Preparation of Layered $Sr_2CuO_{3+\delta}$ by Pulsed Laser Deposition: Rational Synthesis and Doping of a Metastable Copper Oxide Material

Alfredo M. Morales, Peidong Yang, and Charles M. Lieber*

*Department of Chemistry and Division of Applied Sciences
Harvard University, Cambridge, Massachusetts 02138*

Herein we describe the first synthesis of the layered copper oxide material $Sr_2CuO_{3+\delta}$ carried out under low-pressure and low-temperature conditions. Reaction under these mild conditions was achieved using the pulsed laser ablation and deposition (PLD) technique.[1,2] Structural analyses demonstrate that $Sr_2CuO_{3+\delta}$ prepared by PLD adopts a layered tetragonal structure with a repeat unit consisting of a CuO_2 plane and two SrO_δ layers. Investigations of the growth mechanism show that this layered copper oxide phase is a kinetic product in contrast to the thermodynamic one typically produced in solid state reactions. We have exploited this kinetic growth mode to prepare $Sr_{2-x}M_xCuO_{3+\delta}$ solids that have systematic variations in oxygen and cation stoichiometry.

The synthesis of solids using nontraditional reaction conditions can often yield new and exciting materials not accessible from high-temperature reactions typical of traditional techniques.[3-17] In the area of copper oxide superconductivity both low-pressure/low-temperature thin film[7-12] and ultrahigh-pressure/high-temperature[13-17] approaches have yielded new solids that cannot be prepared by conventional methods. The $Sr_{n+1}Cu_nO_{2n+2+\delta}$ family of solids ($n = 1-\infty$) are a particularly interesting case since they represent simple models of the high-T_c materials that contain only CuO_2 and charge compensating $Sr(O)$ layers.[18] This structural simplicity comes at a price: none of these layered copper oxide materials can be prepared by traditional high-temperature syntheses. In contrast, it has been possible to prepare the $n = \infty$ member of this family, $SrCuO_2$, using both ultrahigh-pressure[13-15] and the relatively mild low-pressure/low-temperature conditions of PLD.[9-11] Recent high-pressure studies also indicate that the $n = 1$ material, $Sr_2CuO_{3+\delta}$, can be stabilized in a layered structure,[17,18] although its synthesis has not been investigated using other approaches.

Our studies of the growth and doping of $Sr_2CuO_{3+\delta}$ materials were carried out using a laser ablation system that has been described in detail previously.[9,10] Briefly, targets containing the stoichiometry of metal ions desired in the final products were ablated with a frequency-doubled pulsed Nd:YAG laser, and the ablated material was deposited onto the (100) surface of heated $SrTiO_3$ substrates.[19] The $Sr_{2-x}M_xCuO_{3+\delta}$ (M = Ca^{2+}, Nd^{3+}) targets used in our studies were prepared using conventional high-temperature reactions from stoichiometric mixtures of metal carbonates and oxides.[20] X-ray diffraction (XRD) showed that the targets contained several phases, except for $x = 0$ where the known orthorhombic structure with $a = 12.68$ Å, $b = 3.91$ Å, and $c = 3.48$ Å was obtained.[21]

PLD syntheses carried out at 650–680 °C using these targets produced new single-phase products whose composition and structure were determined using Rutherford backscattering spectroscopy (RBS), XRD, and electron diffraction (ED) (Figure 1). The composition of the $Sr_2CuO_{3+\delta}$ materials determined by RBS was the same (±5%) as the starting stoichiometry of the targets even when the targets contained multiple phases. The Sr:Cu stoichiometry of the film shown in Figure 1, (1.97 ± 0.07): (1.10 ± 0.05), is the same within experimental error as that of the target. More importantly, XRD and ED demonstrate that the materials obtained by PLD have the same structure as that proposed for the layered, $n = 1$ phase $Sr_2CuO_{3+\delta}$. The XRD peaks in Figure 1b can be indexed as the $(00l)$, $l = 2, 4, 6, 8, 10$ lines of the $n = 1$ phase. The c-axis length determined from this data is 12.88 Å. The observation of only $(00l)$ peaks in $\theta–2\theta$ XRD scans shows that the c-axis of $Sr_2CuO_{3+\delta}$ is oriented perpendicular to the (100) $SrTiO_3$ substrate surface. This orientation effect is likely due to lattice matching of $SrTiO_3$ ($a = 3.905$ Å) and $Sr_2CuO_{3+\delta}$ ($a = 3.76$ Å). The structure of our materials was further characterized using transmission ED measurements made along the [001] zone axis. The ED patterns exhibit a square symmetry with $a = 3.8$ Å. The ED data are consistent with the tetragonal structure expected for the layered $n = 1$ phase, but are inconsistent with the orthorhombic structure of the starting material.[22] The XRD and ED results thus confirm that the materials prepared by PLD have the layered $n = 1$ structure.

To rationalize the excellent synthetic control afforded by PLD, we have previously speculated that growth is kinetically con-

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(19) Ablation was carried out using power densities of 1–2 J/cm² and a pulse repetition rate of 10 Hz. The target–substrate distance used in these experiments was 4 cm, although distances between 4 and 6 cm gave similar results. The O_2 or N_2O partial pressure and substrate temperature were varied as described in the text.
(20) Sr_2CuO_3 targets were prepared from stoichiometric amounts of $SrCO_3$ (99.99% Johnson Matthey) and CuO (99.99% Johnson Matthey) that were ground and heated at 1000 °C for 48 h, reground, and heated at 1000 °C for an additional 48 h. The resulting polycrystalline material was ground into a pellet and sintered for 24 h at 1000 °C. Cation-substituted targets, $Sr_{2-x}M_xCuO_x$ (M = Ca^{2+}, Nd^{3+}), were prepared in a similar manner using stoichiometric amounts of $CaCO_3$ or Nd_2O_3.
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(22) If the XRD data was assigned to the (h00) peaks of the orthorhombic phase, the ED would yield a rectangular cell with $b = 3.91$ and $c = 3.48$ Å. Because our data show clearly a square structure, we can rule out this alternative explanation.

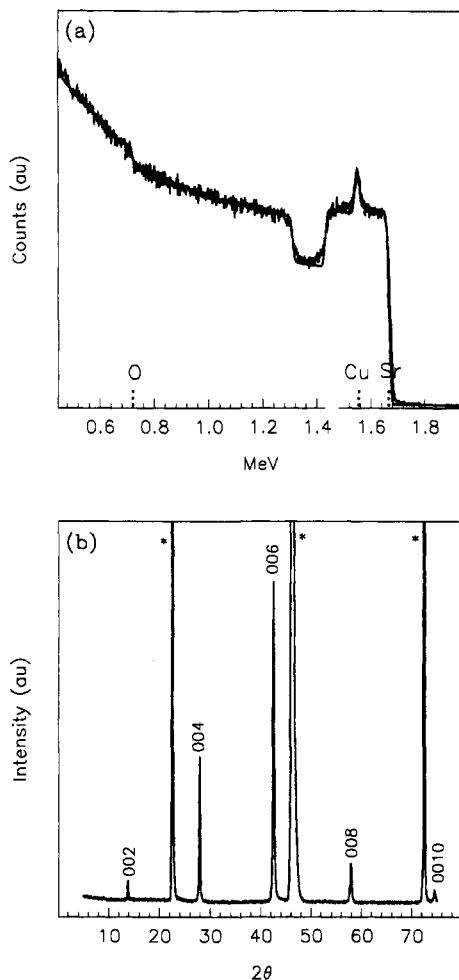*Communications to the Editor*

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Figure 1. (a) RBS data obtained on a $Sr_2CuO_{3+\delta}$ material grown in 210 mTorr of N_2O at 665 °C on a (100) $SrTiO_3$ substrate. The fit (smooth solid line) to the experimental data corresponds to Sr = 1.97 and Cu = 1.10. The RBS data analysis was carried out using the program RUMP from the Department of Materials Science and Engineering, Cornell University. (b) XRD diffraction pattern recorded on a sample grown in 300 mTorr of O_2 at 680 °C. The $SrTiO_3$ substrate (h00) peaks are denoted with asterisks (*).

trolled.[9] To test this idea we have grown amorphous films of $Sr_2CuO_{3+\delta}$ at 400 °C and subsequently annealed them at temperatures up to 680 °C. Since the amorphous films contain Sr + Cu mixed in a 2:1 ratio on the atomic scale, this experiment allows us to determine, in the absence of diffusion constraints, the structure of the thermodynamic crystalline phase. We find that heating the amorphous films to 680 °C (a growth temperature that yields n = 1 phase by PLD) in either 200 mTorr of O_2 or 1 atm of air produces the orthorhombic phase. Furthermore, annealing crystalline n = 1 materials at ≥700 °C leads to a conversion of the layered phase to the orthorhombic one. Hence, we conclude that the layered $Sr_2CuO_{3+\delta}$ phase obtained by PLD is a kinetic product, while the thermodynamic product at our reaction temperatures is the orthorhombic phase.
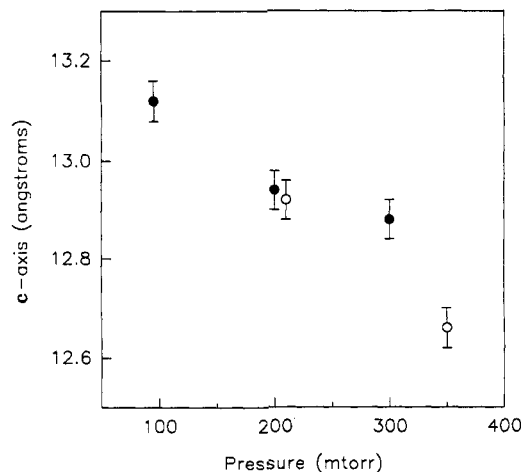

Figure 2. Dependence of the c-axis on the O_2 (●) and N_2O (O) pressure used during film growth.

We have exploited the ability to grow phase pure materials under kinetic control to study doping in this system. Samples of the n = 1 layered phase were grown at 680 °C in O_2 and N_2O pressures ranging from 95 to 350 mTorr to investigate oxygen doping. XRD and ED analyses show that these solids correspond to the pure n = 1 layered phase, and that the c-axis lattice parameter decreases as the pressure of oxidizing gas is increased (Figure 2).[23] We attribute the decrease in c-axis to a systematic increase in copper oxidation state as observed for other copper oxide materials.[24,25] The synthesis of cation-doped solids of the form $Sr_{2-x}M_xCuO_{3+\delta}$ (M = Ca^{2+}, Nd^{3+}) has also been explored by PLD. Preliminary studies show that phase pure n = 1 layered materials are obtained at growth temperatures between 650 and 680 °C for x(M) = 0–0.15.[26] In comparison, high-pressure studies have found that Ca^{2+} destabilizes the n = 1 phase relative to the n = 2 phase, and to our knowledge Nd^{3+} has not been successfully incorporated into this structure by other methods. Taken together, we believe that our studies illustrate clearly that PLD is powerful synthetic approach for solid state chemistry since it provides, through kinetic control, the ability to systematically explore the chemistry of a solid while maintaining a predictable structure.

(23) The c-axis contraction is linear in $P(O_2)$ up to *ca.* 200 mTorr and saturates at higher pressure. This saturation indicates that oxygen doping does not increase above 200 mTorr in O_2. However, the c-axis continues to contract up to a pressure of 400 mTorr when the stronger oxidant N_2O ($E°(N_2O)$ = 1.77 V vs $E°(O_2)$ = 1.23 V) is used during growth.

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(25) Interestingly, resistivity anomalies suggestive of superconductivity are observed in samples prepared at the higher O_2/N_2O pressures. We believe that the nature of these anomalies warrants further investigation.

(26) Impurity phases are observed under these growth conditions when targets containing more than x = 0.15 are employed. It should be possible, however, to extend the range through variations in the growth conditions.