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LETTERS TO THE EDITOR

Thermal-Expansion Mismatch and Intergrowth Types in the System $La_{2-y}Nd_yCuO_4$

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Stabilization of intergrowth structures of the copper-oxide superconductors requires bond-length matching across the intergrowth interface. The influence of thermal-expansion mismatch on the stabilization of T/O vs T' intergrowths in the $La_{2-y}Nd_yCuO_4$ system is demonstrated by firing the coprecipitated hydroxides/carbonates at 500–1050°C. A larger thermal expansion for the (LaNd)–O bond compared to that for the Cu–O bond shifts the T/O–T' phase boundary to a higher y value in $La_{2-y}Nd_yCuO_4$ as the synthesis temperature is increased. Above 950°C, an equilibrium phase diagram is obtained with a new line phase T'' appearing at $y = 0.5$. The T'' phase appears to be an ordered variant of the T' phase and could be doped neither n-type nor p-type.

Introduction

The known copper-oxide superconductors all have intergrowth structures consisting of superconductively active CuO_2 sheets and other inactive layers. For example, the simplest prototype system La_2CuO_4 has CuO_2 sheets alternating with double-rocksalt $(LaO)_2$ layers along the c-axis as

$$|CuO_2|LaO\text{-}LaO|CuO_2|, \qquad (1)$$

where the vertical lines mark the interlayer interface. The stabilization of such an intergrowth requires bond-length matching across the intergrowth interface. The bond-length matching for the T/O phase of La_2CuO_4 can be expressed in terms of the tolerance factor

$$t = (\text{La–O})/\sqrt{2}(\text{Cu–O}), \qquad (2)$$

where La–O and Cu–O are the equilibrium La–O and Cu–O bond lengths. A $t = 1$ will be realized for ideal matching. Although La_2CuO_4 may have t close to unity at the firing temperature $T \approx 1000°C$, the value of t will decrease from unity as the temperature is lowered, since the La–O bond has a larger thermal expansion than the Cu–O bond; $t = 0.869$ at room temperature (*1*), as calculated from the sums of the empirical room-temperature ionic radii (*2*). A $t < 1$ means a bond-length mismatch between the CuO_2 and LaO layers at room temperature that places the La–O bonds under tension and the Cu–O bonds under compression. In La_2CuO_{4+x}, the bond-length mismatch at room temperature is partially relieved by (i) an ordering of the Cu(II)-3d hole into the antibonding $\sigma^*_{x^2-y^2}$ orbitals to give a large octahedral-site axial ratio $c/a > 1$, (ii) the incor-

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poration of some interstitial oxygen within the La_2O_{2+x} layers to give the composition La_2CuO_{4+x}, and (iii) a cooperative tilting of the CuO_6 octahedra to give a macroscopic transition from tetragonal to orthorhombic symmetry (*3*).

Replacement of La^{3+} by other smaller Ln^{3+} = Pr–Gd reduces $t < 1$ sufficiently at the firing temperature that a rocksalt arrangement in the $(LnO)_2$ layer can no longer provide bond-length matching to the CuO_2 layer. In this situation, the O^{2-} ions of the $(LnO)_2$ layers are displaced into the tetrahedral sites of the layer to produce a fluorite Ln–O_2–Ln layer (*4*). The direct electrostatic repulsion between the O^{2-} ions in the tetrahedral sites keeps the fluorite Ln_2O_2 layer stretched compared to that in the rocksalt $(LnO)_2$ layer and relieves the bond-length mismatch. The T' phase of Nd_2CuO_4 has a layer sequence along the c-axis given by

$$|CuO_2|Nd\text{–}O_2\text{–}Nd|CuO_2|. \qquad (3)$$

We recently investigated (*1*) the phase relationships in the system $La_{2-y}Ln_yCuO_4$ (Ln = Pr or Nd) by firing the component oxides at 1050°C. In the $La_{2-y}Nd_yCuO_4$ system, we found at room temperature (i) the orthorhombic T/O La_2CuO_4 structure for $0 \leq y \leq 0.35$ and $t \geq 0.8658$, (ii) the tetragonal $T'Nd_2CuO_4$ structure for $1.2 \leq y \leq 2.0$ and $t \leq 0.8585$, (iii) a line phase at $y \approx 0.5$ designated as T'' having an X-ray pattern similar to that of T', (iv) a two-phase region consisting of T/O and T'' for $0.35 \leq y \leq 0.5$, and (v) a two-phase region consisting of T'' and T' for $0.55 < y < 1.2$. The new T'' phase was proposed to exhibit ordering of La^{3+} and Nd^{3+} cations within the $(La,Nd)_2O_2$ layers.

In an attempt to understand more about the phase relationships as a function of synthesis temperature, we have investigated the $La_{2-y}Nd_yCuO_4$ system by firing the coprecipitated hydroxides/carbonates at 500–1050°C. Our results demonstrate, for the first time, the role of thermal-expansion mismatch on the stabilization of the intergrowth types.

Experimental

La^{3+}, Nd^{3+}, and Cu^{2+} were coprecipitated at pH 7.0 as hydroxides and carbonates by adding K_2CO_3 (*3*) into a nitric acid solution containing required quantities of the ions. The fine precipitate obtained was filtered, washed several times with distilled water and finally with acetone, and dried at 120°C in an air oven. The precursor powder was then fired in air progressively from 500 to 1050°C for about 15 hr at each temperature at an interval of 50–100°C, with intermediate grindings to obtain $La_{2-y}Nd_yCuO_4$. After firing at each fixed temperature for about 15 hr, the sample was cooled and characterized by X-ray powder diffraction recorded at room temperature with a Philips diffractometer and Cu$K\alpha$ radiation. Thermogravimetric analysis was carried out with a Perkin–Elmer Series 7 Thermal Analysis System. The oxygen content was determined by the wet iodometric procedure (*4*); all the phases showed an oxygen content of 4.00 ± 0.02.

Results and Discussion

The decomposition of the hydroxide/carbonate precursors is nearly complete around 600°C and gives $La_{2-y}Nd_yCuO_4$ as revealed by thermogravimetric analysis data (Fig. 1) and X-ray diffraction (Fig. 2). The phases identified by room-temperature X-ray diffraction after firing the precursors at different temperatures are shown in Fig. 3. The stability of the T/O phase field is progressively increased to higher y values in $La_{2-y}Nd_yCuO_4$ as the synthetic temperature is increased. Since the thermal expansion of the Ln–O bond is larger than that of the Cu–O bond, an increase in the synthetic temperature reduces the bond-length mismatch and stabilizes the T/O structure. If

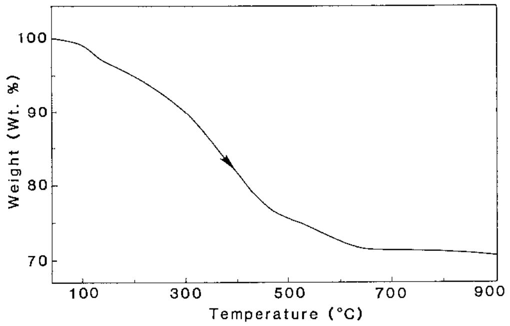

FIG. 1. TGA plot recorded in air at 1°C/min for the coprecipitated hydroxide/carbonate of La_2Cu stoichiometry.

there were no difference in the thermal expansions of the two bonds, then one would anticipate the phase boundary to occur at a constant y value irrespective of the synthesis temperature.

The formation of the T' phase is extended to lower y values in $La_{2-y}Nd_yCuO_4$ as the synthesis temperature is lowered since the thermal-expansion mismatch destabilizes the T/O phase. A two-phase region consisting of T/O and T' phases separates the T/O and T' phase field. This two-phase region has a constant width of $\Delta y \approx 0.2$ at all temperatures below 850°C; above 850°C cation mobility introduces a new T'' phase (see below). Extrapolation of our data in Fig. 3 to lower temperatures leads to the prediction that La_2CuO_4 can be stabilized in the T' structure if the synthesis is carried out below 425°C. Although we could obtain a two-phase mixture consisting of T/O and $T'La_2CuO_4$ at 500°C, we could not achieve single-phase $T'La_2CuO_4$ as our procedure needs a firing temperature of at least 500°C. However, Chou *et al.* (*7*) have shown that $T'La_2CuO_4$ can be obtained by reducing T/O La_2CuO_4 with hydrogen around 300°C followed by reoxygenation below 400°C. This observation lends further support to our demonstration that the thermal-expansion mismatch influences the stabilization of T/O vs T' intergrowths.

Above 850°C the phase relationship is complicated by the stabilization of a new T'' phase—a line phase $La_3NdCu_2O_8$—at $y = 0.5$ within the T/O phase field. The T'' phase has an X-ray diffraction pattern similar to that of $T'Nd_2CuO_4$, but with slightly larger a and c parameters as expected from the larger size of La^{3+} (*1*). It could be doped; neither n-type nor p-type all attempts to substitute Sr^{2+} or Ce^{4+} for La^{3+} or Nd^{3+} resulted in either Sr^{2+}-doped T/O and undoped T' phases or Ce^{4+}-doped T' and undoped T/O phases. We have suggested (*1*) previously that the T'' phase may have an intralayer ordering of La^{3+} and Nd^{3+} ions within the $(La,Nd)_2O_2$ layers. Although neutron diffraction data obtained by Lightfoot *et al.* (*8*) at Argonne National Laboratory on our samples of T'' $La_{1.5}Ln_{0.5}CuO_4(Ln =$ Pr or Nd) indicate the presence of all the O^{2-} ions in the tetrahedral sites as in $T'Nd_2CuO_4$, no cation ordering could be detected. Since both X-ray and neutron diffraction can detect only long-range order, it appears that the cation ordering in the T'' phase is short-range and subtle; a short-range ordering is entirely reasonable in view of a smaller size difference between La^{3+} and Nd^{3+} ions. We suspect that ordering within an individual layer may be quite long-range, but that ordering between layers does not occur.

Cation ordering is also supported by our present experiments, which show that the T'' phase is distinct from the normal T' phase. The occurrence of a normal T' phase at $y \approx 0.5$ is not expected within the T/O phase field (Fig. 3) unless an extra stabilizing force introduces it. We believe that the cation ordering at La : Nd = 3 : 1 within the $(La,Nd)_2O_2$ layers lowers the net energy of the system that stabilizes the T'' phase relative to the T/O phase. Furthermore, the T'' phase is accessible only when the synthesis temperature is above 850°C. A higher synthesis temperature provides a higher mobility of the cations and, hence, the possibility

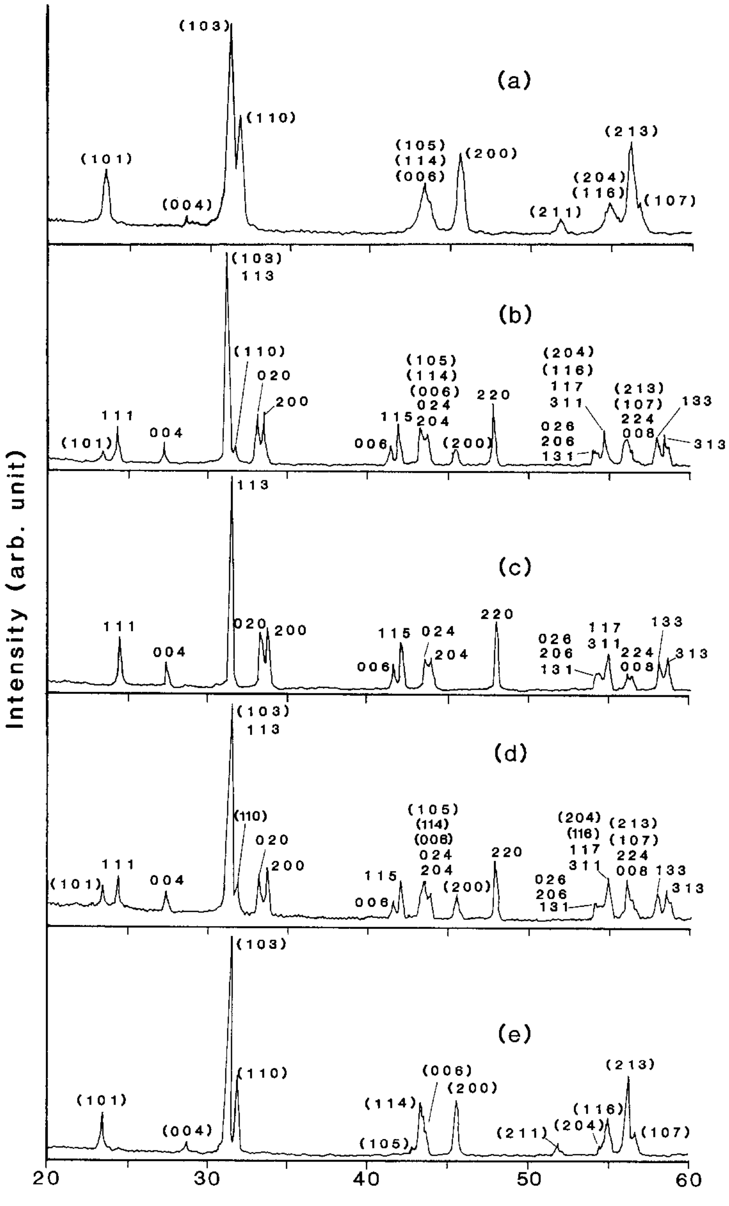

FIG. 2. X-ray powder diffraction patterns recorded at room temperature after firing the coprecipitated hydroxide/carbonate of $La_{1.5}Nd_{0.5}$ stoichiometry at (a) 600°C (T'), (b) 700°C ($T' + T/O$), (c) 800°C (T/O), (d) 900°C ($T/O + T''$), and (e) 1050°C (T''). The *hkl* values within the parentheses are for T' or T'' phases and those without the parentheses are for the T/O phase.

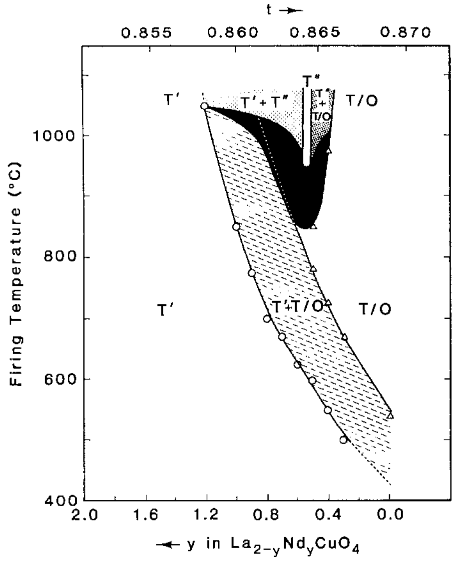

FIG. 3. Phase relationships for the system $La_{2-y}Nd_yCuO_4$ obtained by firing the coprecipitated hydroxide/carbonate progressively at higher temperatures followed by cooling to room temperature. The thickly shaded area around 850–1050°C and $y \approx 0.5$ represents a nonequilibrated region consisting of T/O, T', and T''.

of cation ordering on cooling. Sufficient cation mobility leads to an equilibrium phase diagram at 1050°C. The equilibration temperature is lowered to 950°C around $y \approx 0.5$ (Fig. 3) due to the extra stabilization associated with the T'' phase. In Fig. 3, the thickly shaded region around 850–1050°C and $y \approx 0.5$ represents a nonequilibrated region in which the existence of T', T/O, and T'' is found. Once phase equilibrium is achieved around 1050°C, the equilibrium phase diagram for 1050°C is retained down to room temperature without disproportionation into T/O and T'. Below $T \approx 850$°C, the cations do not have sufficient mobility to order. The determination of the order–disorder transition temperature by diffraction techniques would be difficult in this case since any ordering appears to be short-range.

More interestingly, the composition $La_{1.5}Nd_{0.5}CuO_4$ can be stabilized as single-phase T'(<625°C), T/O (775–850°C), or T'' (>950°C) depending upon the synthesis temperature (Figs. 2 and 3). In view of these experiments at ambient pressure in air, the recent results of Bringly *et al.* (*9*) on the types of intergrowths in $La_{1.4}Nd_{0.6}CuO_{4+x}$ as a function of oxygen pressure can be understood. They have stabilized the T/O phase $La_{1.4}Nd_{0.6}CuO_{4.04}$ by firing the coprecipitated hydroxides at 910°C and 400 bar O_2 and T'' (identified by them as T') $La_{1.4}Nd_{0.6}CuO_{3.98}$ by annealing at 1050°C in air followed by quenching. Since the composition $La_{1.4}Nd_{0.6}CuO_4$ lies close to the T/O phase boundary at 900°C (Fig. 3), the application of moderate oxygen pressure would stabilize single-phase T/O; high oxygen pressure increases the oxygen content above 4.0, which oxidizes the CuO_2 sheets and therefore decreases the Cu–O bond-length and shifts the T/O phase boundary to higher y values by relieving the bond-length mismatch. For a relatively short firing time at 900°C, there would be no formation of the T'' phase since it needs sufficient cation mobility and equilibration; however, at 1050°C the T'' phase would be rapidly formed.

Acknowledgments

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References

1. A. MANTHIRAM AND J. B. GOODENOUGH, *J. Solid State Chem.* **87,** 402 (1990).
2. R. D. SHANNON, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
3. J. M. LONGO AND P. M. RACCAH, *J. Solid State Chem.* **6,** 526 (1973); B. GRANDE, H. MÜLLER-BUSCHBAUM, AND M. SCWEIZER, *Z. Anorg. Allg. Chem.* **428,** 120 (1977).
4. H. MÜLLER-BUSCHBAUM AND W. Z. WALLSCHLAGER, *Z. Anorg Allg. Chem.* **414,** 76 (1975).
5. E. TAKAYAMA-MUROMACHI, Y. UCHIDA, AND K. KATO, *Physica C* **165,** 147 (1990).
6. A. MANTHIRAM, J. S. SWINNEA, Z. T. SUI, H.

STEINFINK, AND J. B. GOODENOUGH, *J. Amer. Chem. Soc.* **109,** 6667 (1987).

7. F. CHOU, J. H. CHO, L. L. MILLER, AND D. C. JOHNSTON, *Phys. Rev. B* **42,** 6172 (1990).

8. P. LIGHTFOOT, SHIYOU PEI, AND J. D. JORGENSEN, private communication.

9. J. F. BRINGLY, S. S. TRAIL, AND B. A. SCOTT, *J. Solid State Chem.* **88,** 590 (1990).