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The Influence of Oxygen Activity on T, T', and T^* Phase Stabilities in $(La,RE)_2CuO_4$ Systems

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The effect of oxygen activity on the formation of $(La,RE)_2CuO_4$ (RE = rare earth) solid–solutions has been investigated. Compositions from the $(La,Nd)_2CuO_4$ and $(La,Dy,M)_2CuO_4$ (M = Ce, Th) systems, for example, can be prepared in either the T and T' or T^* and T' structure types, respectively, at different oxygen contents but identical cation stoichiometries, thereby considerably extending the stability field of each structure. These results in part explain some of the differences in several published "equilibrium" phase diagrams for the $(La,Nd)_2CuO_4$ system. © 1990 Academic Press, Inc.

Introduction

Variations in oxygen stoichiometry are known to dramatically affect the transport properties of all of the known high-T_c materials. For example, $La_2CuO_{4+\delta}$ and $Nd_{1.85}Ce_{.15}CuO_{4-\delta}$ transform from insulator to superconductor with changes as small as $\delta \leq 0.05$, or ~1% of the total oxygen content (*1*). In the present work, we have examined the effect of oxygen activity on solid–solutions of the type $La_{2-x}Nd_xCuO_4$ and $La_{2-x}Dy_xCuO_4$ (Ce- and Th-doped). We find that subtle stoichiometry changes occur in the oxygen sublattice depending upon oxygen activity and temperature during processing. These small variations in oxygen content influence the precise location of the T/T' or T'/T^* phase boundaries in these systems, thereby stabilizing two different structure types at a fixed cation composition. These observations will aid in the design of phase selective synthetic routes to the T, T', and T^* phases.

T/T' Phase Transition

Although there is some disagreement in the literature (*2–5*), we find that the equilibrium phase diagram of $La_{2-x}Nd_xCuO_{4+\delta}$ in air at 1050°C (*2*) consists of a simple binary system containing the T structure for $0.0 \leq x \leq 0.4$ and the T' structure for $0.5 \leq x \leq 2.0$, separated by a narrow two-phase region. We have examined the crystal chemistry of this system under various synthetic conditions ($700°C \leq T \leq 1150°C$; $0 \leq P_{O_2} \leq 400$ bar) near the phase boundary and have found that it is sensitive to both oxygen fugacity and temperature.

Figure 1a shows the X-ray powder diffraction profile of $La_{1.4}Nd_{.6}CuO_{4.04}$ prepared

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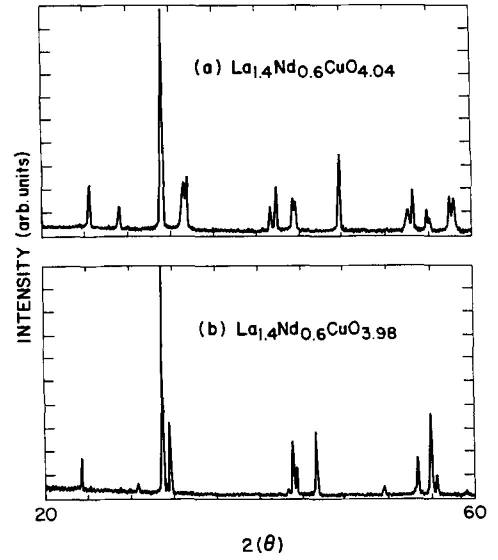

FIG. 1. X-ray powder diffraction profiles of (a) the T and (b) the T'phase at composition $La_{1.4}Nd_{.6}CuO_{4\pm\delta}$. The observed oxygen stoichiometries are indicated.

from the coprecipitated hydroxides (2) in 400 bar O_2 at 910°C. The pattern is that of single phase material having the T structure with orthorhombic lattice parameters a = 5.339 Å, b = 5.388 Å, and c = 13.073 Å. Since the solid–solution boundary in air at 1050°C occurs at $x = 0.4$ (2), the T phase field extends to considerably greater Nd content under high oxygen fugacity. Further, we find that this T phase can be stabilized to $x \lesssim 0.7$ at 900°C and 400 bar O_2. The use of mixed hydroxide precursors is important in these experiments, making it possible to prepare single phase material in a single-step process (48 hr). High P_{O_2} reactions using mixed oxides usually resulted in incompletely reacted phase assemblages.

Heating the T phase ($x = 0.6$) in air at 1050°C for 5 days, and then rapidly quenching it, produced material with the T' diffraction profile shown in Fig. 1b. Its overall stoichiometry is $La_{1.4}Nd_{.6}CuO_{3.98}$, with lattice parameters a = 3.991 Å and c = 12.460 Å. The T phase with higher La content, e.g., $La_{1.5}Nd_{.5}CuO_{4.01}$, forms at 950°C and 1 atm O_2. Annealing this material at 1050°C in air, followed by rapid quenching, results in its conversion to a T' phase with the composition $La_{1.5}Nd_{.5}CuO_{3.98}$.

Remarkably, the oxygen stoichiometries determined by iodometric titration (6) of the T and T' phases in the $La_{2-x}Nd_xCuO_{4+\delta}$ system differ by only $\delta = 0.03$ and 0.06, respectively, for $x = 0.5$ and 0.6. TGA of $La_{1.4}Nd_{.6}CuO_{4.04}$ in N_2 at 5°/min reveals that the T phase is stable to ~850°C, after having lost oxygen to the extent $\Delta\delta = -0.04$. On further heating, a phase transition to T' occurs with a concomitant change in oxygen stoichiometry $\Delta\delta = -0.06$ between 850 and 1025°C. In general, TGA analyses of the $La_{2-x}Nd_xXCuO_{4-\delta}$ solid–solution compositions close to the phase boundary indicate that the T phase is stable for $\delta > 0$, but that T' occurs for $\delta < 0$, with the $T \rightarrow T'$ transition occurring for $\delta \approx 0$. The reversibility of the transition was checked by heating the T' phase, $La_{1.4}Nd_{.6}CuO_{3.98}$, at 910°C in 400 bar O_2 for 48 hr, completely converting it to the T structure.

T^*/T' Phase Transition

Previously, we showed that pure T^* phases can be isolated in the $La_{2-x}Dy_xCuO_4$ system for $0.8 \leq x \leq 1.0$ (2). This system can be doped with divalent cations (7). We have now found it possible to also dope it with tetravalent (M = Ce or Th) cations. However, it is found that small concentrations of Ce and Th induce a phase transition from the T^* to the T' structure, but that the transition point can be controlled by the oxygen fugacity. For example, in the $La_{1.2}Dy_{.8-x}M_xCuO_{4+\delta}$ systems, a $T^* \rightarrow T'$ transition occurs for $x \approx 0.05$ for samples prepared in air at 1050°C. However, when the materials are prepared in 1 atm O_2 at 950°C, the limit of Ce and also Th-doping into T^* is $x = 0.10$, and it extends to $x \simeq$

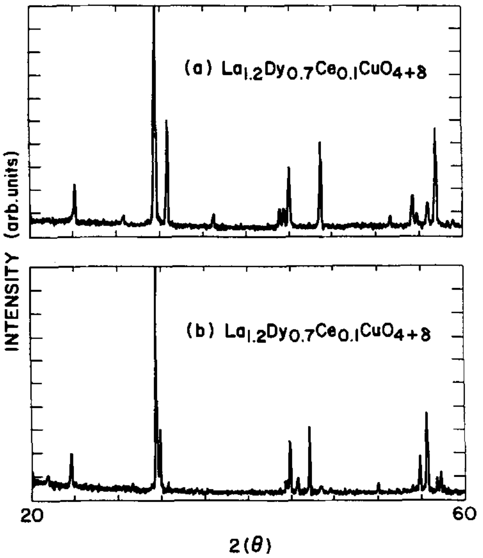

FIG. 2. X-ray powder diffraction profiles of (a) the T^* and (b) the T' phase at composition $La_{1.2}Dy_{.7}Ce_{.1}CuO_{4+\delta}$.

0.15 at 900°C in 350 bar O_2. Figures 2a and 2b show the X-ray powder diffraction profiles of $La_{1.2}Dy_{.7}Ce_{.1}CuO_{4+\delta}$ prepared at 950°C in $P_{O_2} = 1$ atm and $P_{O_2} \approx 0$ atm (N_2 atm), respectively. The sample prepared in oxygen contains only a T^* phase with lattice parameters $a = 3.868$ Å and $c = 12.463$ Å, while that prepared in nitrogen is T' with $a = 3.961$ Å and $c = 12.16$ Å. The T'/T^* phase boundary, therefore, is also extremely sensitive to oxygen fugacity: T^* is stabilized at higher P_{O_2}, whereas T' forms under more reducing conditions. Due to their poor solubility in hydrochloric acid and the complications introduced by Ce^{4+}, the overall oxygen contents of the doped solid–solutions could not be determined reliably by iodometric titration.

Since Dy^{3+} (1.08 Å) and Th^{4+} (1.09 Å) are virtually the same size (*8*), tolerance factor arguments based on ionic size alone (*2*) cannot explain the shift in the T^*/T' phase boundary. Although the driving force for the transition is not completely clear, it could be related to electronic factors which also make the T^* phase resistant to electron doping. In this context, it is interesting that iodometric analyses of the T^* phase $La_{1.2}Dy_{.7}Th_{.1}CuO_{4+\delta}$ prepared in O_2 at 950°C gave $\delta = 0.06$, so that the apparent electron doping by Th is compensated by uptake of excess oxygen such that the formal copper valence remains above or close to two.

Discussion

The sensitive dependence of phase equilibria on reaction or annealing conditions is the likely cause of disagreements in the literature regarding the phase diagram of $La_{2-x}Nd_xCuO_4$. For example, Manthiram *et al.* (*3*) observed a much wider two-phase region ($0.6 \leq x \leq 1.1$) for samples heated and slowly cooled in oxygen. In this region they observe T', but apparently also a new phase, denoted T''. The T'' compound exhibits a narrow homogeneity range near $x = 0.5$. Its diffraction pattern is similar to T', but differs in that a unique ordering of rare earth cations is postulated (*3*). In phase diagram work carried out at 950°C in air, Singh *et al.* (*4*) observed the T structure in the range $0 \lesssim x \lesssim 0.17$, and T' for $0.25 \lesssim x \lesssim 2$, whereas Wang *et al.* (*5*) report a two-phase region $0.4 \leq x \leq 1.1$ for samples prepared in oxygen at 1100°C.

Although we have observed the two-phase region reported by Manthiram *et al.* (*3*) for $0.8 \leq x \leq 1.0$, we find that prolonged heating (>100 hr) in air at 1050°C, with several intermediate regrindings, produces single-phase T' if the samples are quenched. These results, as well as those obtained by Singh *et al.* (*4*) and Wang *et al.* (*5*), indicate that the T' solid solubility field narrows at higher temperature and/or higher oxygen activity. In view of the present results, it is clear that phase relationships in $La_{2-x}Nd_xCuO_4$ depend strongly upon synthesis and annealing conditions, and that the dissimilar reports need not be considered contradictory, especially since each study was carried out differently. Phase relationships in these systems are complex, and by judicious choice of synthetic conditions, the stability/metastability fields of the closely related *T*, *T'*, and *T** phases can be manipulated considerably. Indeed, it has been shown (*9*) that $La_{1.85}Ce_{.15}CuO_4$ can be synthesized with the *T'* structure at low temperature (600°C), and even a *T'* form of La_2CuO_4 has been prepared through a unique low temperature kinetic channel (*10*).

The oxygen activity effects observed in our experiments occur for compositions adjacent to the transition boundaries determined in air. Since two structure types have similar free energies near their phase boundary, it is perhaps not surprising that the resulting small shifts in oxygen stoichiometry brought about by fugacity change are so effective in steering phase selection. A substoichiometric oxygen content is destabilizing to the *T* structure, with its higher cation–oxygen coordination numbers, while this favors the *T'* structure. A similar argument can be made for *T** vs *T'*. These effects are also consistent with the observed doping preferences of the *T*, *T'*, and *T** phases (*11*).

The results we have obtained can be fit neatly into the simple framework of the tolerance factor model (*2, 3*). Tolerance factors for the two solid–solution systems shift in the expected directions, i.e., toward the previously determined (*2*) stability fields in air ($\delta \approx 0$) when recalculated on the basis of the amount of Cu^{3+} (Cu^{1+}) created by the oxygen excess (deficiency). This result lends consistency to the tolerance factor correlation, the physical and chemical foundation of which has been discussed previously by us (*2*) and by Manthiram and Goodenough (*1, 3*).

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