Crystal Chemistry of the $La_{2-y}Ln_yCuO_4$ (Ln = Pr, Nd) Systems

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An investigation of the value of the room temperature crystallographic tolerance factor t at which stability of the La_2CuO_4 T-tetragonal structure becomes unstable relative to the Nd_2CuO_4 T'-tetragonal structure in the systems $La_{2-y}Ln_yCuO_4$, Ln = Pr or Nd, has led to the discovery of a new T''-tetragonal phase. It has a powder X-ray diffraction pattern like that of the T' phase, but with a slightly larger c parameter than that obtained by extrapolation from the T' phase field. Its occurrence as nearly a line phase at $y \approx 0.5$ suggests cation ordering within a Ln–O layer; with a larger size difference between La^{3+} and the Ln^{3+} ion, interlayer ordering occurs to give either a two-phase sample T/O + T' or the hybrid T* phase. © 1990 Academic Press, Inc.

Introduction

All the known copper–oxide superconductors have intergrowth structures consisting of superconductively active layers alternating with inactive layers. The simplest structures of this class are illustrated by the prototype p-type and n-type superconductors $La_{2-y}Sr_yCuO_4$ and $Nd_{2-y}Ce_yCuO_4$.

La_2CuO_4 has a T-tetragonal structure at high temperatures and undergoes a displacive transition to orthorhombic symmetry below a transition temperature T_t; we refer to this structure type as the T/O phase. In the T-tegragonal structure, the active layer is a single CuO_2 plane consisting of a square Cu array bridged by 180° Cu–O–Cu bonds; the inactive layer is composed of two (001) rocksalt LaO planes in which the oxygen atoms coordinate the Cu along the c-axis and the La atoms are coordinated by four oxygens of a neighboring CuO_2 plane as well as by five oxygens within the La–O layers. A cooperative tilting of the CuO_6 octahedra about a [110] axis reduces the symmetry from tetragonal to orthorhombic and bends the Cu–O–Cu bonds from 180° (*1*).

Nd_2CuO_4 has a T'-tegragonal structure at all temperatures. Here also the active layer is a single CuO_2 plane; but a displacement of the c-axis oxygen of the T-phase to the tetrahedral interstices between the two planes of Nd^{3+} ions creates a fluorite-type inactive layer (*2*). In the T' phase the copper have only four square-coplanar oxygen neighbors within a CuO_2 sheet.

Stabilization of an intergrowth structure requires a matching of the bonds across the interface between adjacent layers. In the T phase of La_2CuO_4, a measure of the bond-length matching is the tolerance factor

$$t = (La–O)/\sqrt{2}\ (Cu–O). \qquad (1)$$

Ideal matching corresponds to $t = 1$; but it can only occur at one temperature because of the different thermal expansions of the La–O and Cu–O bond lengths. A larger La–O thermal expansion means that t decreases with decreasing temperature. Already at room temperature, La_2CuO_4 has a

$t = 0.869 < 1$ as calculated from the sums of the empirical room temperature ionic radii (3). A $t < 1$ means a bond-length mismatch that places the CuO$_2$ sheets under compression and the LaO layers under tension. These stresses are partially relieved by ordering of the Cu(II)–3d hole into the antibonding $\sigma^*_{x^2-y^2}$ orbitals of Cu–3$d_{x^2-y^2}$ and O–2$p_{\sigma x}$, 2$p_{\sigma y}$ parentage. This ordering accounts for the large tetragonal ($c/a > 1$) distortion of the CuO$_6$ octahedra; it is already accounted for in the empirical Cu(II) room temperature ionic radius, which means the CuO$_2$ layers would remain under compression at and below room temperature if the structure were to remain tetragonal. In fact, the cooperative tilting of the CuO$_6$ octahedra in the orthorhombic distortion below T_t occurs to relieve the bond-length mismatch (4, 5).

Replacement of La^{3+} by smaller lanthanide ions, Ln = Pr–Gd, reduces $t < 1$ sufficiently that nature relieves the mismatch by forming the T' phase. Placement of all the c-axis oxygen into a single plane of lanthanide tetrahedral sites via the c-axis stacking sequence

$$-CuO_2-Nd-O_2-Nd-CuO_2- \quad (2)$$

causes an expansion of the basal plane; this expansion places the CuO$_2$ sheets under tension, at least in the case of Ln = Pr or Nd if not for Ln = Gd, and the T' phase remains tetragonal to lowest temperatures.

As pointed out elsewhere (4), the existence of a compressive stress on the CuO$_2$ planes in the T phase allows p-type doping with either an interstitial oxygen in the La–O layer or substitution of La^{3+} by a larger M^{2+} ion, but it inhibits n-type doping; a tensile stress on the CuO$_2$ planes in the T' phase allows n-type doping, but it inhibits p-type doping.

In a mixed-lanthanide system La$_{2-y}$Ln$_y$-CuO$_4$, there is no doping of the CuO$_2$ sheets. For the smaller lanthanides Ln = Sm–Dy, particularly for Tb and Dy with $y \approx 1$, a new

hybrid structure is formed (6, 7); in this phase, which is designated the T*-tetragonal structure (6), the inactive Ln–O layers alternate between the (001) rocksalt LaO layers of the T structure and the fluorite-type layers of the T' structure. Neutron-diffraction data (8) for a T* sample La$_{1.25}$Dy$_{0.75}$-CuO$_4$ has verified that the smaller Ln^{3+} ions are ordered into the fluorite-type layers as required for bond-length matching.

The phase relationships in the systems La$_{2-y}$Ln$_y$CuO$_4$ with larger Ln = Pr and Nd atoms have not been investigated systematically. We report an investigation into the values of t at which the transition from T to T' occurs. A previous investigation (9) of these systems was made before the discovery (6) of the T* structure; it reported an abrupt transition, with no two-phase region specified, from the T/O to the T' phase at $y = 0.75$ and 0.25, respectively, for Ln = Pr and Nd. With the smaller size difference between La^{3+}, Pr^{3+}, and Nd^{3+}, we anticipated there would be no T* phase, only two solid–solution ranges, one with the T/O and the other with the T' structure, in which the Ln^{3+} ions are randomly distributed. Of particular interest to us was the value of t at which a two-phase (T + T') compositional range occurs on increasing y. In this investigation, we discovered a new T'' phase between the T and T' phase fields; this new T'' phase could not be doped either p-type or n-type by cation substitution.

Experimental

La$_{2-y}$Ln$_y$CuO$_4$ (Ln = Pr–Gd) samples were obtained by firing the required quantities of intimately mixed La$_2$O$_3$, Ln$_2$O$_3$, or Pr$_6$O$_{11}$ and CuO at 950°C for 15 hr; the product was ground, pelletized, and refired at 1060°C for 15–30 hr. The pellets were finally annealed in 1 atm O$_2$ at 900°C for 4 hr followed by stopping at 700, 500, 350, and 250°C each for about 12 hr before cooling to 100°C. Doping of La$_{2-y}$Ln$_y$CuO$_4$ with Sr^{2+}

or Ce^{4+} was carried out in a similar way. All products were characterized by X-ray powder diffraction recorded with a Philips diffractometer and $CuK\alpha$ radiation. The average formal oxidation state of Cu and the oxygen content were obtained by iodometric titration (10). All the $La_{2-y}Ln_yCuO_{4+x}$ samples annealed in 1 atm O_2 showed the presence of an excess oxygen content x; the total oxygen content of these samples remained constant at 4.02 ± 0.005. At these concentrations, the excess oxygen does not appear to oxidize the CuO_2 sheets.

Results and Discussion

The variations with the tolerance factor t or y of the room temperature lattice parameters for the $La_{2-y}Nd_yCuO_4$ system are shown in Fig. 1. The orthorhombic T–La_2CuO_4 structure is found for $0 \le y \le 0.35$ and $t \ge 0.8658$. The orthorhombic distortion increases with y due to an increasing tensile stress (decreasing t) introduced by the smaller Nd^{3+} ions in the rocksalt layer. A fluorite-type arrangement of the Ln–O layers for $y \ge 1.2$ gives a stable bond-length matching with the CuO_2 sheets; therefore the T′–Nd_2CuO_4 structure is found for $1.2 \le y \le 2.0$ where a $t \le 0.8585$ would have been required of the T phase. The lattice parameters, c/a ratio, and cell volume decrease monotonically with y in both the T and T′ structures. However, discontinuities in the parameters are associated with the T to T′ phase transition. The T′ structure has a smaller c-axis and c/a ratio and a larger a-axis and cell volume compared to the T structure. The stronger electrostatic repulsion between the O^{2-} ions in the tetrahedral sites of the fluorite layer causes an increase in the a parameter that is not fully compensated by the decrease in the c-axis introduced by the movement of the c-axis oxygen into the tetrahedral sites in the T′ structure. For a given t, the T′ structure therefore adopts a larger volume than the T structure.

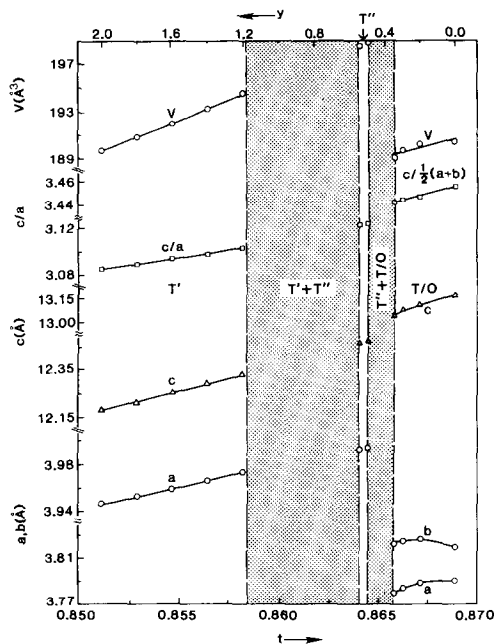

FIG. 1. Variation of room temperature lattice parameters with t or y for the system $La_{2-y}Nd_yCuO_4$ annealed in 1 atm O_2; t values were obtained with the nine-coordinated radius for La^{3+} and Nd^{3+} for all values of y. For comparison, the a and b parameters for the T/O phases are plotted by dividing the actual orthorhombic parameters by $\sqrt{2}$.

The intermediate region $0.35 \le y \le 1.2$ shows interesting phase relationships. The X-ray diffraction patterns (Fig. 2) for the region $0.6 \le y \le 1.1$ reveal the presence of two similar tetragonal phases with only a small difference in their lattice parameters (Fig. 2b). The one with the smaller lattice parameters is like the T′ phase found for $y = 1.2$ (Fig. 2a); the one with the larger lattice parameters corresponds to the single phase found with $y \approx 0.5$ (Fig. 2c). The X-ray diffraction pattern for the single phase occurring in the narrow range $0.5 \le y \le 0.55$ is similar to that of the T′ phase except for slightly larger c parameter than is obtained by extrapolation from the T′ phase field. However, the occurrence of a two-phase region between the T′ phase occurring be-
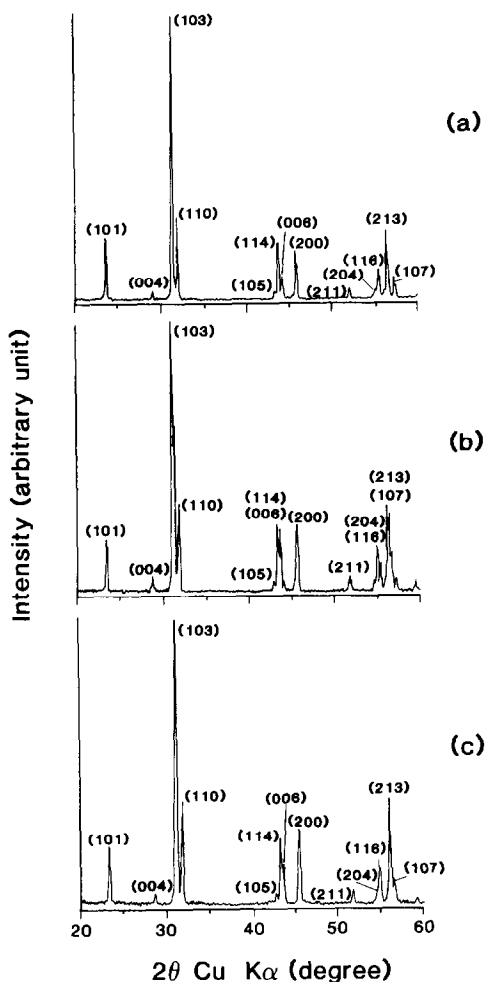
FIG. 2. X-ray powder diffraction patterns for La$_{2-y}$Nd$_y$CuO$_4$: (a) y = 1.2 (T' phase) (b) y = 0.8 (T' and T" phases), and (c) y = 0.5 (T" phase).

tween $1.2 \leq y \leq 2.0$ and the phase appearing between $0.5 \leq y \leq 0.55$ indicates that the phase found at $y = 0.5$ is different from that found at $y = 1.2$. We designate the new phase at $0.5 \leq y \leq 0.55$ the T"-tetragonal phase. Its structure has yet to be determined from single-crystal or neutron-diffraction data. Nevertheless it can be distinguished readily from a T* phase. We therefore presume that any ordering between Nd^{3+} and La^{3+} ions in the T" phase occurs within a Ln–O layer, not between layers. The fact that the T" phase appears to be a line phase with a probably limited solid-solubility range $0.5 \leq y \leq 0.55$ (Fig. 1) is compatible with a cation ordering within the Ln–O layers of a T" phase. In contrast to Singh et al. (9), the compositional range $0.35 < y < 0.5$, which corresponds to $0.8658 \geq t \geq 0.8645$, was found to be two-phase (T/O + T").

Remarkably, pellets of compositions $0.5 < y \leq 1.1$ that had been quenched from 1060°C to room temperature in air disintegrate spontaneously into a fine powder within a few minutes at room temperature in air. This phenomenon was rapid for compositions in the middle of the T' + T" two-phase region with $y \approx 0.8$; it becomes slower and less pronounced upon moving to either side toward the limit of the two-phase region. This observation indicates that, at the firing temperature ($\sim$1060°C), disordering of the cations and/or of the O^{2-} ions within the Ln–O layers stabilizes a single-phase material via a large entropy term in the free energy; upon cooling to lower temperatures, ionic ordering within the Ln–O layers can occur at room temperature, probably giving a "spinodal" decomposition into the phases T' and T" (11). The room temperature decomposition into T' and T" phases was always observed for compositions in the range $0.6 \leq y \leq 1.1$ even if the phase was quenched directly into liquid nitrogen from 1060°C.

When our manuscript was in preparation, a preprint was received from Bringley et al. (12) discussing the phase relationship in the La$_{2-y}$Ln$_y$CuO$_4$ systems. Although our results are in substantial agreement, we differ from their observation/interpretation for the region $0.6 \leq y \leq 1.1$ with Ln = Nd. They claim the formation of a mixture of T' and metastable T* phases for $y \approx 1.0$ if prepared around 950°C for 3 days. Similar experiments were subsequently carried out by us for $y = 1.0$ at 950°C for 2 days; they resulted in the formation of predominantly T' and T" phases with traces of T, but not T*. Anneal-
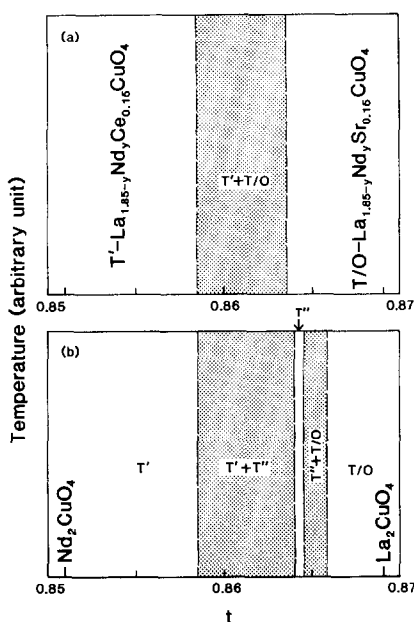
FIG. 3. Phase diagrams for the (a) doped $La_{1.85-y}$ $Nd_ySr_{0.15}CuO_4$ and $La_{1.85-y}Nd_yCe_{0.15}CuO_4$ systems and (b) undoped $La_{2-y}Nd_yCuO_4$ system.

FIG. 4. Variation of room temperature lattice parameters with t or y for the system $La_{2-y}Pr_yCuO_4$ annealed in 1 atm O_2; t values were obtained with the nine-coordinated radius for La^{3+} and Pr^{3+} for all values of y. For comparison, the a and b parameters for the T/O phases are plotted by dividing the actual orthorhombic parameters by $\sqrt{2}$.

ing for 1 week in air at 950 or at 1100°C resulted in the vanishing of the T-phase component, but the presence of both T' and T" phases persisted. The larger Nd^{3+} ions in a fluorite-type arrangement would give a much larger stretching in the basal plane than the La^{3+} ions in the rocksalt arrangement; only smaller Ln^{3+} ions such as Gd^{3+}–Dy^{3+} give a stretching of the fluorite layer comparable to that in a LaO rocksalt layer and hence the good bond-length matching between fluorite and rocksalt layers required to stabilize the T* structure. These considerations rule out the occurrence of a T* phase for $LaNdCuO_4$ or $LaPrCuO_4$.

The new T" phase having a larger a parameter would keep the CuO_2 sheets under tension and the Ln–O layers under compression. Therefore it is expected that the T" phase cannot be doped p-type. Accordingly

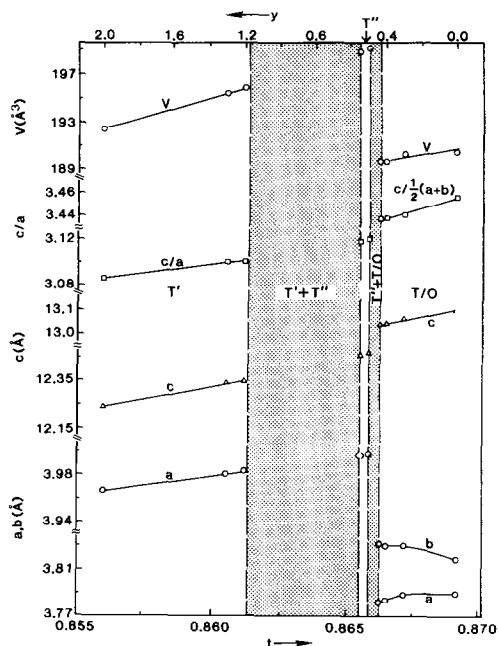our attempts to synthesize $La_{2-y-z}Nd_ySr_z$-CuO_4 with $0.858 < t < 0.864$ resulted in the formation of undoped T' and hole-doped T-phases (Fig. 3). On the other hand, the larger tensile stress on the CuO_2 sheets of the T" phase can be expected to allow n-type doping. However, all our attempts to synthesize $La_{2-y-z}Nd_yCe_zCuO_4$ with $0.858 < t < 0.864$ resulted in an undoped T-phase and an electron-doped T'-phase (Fig. 3) rather than electron-doped T" and/or T" + T'. This result is consistent with cation ordering in the T" phase. Doping would tend to retain a disordered cation array.

Investigation of the $La_{2-y}Pr_yCuO_4$ system showed the phase relationships of Fig. 4; they are similar to those found for $La_{2-y}Nd_yCuO_4$ (Fig. 1). If the phase boundaries

for the T/O and T' phase fields are determined by the tolerance factor t of Eq. (1), then the T/O and the T' phase boundaries would be expected to move to higher values of y if all the Pr is present as Pr^{3+}, which has a larger ionic radius than Nd^{3+}. On the other hand, the T″ phase would remain at $y \approx 0.5$ if cation ordering within the Ln–O layers plays a role in stabilization of the phase. Indeed, the T″ phase remains at $y \approx 0.5$ and the T/O to T″ + T/O phase boundary moves to higher y value as expected. However, the T' to T' + T″ phase boundary does not appear to be shifted. This observation may simply indicate that the t parameter is not a critical determinant of the T' + T″ two-phase domain since it applies strictly only to the T/O phase.

Our attempts to synthesize similar T″ phases in the systems $La_{2-y}Ln_yCuO_4$ (Ln = Sm or Gd) by choosing a y corresponding to a $t \approx 0.864$ resulted in the formation of a two-phase mixture of the T/O and T' phases. It appears that a larger size difference between the La^{3+} and Ln^{3+} ions does not favor an intralayer cation ordering, but an interlayer cation separation.

Acknowledgments

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