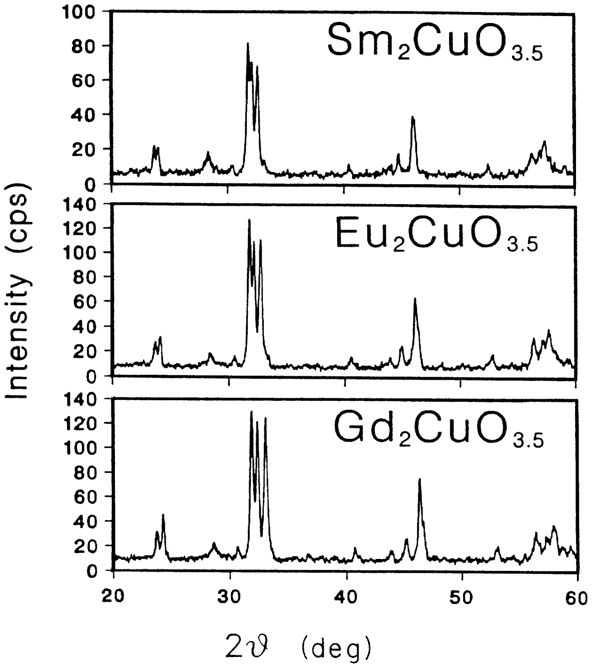


FIG. 5. Powder x-ray diffraction patterns of $L_2CuO_{3.5}$, where L=Sm,Eu, and Gd.

(*Immm*) Sr_2CuO_3 unit cell. The lattice parameters are listed in Table I. A significant increase in cell volume was observed in the La, Pr, and Nd samples relative to those of the respective L_2CuO_4 starting materials. *S*-phase $La_2CuO_{3.67}$ has a compressed *c* axis and elongated *a* and *b* axes and a cell volume approximately 6% larger than the original *T*-phase La_2CuO_4. The unit-cell volumes of $Pr_2CuO_{3.5}$ and $Nd_2CuO_{3.5}$, on the other hand, are only about 1% larger than the original *T*′-phase cell volumes. The $L_2CuO_{3.5}$ compounds have the same stoichiometry as the known compounds $Ca_2(Fe,Mn)O_{3.5}$.[14,15]

B. Nd_2CuO_4-type (*T*′-phase) $La_2CuO_{4+\delta}$

T′-phase $La_2CuO_{4+\delta}$ samples were obtained from the above *S*-phase $La_2CuO_{3.67}$ samples by heating under an oxygen flow at relatively low temperatures. Figure 6(a) shows a typical TGA profile for a $La_2CuO_{3.67}$ sample heated in an oxygen flow of 40 cm^3/min as the temperature increased from 50 to 850 °C at a rate of 5 °C/min. Remarkably, the oxygen content increases to 4.42 at $\simeq$300 °C, far above the stoichiometric value of 4, then decreases with further increase in temperature. Surprisingly, x-ray diffraction analysis revealed that if the experiment is interrupted when the temperature is 300 to 500 °C and the sample cooled to room temperature, the sample showed the *T*′ structure rather than *T* structure of the La_2CuO_4 starting material. On the other hand, samples obtained by interrupting the experiments at temperatures above 600 °C showed the *T* structure. The *T*′ structure appears to be metastable, since once the *T* structure has formed at the higher temperatures, the *T*′ structure and associated large oxygen excess do not reappear upon

TABLE I. Summary of samples studied by powder x-ray diffraction at 295 K.

Sample	Structure	a (Å)	b (Å)	c (Å)	V (Å^3)
$La_2CuO^a_{4.00}$	T	3.792^b	3.825^b	13.170	191.02^b
$Pr_2CuO^a_{4.00}$	T'	3.958		12.288	192.50
$Nd_2CuO^a_{3.99}$	T'	3.937		12.150	188.32
Sr_2CuO_3	S	3.906	3.496	12.684	173.21
$La_2CuO_{3.67}$	S	4.278	3.870	12.241	202.68
$Pr_2CuO_{3.49}$	S	4.254	3.794	12.005	193.76
$Nd_2CuO_{3.50}$	S	4.238	3.768	11.919	190.33
$La_2CuO_{4.10}$	T'	4.004		12.546	201.18
$La_2CuO_{4.20}$	T'	4.007		12.549	201.46
$La_2CuO_{4.33}$	T'	4.009		12.547	201.69
$La_2CuO_{4.06}$	T	3.804		13.152	190.29
$La_2CuO_{4.03}$	T	3.802		13.150	190.03

[a] Starting materials.

[b] The a and b axes have been reduced by $1/\sqrt{2}$ for comparison with the other compounds.

slowly cooling, as illustrated in Fig. 6(a); here, the cooling rate was 1 °C/min. Shown in Fig. 6(b) is a differential thermal analysis (DTA) profile of a $La_2CuO_{3.67}$ sample under oxygen. The data clearly reveal that there are phase transitions at ≃200–300 °C and 500–520 °C, which we interpret as the S- to T'- and T'- to T-structure-phase transitions, respectively. Different oxygen contents in the T'-phase compounds can be obtained by varying the oxygen annealing temperature (300–500 °C) and annealing

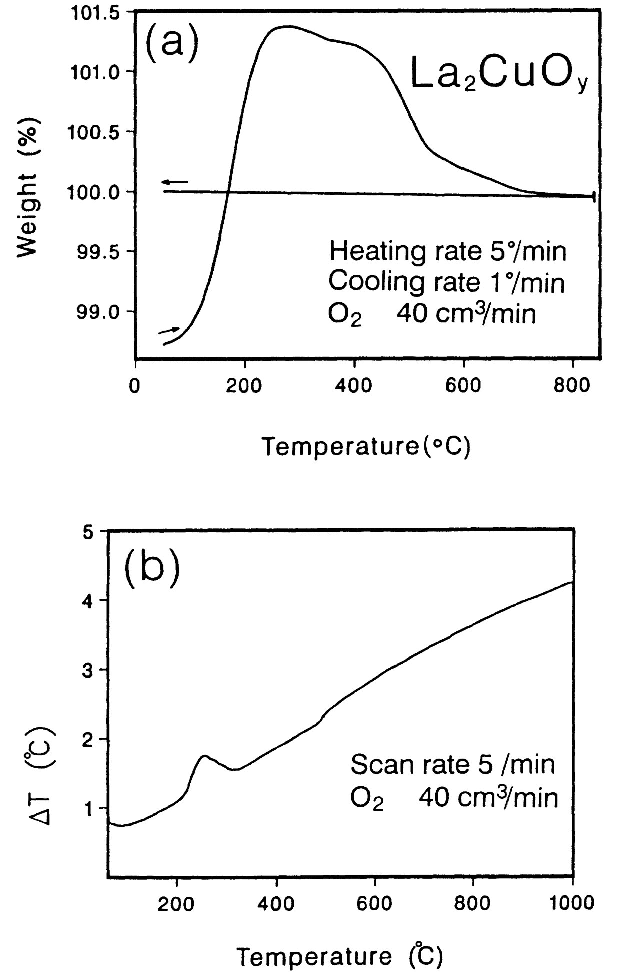


FIG. 6. (a) Weight of $La_2CuO_{3.67}$ vs temperature in an O_2 atmosphere as the temperature is increased at a rate of 5 °C/min in the TGA, and then decreased at 1 °C/min (horizontal line); (b) differential thermal analysis scan of $La_2CuO_{3.67}$ in oxygen at a heating rate of 5 °C/min and with an oxygen flow rate of 40 cm^3/min.

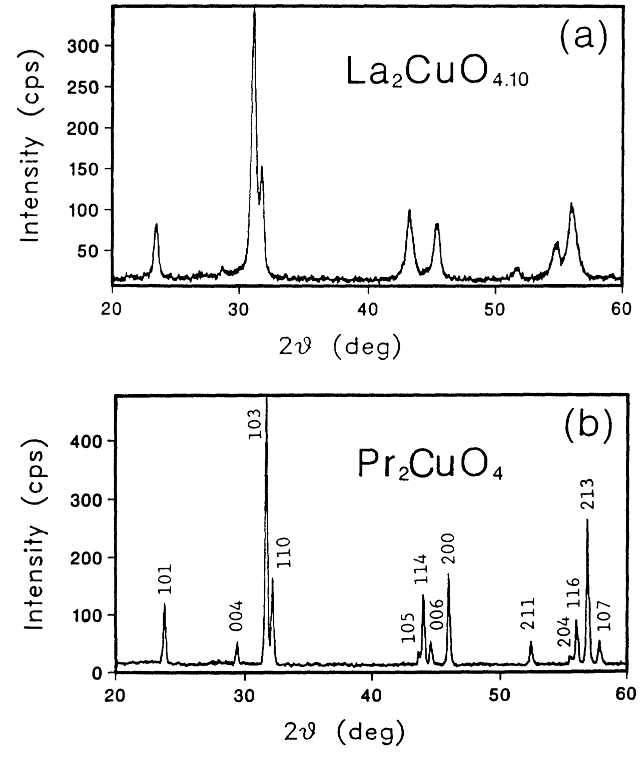


FIG. 7. Powder x-ray diffraction patterns (Cu $K\alpha$ radiation) of (a) T'-phase $La_2CuO_{4.10}$ and (b) T'-phase Pr_2CuO_4.

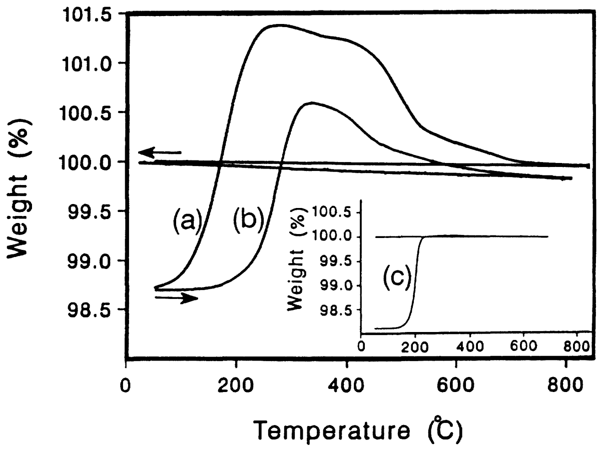


FIG. 8. Weight of $La_2CuO_{3.67}$ (a), $La_{1.1}Dy_{0.9}CuO_{3.61}$ (b), and $Nd_2CuO_{3.5}$ (c), in flowing oxygen (40 cm^3/min) vs temperature; the heating/cooling rates were 5/1, 5/1, and (10 °C/min)/(10 °C/min), respectively.

time. Based on our data so far, the oxygen homogeneity range for the T' structure is 4.10–4.42. Additional treatments such as vacuum annealing and Zr gettering at different temperatures failed to reduce δ in single-phase samples below 0.10; such attempts led to contamination by the S phase. The excess-oxygen T'-phase samples are stable with time; for example, a sample with $\delta=0.33$ did not change its oxygen content after storage for two months in a desiccator.

The x-ray diffraction pattern for T'-phase $La_2CuO_{4.10}$ is shown in Fig. 7(a). Broadened peaks are apparent, which arise for the same reasons as for S-phase $La_2CuO_{3.67}$ cited above. One may compare the pattern in Fig. 7(a) with that of T'-type Pr_2CuO_4, which is shown in Fig. 7(b). The pattern in Fig. 7(a) was indexed on the T' unit cell, and the lattice parameters are shown in Table I. There is a 1.5% reduction in unit-cell volume upon transforming from the S to the T' structure, accompanied by an increase in the c-axis parameter.

C. Nd_2CuO_4-type (T' phase) $L_2CuO_{4+\delta}$ (L=Pr,Nd,Sm,Eu,Gd)

By annealing S-phase $L_2CuO_{3.5}$ in oxygen at temperatures higher than 300 °C, the samples quickly gain oxygen and transform back to the T' structure $L_2CuO_{4+\delta}$, where $\delta=0.01$, 0.03, 0.01, -0.02, and -0.02 for the above respective L compounds. Figure 8 (curve c) shows a typical TGA profile for $Nd_2CuO_{3.5}$ obtained upon heating in oxygen at 10 °C/min; data for $La_2CuO_{3.67}$ (curve a) and $La_{1.1}Dy_{0.9}CuO_{3.61}$ (curve b, see below) are shown for comparison.

D. K_2NiF_4-type (T-phase) $La_2CuO_{4+\delta}$

T-phase $La_2CuO_{4+\delta}$ samples were made from S-phase $La_2CuO_{3.67}$ by heating in an oxygen flow from 50 °C up to a maximum temperature T_{max} ranging from 650 to 925 °C, followed by cooling to room temperature; the weights of the samples were monitored as shown above in Figs. 6(a) and 8. Samples with different oxygen contents were obtained by varying T_{max} and the heating and cooling rates; oxygen contents between 4.06 ($T_{max}=650$ °C) and 3.99 ($T_{max}=925$ °C) were obtained, as shown in Table II, where the heating and cooling rates are also shown for each sample. The samples with higher oxygen contents tend to exhibit smaller orthorhombic distortions than the more stoichiometric samples. This can be seen directly from the x-ray patterns as shown in Fig. 9, where the pattern for $La_2CuO_{4.06}$ [Fig. 9(b)] is compared with that of the La_2CuO_4 starting material [Fig. 9(a)]. Since the former sample showed very little orthorhombic distortion, we indexed the x-ray pattern on a tetragonal lattice (Table I). The decrease in orthorhombicity with in-

TABLE II. Summary of samples treated by hydrogen and subsequent oxygen annealing. Oxygen contents were measured by TGA with an accuracy of ±0.01.

Sample	Structure	T_{max} (°C)	Time (h)	O_2 heating/cooling rate (°C)
$La_2CuO_{4.10}$	T'	500	2	5/5+He, 500 °C, 1 h (40/100)
$La_2CuO_{4.10}$	T'	500	2	5/5+He, 500 °C, 1 h (20/100)
$La_2CuO_{4.20}$	T'	500	$\frac{1}{6}$	5/5
$La_2CuO_{4.21}$	T'	500	2	5/5
$La_2CuO_{4.33}$	T'	280	8	5/100
$La_2CuO_{4.42}$	T'	300	1	1/100
$La_2CuO_{3.99}$	T	925	$\frac{1}{6}$	100/quench
$La_2CuO_{4.01}$	T	850	$\frac{1}{6}$	100/quench
$La_2CuO_{4.01}$	T	800	$\frac{1}{6}$	100/quench
$La_2CuO_{4.02}$	T	740	$\frac{1}{6}$	100/quench
$La_2CuO_{4.02}$	T	650	2	5/40+He, 650 °C, 30 min (40/100)
$La_2CuO_{4.02}$	T	620	24	100/quench
$La_2CuO_{4.03}$	T	700	$\frac{1}{6}$	100/quench
$La_2CuO_{4.05}$	T	650	0	5/10+He, 650 °C, 1 h (40/100)
$La_2CuO_{4.06}$	T	650	$\frac{1}{6}$	5/1

creasing oxygen content is consistent with the decrease in the orthorhombic-tetragonal transition temperature with increasing oxygen content reported previously.[16] For values of T_{max} lower than 650 °C, the x-ray patterns showed broader peaks than in Fig. 9(a), although the broadening was not enough to smear two orthorhombically split peaks such as the (020) and (200) peaks into one peak. By increasing T_{max} to 925–1100 °C and annealing for more than 15 h, the samples became indistinguishable from the original La_2CuO_4 starting material.

E. Additional experiments

Most of the samples above were prepared in small quantities (~100 mg) in the TGA for crystallographic, magnetic, and electronic transport studies. We have found that the detailed synthetic procedures enumerated above using the TGA may not be suitable for synthesis of large (3–15 g) single-phase powder samples of S- and T'-phase La_2CuO_x in conventional tube furnaces, because of sensitivity of the product structure and composition to the temperature and gas flow rate.

In order to improve the crystallinity of our S-phase and T'-phase La_2CuO_x samples, various annealing procedures were tried. Some were successful in improving the crystallinity. For example, the x-ray pattern for S-phase $La_2CuO_{3.76}$ showed no change after annealing in a sealed evacuated quartz tube at 300 °C for 24 h. However, increasing the annealing temperature to 500 °C (24 h) improved the crystallinity as seen by sharpening of some x-ray diffraction peaks, as shown in Fig. 10, and caused the oxygen content to decrease to 3.66; slight sample decomposition may also have occurred as evidenced by the emergence of the weak peak at $2\theta \simeq 39°$ which may belong to La_2O_3. Annealing T'-phase samples in sealed evacuated quartz tubes at 300–400 °C for more than 15 h has little effect other than to induce growth of small amounts of the S phase, but raising the temperature close to 500 °C also causes T-phase impurity to form.

Exposing the T^*-type compounds $La_{1.1}Dy_{0.9}CuO_4$ and $La_{1.3}Tb_{0.7}CuO_4$ to hydrogen led to similar behavior as seen for the L_2CuO_4 compounds above. TGA scans for the Dy compound are shown in Fig. 11. From Fig. 11(b), isothermal annealing in 5 mol % H_2/He at 300 °C leads to a compound with oxygen content 3.61; powder x-ray diffraction patterns indicate an S-type structure for each compound, with broadened diffraction peaks as in $La_2CuO_{4-\delta}$ above. Subsequent oxidation causes the original T^* structure to be recovered, but with an oxygen content up to 4.12 [Fig. 11(c)]. The data taken on cooling in Fig. 11(c) suggest that the compositions with oxygen contents above 4 are metastable.

Magnetization measurements in an applied magnetic field of 50 G were carried out at 5 K. These measurements showed no evidence for superconductivity in any of our samples.

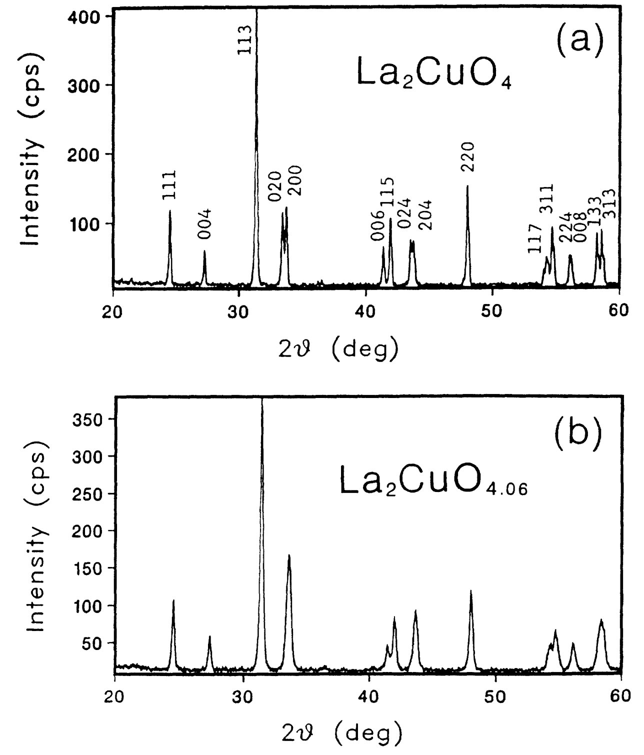


FIG. 9. Powder x-ray diffraction patterns (Cu $K\alpha$ radiation) of (a) T-phase La_2CuO_4 starting material and (b) T-phase $La_2CuO_{4.06}$ obtained by heating the S phase to 650 °C in oxygen (see Table II). The orthorhombic distortion as revealed, e.g., in the splitting of the (020)/(200) peaks, is smaller in (b).

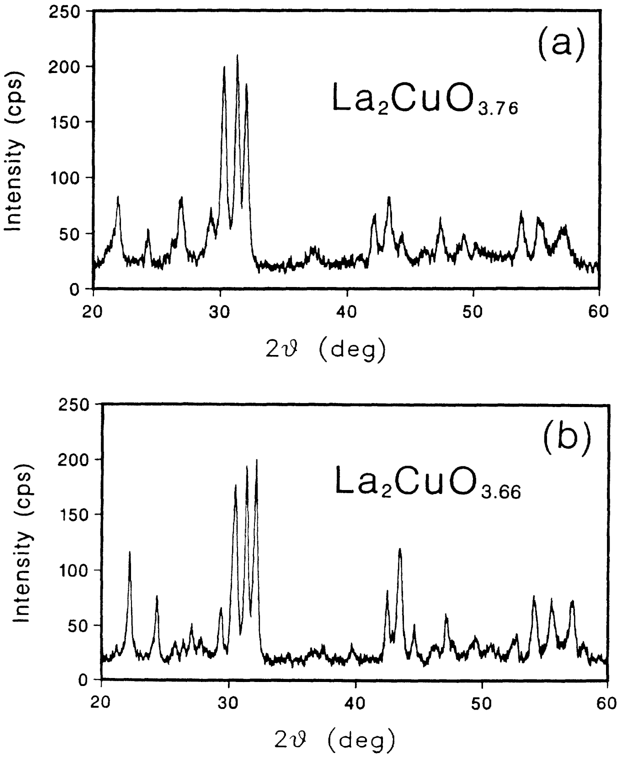


FIG. 10. Powder x-ray diffraction patterns (Cu $K\alpha$ radiation) of S-phase (a) $La_2CuO_{3.76}$ obtained in a tube furnace and (b) $La_2CuO_{3.66}$ obtained by annealing the sample in (a) in a sealed evacuated quartz tube at 500 °C for 24 h.

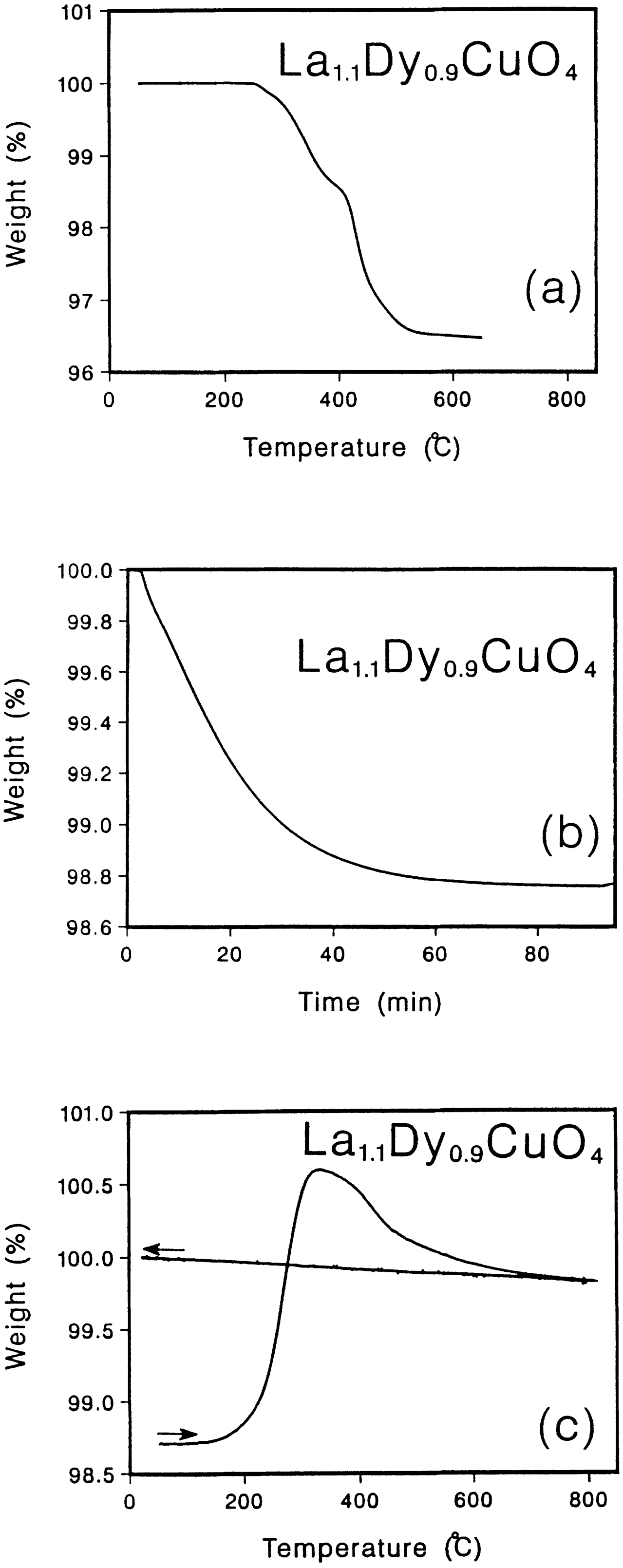


FIG. 11. TGA scan of T^*-type $La_{1.1}Dy_{0.9}CuO_4$ in 5 mol % H_2/He at a heating rate of 5 °C/min (a), isothermal TGA scan of T^*-type $La_{1.1}Dy_{0.9}CuO_4$ in 5 mol % H_2/He at 300 °C (b), and TGA scan of $La_{1.1}Dy_{0.9}CuO_{3.61}$ in O_2, with a heating rate of 5 °C/min and a cooling rate of 1 °C/min (c).

DISCUSSION

The lattice parameters and structures of the samples synthesized in this work are summarized in Table I. There are significant changes in the lattice constants between the S, T', and T phases. For La_2CuO_x, the transition from the T to the S structure, which has elongated a and b axes and a compressed c axis relative to the T structure, resulted in a large increase ($\simeq 6\%$) in the unit-cell volume. The shortened c axis is associated with oxygen loss from the CuO_2 plane, as in $La_{2-x}Sr_xCuO_{4-y}$.[17] When T'-phase $La_2CuO_{4+\delta}$ transforms to the T structure, a large decrease of $\simeq 4.3\%$ in the cell volume occurs. A similar cell volume decrease was observed in a study of the $La_{2-x}Nd_xCuO_4$ system,[18] in which a T to T' phase transition was induced by increasing x above 0.5. If we interpret[19] the T to T' transition in terms of a competition between La and Cu ions for bonding with the out-of-CuO_2-plane oxygens, then in our case this competition must depend on the oxygen content.

When the S phase transforms to the T' structure, two kinds of events occur: filling of the vacant oxygen sites in the Cu-O plane of the S phase and translation of the apical oxygens to the faces of the unit cell. The conversion of the T' phase to the T phase involves only the latter rearrangement; most of the excess oxygen in T'-phase $La_2CuO_{4+\delta}$ is also removed during this process. The S phase is closer in structure to the T phase than the T' phase, as seen in Fig. 1. Indeed, in the system $(Nd_2CuO_4)_{1-x}(Sr_2CuO_3)_x$,[4] the structure transforms from S to T to T' with decreasing x. For our La_2CuO_x system, the phase transformation is from S to T' and then to T; the reason for the different transition order in the two systems is not clear, although in our case the excess oxygens in the T' phase apparently stabilize this structure. On the other hand, the T' structure of $La_2CuO_{4+\delta}$ appears only to be metastable, since once the T structure is formed at the higher temperatures, it does not transform back to T' on cooling. Our room-temperature lattice parameter data for T-phase samples exhibit a decrease in orthorhombic distortion with increasing δ, consistent with previous observations[16] which showed that the orthorhombic-tetragonal phase transition temperature decreases with increasing oxygen content.

Our T-phase $La_2CuO_{4+\delta}$ samples contain excess oxygen up to $\delta=0.06$ and were produced without the high oxygen pressures needed previously to obtain $\delta > 0$. Samples of $La_2CuO_{4.03}$ (Ref. 7) and $La_2CuO_{4.08}$ (Ref. 6) made under high oxygen pressure showed bulk superconductivity below $\simeq 40$ K. These results are in strong contrast to the properties of our samples, which do not exhibit any evidence for superconductivity. From a single-crystal neutron diffraction study on $La_2CuO_{4.03}$,[20] the excess oxygen is proposed to be located at an interstitial site in the form of peroxide $(O_2)^{2-}$ ions which are almost tetrahedrally coordinated to four nearest-neighbor La ions. On the other hand, an x-ray photoelectron spectroscopy study suggested that the excess oxygen is present as superoxide ions O_2^- in the near-surface region.[21] The observed absence of superconductivity in our

T-phase $La_2CuO_{4+\delta}$ samples implies that the detailed structure is different than in samples produced under high oxygen pressure.

The enormously high oxygen content T'-phase system $La_2CuO_{4+\delta}$ $(0.10 \leq \delta \leq 0.42)$ shows nonsuperconducting behavior also; it is not clear yet whether this system can be electron-doped to become superconducting. Because the S- and T'-phase limits are close to $La_2CuO_{4-1/3}$ and $La_2CuO_{4+1/3}$, respectively, it seems possible that some of the oxygen may fill vacant sites in the form of peroxide ions $(O_2)^{2-}$, such that the Cu atoms retain an oxidation state close to $+2$ when $\delta > 0$. This is consistent with preliminary resistivity data which suggest that the $La_2CuO_{4+\delta}$ compounds are insulators.[13]

S-phase $L_2CuO_{3.5}$ (L=Pr,Nd) and $La_2CuO_{3.67}$ also have an excess of oxygen compared to the prototype Sr_2CuO_3 stoichiometry. The lattice positions of the excess oxygens are not yet known. For S-phase $La_2CuO_{3.67+\delta}$, new x-ray diffraction peaks (e.g., at $2\Theta \simeq 27°$) arise compared to the $L_2CuO_{3.5}$ x-ray patterns, implying a lower symmetry of the unit cell of the former with respect to the latter compounds. Similar extra peaks were also observed for T'-phase $La_2CuO_{4+\delta}$ with $\delta > 0.1$. These peaks do not appear for $L_2CuO_{4+\delta}$ (L=Pr,Nd) in which δ is closer to zero. $L_2CuO_{3.5}$ phases were also found for L=Sm, Eu, and Gd, but the structure(s) of these compounds is different from the S structure and is not yet known. Finally, the new S-type compound $La_{1.1}Dy_{0.9}CuO_{3.61}$, formed from the T^* phase, has an oxygen stoichiometry intermediate between the above values of 3.5 and 3.67; the original T^* structure is recovered upon oxidizing this material, although the maximum oxygen content is 4.12, intermediate between the maximum value for T'-type $La_2CuO_{4+\delta}$ (4.42) and $Nd_2CuO_{4+\delta}$ (4.03).

In the context of the above possibility that (some of) the excess oxygen in the T'- and/or T-type $La_2CuO_{4+\delta}$ compounds could be present only on the surface of the grains, this issue is being addressed via neutron diffraction structural refinements of the new materials which are currently underway.[22] Another possible source of systematic error in the absolute values of the oxygen contents measured for the various phases is the presence of additional phases in the starting materials and/or products which are undetected by x-ray analysis.

SUMMARY

Herein, we reported the synthesis of new $L_2CuO_{4-\delta}$ L=La,Pr,Nd,Sm,Eu,Gd) systems, obtained by mild hydrogen reduction of the parent L_2CuO_4 compounds. $La_2CuO_{3.67}$ and $L_2CuO_{3.5}$ (L=Pr,Nd) have structures related to that of orthorhombic Sr_2CuO_3, which contains Cu-O chains running in the a-axis direction, but the structures of the Sm, Eu, and Gd compounds are unknown as yet. The new T'-phase system $La_2CuO_{4+\delta}$, which formed on oxidation of $La_2CuO_{3.67}$ below 500 °C, has an exceptionally high oxygen excess $0.10 \leq \delta \leq 0.42$. Oxidizing the $L_2CuO_{3.5}$ (L=Pr,Nd,Sm,Eu,Gd) compounds transforms them back to their original T' structures. Heating the T'-phase $La_2CuO_{4+\delta}$ above $\simeq 500$ °C in oxygen causes it to transform to T-phase $La_2CuO_{4+\delta}$ which can also contain an oxygen excess $(-0.01 \leq \delta \leq 0.06)$; the samples with the larger δ values showed smaller degrees of orthorhombic distortion than conventionally prepared T-phase La_2CuO_4, consistent with previous work.[16] None of the samples studied showed any superconductivity from magnetization measurements in a field of 50 G. The lattice parameters from powder x-ray diffraction for some of the above materials are reported. Detailed neutron diffraction structural analyses[22] and physical property measurements[13] of the new materials are in progress.

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