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# Energetics of T, T′, and T* Phases in Some Rare Earth Cuprates

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The enthalpies of solution in molten $2PbO \cdot B_2O_3$ at 704°C of $Nd_2CuO_4$ (T′), $(La_{1-x}Nd_x)_2CuO_4$ (T or T′), $(La_{0.60}Dy_{0.35}Ce_{0.05})_2CuO_4$ (T′ and T*), and $(La_{0.60}Dy_{0.35}Th_{0.05})_2CuO_4$ (T′ and T*) have been measured. The enthalpy of formation (from oxides) at 700°C of $(La_{1-x}Nd_x)_2CuO_4$ ($0 \le x \le 1$) varies from −20 to −7 kJ mol$^{-1}$, depending on composition. The enthalpy of the T′ to T transition in $(La_{0.75}Nd_{0.25})_2CuO_4$ is +6.3 ± 2.8 kJ mol$^{-1}$. Extrapolated enthalpies of transition from T′ to T are +3 ± 8 kJ mol$^{-1}$ for $La_2CuO_4$ and +28 ± 10 kJ mol$^{-1}$ for $Nd_2CuO_4$. The enthalpy of mixing in the T′ phase of $(La_{1-x}Nd_x)_2CuO_4$ is positive, with a regular enthalpy interaction parameter of +51.8 kJ mol$^{-1}$. The positive enthalpy of mixing argues against cation ordering being important in this system. The enthalpies of transition of T* to T′ of $(La_{0.6}Dy_{0.35}Th_{0.05})_2CuO_4$ and $(La_{0.6}Dy_{0.35}Ce_{0.05})_2CuO_4$ are +38 ± 5 and +51 ± 6 kJ mol$^{-1}$, respectively. There is a linear dependence of the enthalpy of transition ($\Delta H$) between T′ and T (or T* and T′) phases on the volume of transition ($\Delta V$), $\Delta H$ (kJ mol$^{-1}$) = 37.4 + 9.27 $\Delta V$ (cm$^3$ mol$^{-1}$).


## Introduction

There are three related structure-types with stoichiometry $(RE)_2CuO_4$ ($RE$ = rare earth). Each of them consists of isolated sheets of either 4-fold (T′ structure), 5-fold (T* structure), or 6-fold (T structure) oxygen-coordinated copper cations (*1*) (see Figure 1). The phase with the largest $RE$ cation (La) crystallizes in a distorted $K_2NiF_4$ T structure (*2*, *3*). Phases with rare earth ions of intermediate size (Pr–Gd) assume the T′ structure of $Nd_2CuO_4$ (*4*). A third structure denoted T* is observed with certain combinations of rare earth and alkaline earth cations (e.g., $(La_{0.60}Dy_{.35}Ce_{.05})_2CuO_4$). Layers of rare earth ions isolate the copper layers in all three structures. Coordination of $RE$ ions is ninefold for the T structure in rocksalt-like La–O layers (four oxygens of the neighboring $CuO_2$ planes and five oxygens within the (001) rocksalt La–O planes) and eightfold for the T′ structure in $NdO_2$ fluorite-type layers. Both types of coordination are found in the T* structure, on opposite

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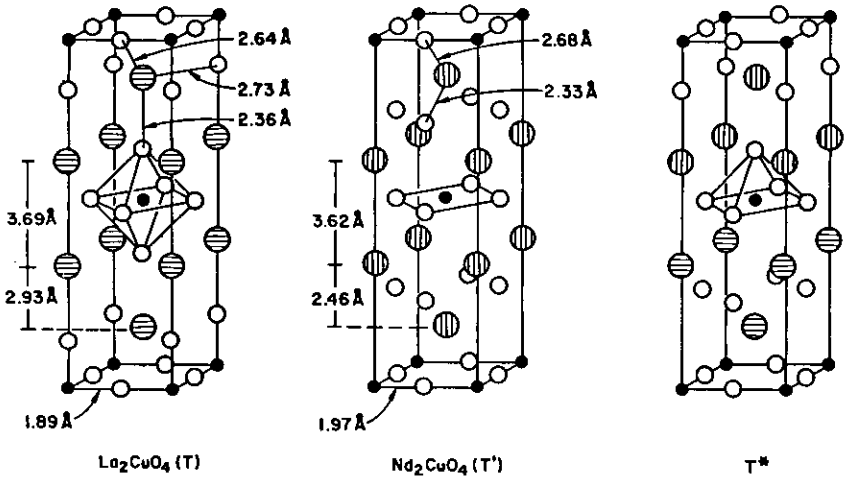


FIG. 1. T, T', and T* structures. Cu, solid circles; oxygen, open circles; and rare earth, shaded circles.

sides of each copper layer (see Fig. 1). Neutron diffraction studies have shown that the T* is a hybrid of the T and T' structures (*5, 6*) with *RE–O* rocksalt and $RE$–$O_2$ fluorite-type layers separated by $CuO_5$ square pyramids. In the T and T' structures, $CuO_6$ and $CuO_4$ bipyramids and squares occur, respectively. All these copper–oxygen polyhedra share corners in the (001) plane.

Manthiram and Goodenough reported recently (*16*) the possible existence of a new T'' phase with $(La_{0.75}Nd_{0.50})_2CuO_4$ composition in the $(La_{1-x}Nd_x)_2CuO_4$ system. This T'' phase appears to be an ordered variant of the T' phase (*16*) with intralayer ordering of $La^{+3}$ and $Nd^{+3}$ cations within the $(La, Nd)_2O_2$ layers. However, their X-ray diffraction and neutron data could not confirm the existence of an ordered T'' phase (*16*).

Recently phases with *RE* = Y, Dy, Ho, Er, Tm were found to crystallize in the T'-$Nd_2CuO_4$ structure under a pressure of 6 MPa at 950°C (*7*). Under ambient pressure, when *RE* is smaller in size than Gd, the T' structure does not appear and other phase mixtures form. In addition, oxygen activity was found to have a strong influence on the crystal chemistry of these phases (*14*).

The above structures show a richness of electrical behavior including insulating, semiconducting, metallic, and supeconducting properties. This variety of transport properties is related to the nature and degree of doping, oxygen stoichiometry, and, more generally, to the resulting defect chemistry. In T type structures, in the conducting and superconducting state, charge carriers are holes (*8–10*). In contrast certain T' compounds doped with Ce and Th, $(RE_{1-x}Me_x)_2CuO_{4-\delta}$ (*RE* = Pr, Nd, Sm, Eu, *M* = Ce, Th) (*11*), are claimed to be electron-type superconductors (*11–13, 31*).

In an effort to understand the crystal chemistry, phase stability, and doping preferences of T, T', and T* phases, a simple ionic model was developed (*1*) in which a perovskite-like tolerance factor ($t$) was found to be a predictor of T, T', and T* stability limits. Although a simple ionic model furnishes geometrical reasons for stability of T, T', and T* structures, it can not be readily quantified to make energetic or thermodynamic predictions of stability.

This study addresses energetics of phase transition between T′ and T and T′and T* structures and energetics of formation of several T and T′ phases from their component oxides using high temperature reaction calorimetry. Series of solid solutions $(La_{1-x}Nd_x)_2CuO_4$ with both T and T′ structures were investigated together with $(La_{0.6}Dy_{0.35}Th_{0.05})_2CuO_4$ (T* and T′) and $(La_{0.6}Dy_{0.35}Ce_{0.05})_2CuO_4$ (T* and T′).

There is still a controversy regarding the phase diagram in the $(La_{1-x}Nd_x)_2CuO_4$ (T–T′) system (*1*, *14–16*). In contrast to earlier workers, Manthiram and Goodenough (*15,16*) have shown that the T′–T phase boundary depends on temperature (solubility of $Nd^{3+}$ increase in the T phase with increasing temperature) and they report the existence of a two phase region (T′ + T) approximately $x = 0.1$ wide. They place, as discussed above, the tetragonal, line T″ phase at $x = 0.25$ above 900°C. The present paper also addresses the question of the existence of the T″ phase.

## Experimental

### *Sample Preparation*

Table I contains conditions of preparation for all samples. Full experimental details of sample preparation are provided elsewhere (*1*, *14*). Sample identification was based on powder X-ray diffraction patterns obtained on a Siemens D500 diffractometer at IBM or a Scintag PAD V diffractometer at Princeton, both using Cu$K\alpha$ radiation. X-ray diffraction patterns of most of the samples were taken immediately before calorimetric experiments. Only one sample of T-$(La_{0.7}Nd_{0.3})_2CuO_4$, initially prepared under 400 bar of oxygen (*14*), was found to decompose to a mixture of T and T′ phases at room temperature after 3 days. Two new syntheses gave the same result; after 2–3 days at room temperature T-$(La_{0.7}Nd_{0.3})_2CuO_4$ decomposed to a mixture of T′ and T at ambient pressure. This sample was excluded from calorimetric investigation, although pure T′-$(La_{0.7}Nd_{0.3})_2CuO_4$ was used.

The samples were checked by X-ray diffraction to see if they maintained the structure after 10–15 hr equilibrium in the calorimeter at 704°C. All $(La_{1-x}Nd_x)_2CuO_4$ solid solutions including T- and T′-$(La_{0.75}Nd_{0.25})_2CuO_4$, failed to transform during equilibration at 704°C in the calorimeter. On the other hand, two samples of T′-$La_2CuO_4$ (A and B, see below), prepared according to the procedure described by Chou *et al.* (*17*), transformed entirely to the T structure after 40 min at 704°C. Transposed temperature drop calorimetry was used for these samples to determine the enthalpy of T′ ⇒ T transition, see below.

The oxygen content in our samples was $4.00 \pm 0.02$ (*14*) based on iodometric titration and thermogravimetric analysis, in agreement with recently published results of Manthiram and Goodenough (*16*). Although small variations in oxygen stoichiometry may have subtle effects on transport properties, phase relations, and energetics, the variations in oxygen content in these samples (<0.02) are too small to be resolved in the calorimetric measurements. In the discussions which follow, we neglect any possible effects of such small variations of oxygen stoichiometry on phase stability.

### *Calorimetry*

Solution calorimetric measurements were performed at 704°C in molten $2PbO \cdot B_2O_3$ solvent. The high temperature twin Calvet type solution calorimeter and the technique used have been described previously (*18*). For solution calorimetry, a sample of 20–30 mg was suspended in a platinum sample holder 1 cm above molten solvent for 8–15 hr to reach thermal equilibrium. Only in the case of T′-$(La_{0.6}Dy_{0.35}Ce_{0.05})_2CuO_4$ did the sample partially (10%–20%) convert to T* after 8–9 hr at 704°C. However, after 2 hours annealing in air, the sample retained the T′ structure. In this case, solution calorimetry

TABLE 1

SAMPLE SYNTHESIS CONDITIONS

| Sample | Structure | Method of preparation,[a] atmosphere, temperature, time |
|---|---|---|
| $(La_{0.85}Nd_{0.15})_2CuO_4$ | T | Dry from carbonates and CuO, air, 1 atm, 950°C, 20 hr + 1050°C, 40 hr + 700°C, 40 hr, quench |
| $(La_{0.75}Nd_{0.25})_2CuO_4$ | T | oxygen, 1 atm, 900°C, 10 hr |
| $(La_{0.75}Nd_{0.25})_2CuO_4$ | T′ | air, 1 atm, 1050°C, 5 days, quench |
| $(La_{0.7}Nd_{0.3})_2CuO_4$ | T′ | air, 1 atm, 1050°C, 5 days, quench |
| $(La_{0.6}Nd_{0.4})_2CuO_4$ | T′ | air, 700°C, 20 hr |
| $(La_{0.5}Nd_{0.5})_2CuO_4$ | T′ | air, 825°C, 20 hr |
| $(La_{0.35}Nd_{0.65})_2CuO_4$ | T′ | air, 1050°C, 16 hr, quench |
| $(La_{0.25}Nd_{0.75})_2CuO_4$ | T′ | air, 1050°C, 16 hr, quench |
| $(La_{0.125}Nd_{0.875})_2CuO_4$ | T′ | air, 1050°C, 16 hr, quench |
| $Nd_2CuO_4$ | T′ | Dry from carbonate and oxide, air, 1 atm, 1000°C, 60 hr + 1100°C, 20 hr, quench |
| $La_2CuO_4$ (A) | T′ | Oxidation of S-$La_2CuO_{3.6}$, oxygen, 1 atm, 450°C, 5 hr |
| $La_2CuO_4$ (B) | T′ | Oxidation of S-$La_2CuO_{3.6}$, oxygen, 1 atm, 400°C, 10 hr |
| $(La_{0.6}Dy_{0.35}Th_{0.05})_2CuO_4$ | T′ | air, 1050°C, 36 hr |
| | T* | oxygen, 950°C, 48 hr |
| $(La_{0.6}Dy_{0.35}Ce_{0.05})_2CuO_4$ | T′ | argon, 910°C, 16 hr |
| | T* | oxygen, 950°C, 48 hr |

[a] Where not otherwise indicated, samples were prepared from oxides and hydroxides (+).

experiments were performed as follows. First the calorimeter was equilibrated with all necessary glassware and solvent. Then the sample and its support were lowered over the solvent only 90 min before calorimetry.

The T, T′, and T* phases investigated dissolved readily in molten $2PbO \cdot B_2O_3$. Commerical hexagonal $Nd_2O_3$ (Aesar 99.99% AAS grade) powder formed a precipitate, probably $NdBO_3$, during calorimetry, as confirmed by X-ray diffraction of a blue material found in the sample holder after the solution experiment. Similar behavior has been observed for $La_2O_3$ previously in this laboratory (*19*). As for $La_2O_3$, preparation of $Nd_2O_3$ using an aqueous precipitation route resulted in an oxide which could be dissolved without precipitation of $NdBO_3$. The commercial $Nd_2O_3$ powder was dissolved in nitric acid. The solution was heated to dryness on a hot plate and then carefully heated with a flame to drive off nitrogen oxides. The sample was heated at 1100°C for 20 hr. X-ray diffraction confirmed single phase hexagonal $Nd_2O_3$. Hexagonal $Nd_2O_3$ was also preserved during overnight equilibration in the calorimeter at 704°C before dissolution experiments. Only this initial porous $Nd_2O_3$ could dissolve readily; when it is ground, it showed precipitation of $NdBO_3$. Slow kinetics of dissolution of $NdBO_3$ (if formed) apparently play an important role and the morphology of the sample apparently controls of kinetics of dissolution (*19*). Since the porous material dissolved more slowly after grinding, the presence of air spaces between the particles appears more important than particle size itself.

Enthalpies of solution of $La_2O_3$ and CuO used in this study were taken from experiments performed earlier in this laboratory (*19*).

Since two samples, T′-$La_2CuO_4$(A and B), transform to T phases after only 40 min

at 704°C, we used the transposed temperature drop method to measure the enthalpy of T′ ⇒ T transition. A sample (~25 mg powder enclosed in an ~30 mg platinum capsule) was dropped from room temperature through a hollow silica tube into an empty Pt crucible in the hot calorimeter (704°C). The measured heat effect was the sum of the heat contents of the platinum and the sample plus the enthalpy of any reaction or phase transition which occurred rapidly at calorimetric temperature. A second drop of this same sample (retrieved) gave heat content terms only. The difference between the first and second drop gave the enthalpy of reaction at room temperature. However, these data had to be corrected for weight loss related to the release of volatiles during the first drop; see below.

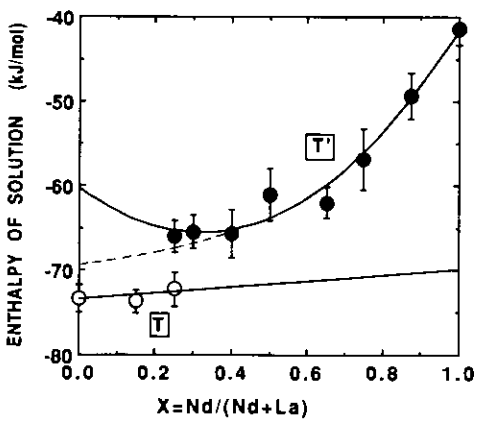


FIG. 2. Enthalpy of solution of $(La_{1-x}Nd_x)_2CuO_4$ in $2PbO \cdot B_2O_3$ at 704°C. T′ phase solid circles; T phase open circles. Curve is described by Eq. (3) and straight line by Eq. (4). The dashed line represents heat of solution of T′ phase extrapolated (hand drawn) to $La_2CuO_4$ composition as a smooth curve with the least curvature required by the data.

*High Temperature Mass Spectrometry*

The thermal stability of the $La_2CuO_{4+x}$ powders was studied by Knudsen Effusion Mass Spectrometry (KEMS). The instrumentation of the high temperature mass spectrometer system is described in detail elsewhere (*29*, *30*). Several important features are incorporated in this system, resulting in an exceptionally high sensitivity. These include a differentially pumped ultra-high-vacuum environment for both the mass spectrometer and furnace, the use of digital modulation techniques, and fully automated instrumentation.

Samples, 1 mg in size, were weighed into a platinum cup with 1 μg precision and placed in a platinum-lined Knudsen cell. The cell was heated at 2°C/min from 25 to 623°C. A Pt vs 90% Pt–10% Rh thermocouple was used for temperature measurement and control. The molecular beam from the Knudsen cell was modulated at 20 Hz, followed by ionization using 30-eV electrons. The ion currents (counts/sec), which are proportional to the gas flux through the orifice, were measured for the significant vapor species, $H_2O$, $O_2$, and $CO_2$, with an automated quadrupole mass spectrometer. After heating, the samples were reweighed and the weight loss used for calibration of the integrated ion signals.

## Results and Discussion

*T′ to T Transition*

The heats of solution of the $(La_{1-x}Nd_x)_2CuO_4$ solid solution ($0 \leq x \leq 1$) at 704°C in the lead borate solvent are given in Table II and Figure 2. The enthalpy of formation of $(La_{1-x}Nd_x)_2CuO_4$ solid solutions from the oxides was calculated from enthalpies of solution according to the reaction

$$(1 - x)La_2O_3 + xNd_2O_3 + CuO \Rightarrow (La_{1-x}Nd_x)_2CuO_4 \quad (1)$$

using the equation

$$\Delta H_f = (1 - x)\Delta H_{sol}(La_2O_3) + x\Delta H_{sol}(Nd_2O_3) + \Delta H_{sol}(CuO) - \Delta H_{sol}(\text{solid solution}). \quad (2)$$

All enthalpies of formations are definitely negative. This confirms that the entire se-

TABLE II

ENTHALPY OF SOLUTION (IN $2PbO \cdot B_2O_3$ AT 704°C) AND ENTHALPY OF FORMATION (FROM OXIDES) OF $(La_{1-x}Nd_x)_2CuO_4$ SOLID SOLUTIONS

| Composition $x$ | Structure | $\Delta H$ (solution) (kJ mol$^{-1}$) | $\Delta H$ (formation from oxides) (kJ mol$^{-1}$) |
|---|---|---|---|
| 0.00 | T-$La_2CuO_4$ | −73.3 ± 1.6[a] (20)[b] | −19.4 ± 4.7[c] |
| 0.15 | T | −73.7 ± 1.3 (4) | −13.4 ± 4.1 |
| 0.25 | T | −72.3 ± 2.0 (10) | −11.1 ± 4.1 |
| 0.25 | T′ | −66.0 ± 1.9 (7) | −17.5 ± 4.6 |
| 0.30 | T′ | −65.5 ± 2.0 (6) | −16.1 ± 4.5 |
| 0.40 | T′ | −65.7 ± 2.9 (5) | −12.2 ± 4.6 |
| 0.50 | T′ | −61.1 ± 3.1 (6) | −13.2 ± 4.8 |
| 0.65 | T′ | −62.0 ± 1.8 (5) | −6.7 ± 4.4 |
| 0.75 | T′ | −56.8 ± 3.7 (4) | −8.2 ± 5.8 |
| 0.875 | T′ | −49.3 ± 2.7 (7) | −11.1 ± 5.7 |
| 1.00 | T′-$Nd_2CuO_4$ | −41.5 ± 1.9 (11) | −14.3 ± 6.0 |
| $Nd_2O_3$ | A-hexagonal | −89.1 ± 5.7 (10) | — |
| $La_2O_3$ | A-hexagonal | −126.0 ± 4.4 (7) | — |
| CuO | tenorite | +33.3 ± 0.4 (10) | — |

[a] Two standard deviations of mean.
[b] Number of experiments performed.
[c] Propagated error of $Nd_2O_3$, $La_2O_3$, CuO, and solid solutions.

ries, $(La_{1-x}Nd_x)_2CuO_4$, is thermodynamically stable relative to the component oxides because the entropy change is expected to be small. The enthalpy of formation can be interpreted as follows. Introduction of $Nd^{3+}$ cations to $T - La_2CuO_4$ destabilizes this structure relative to the component oxides from −19.4 kJ mol$^{-1}$ at $x = 0$ to −11.1 kJ mol$^{-1}$ at the limit of the T phase, $x = 0.25$. The heats of solution fall on a straight line within experimental error. The T′ phase, extending from $x = 0.25$ to $x = 1$, shows definite curvature in $\Delta H_{sol}$, consistent with a positive heat of mixing in the solid solutions and a maximum (greatest destabilization) in the heat of formation from the oxides.

In the T phase,

$$\Delta H_{sol} = -73.6\ (\pm 0.7) + 3.5\ (\pm 4.5)x, \quad (3)$$

and in the T′ phase,

$$\Delta H_{sol} = -60.3\ (\pm 3.7) - 33.3\ (\pm 13.7)x + 51.8\ (\pm\ 11.0)x^2. \quad (4)$$

Equation (3) is consistent with zero enthalpy of mixing in the T phase, though the small extent of this phase ($0 \leq x \leq 0.25$) limits the accuracy of this conclusion. Equation (4) implies a positive enthalpy of mixing in the T′ phase, with a regular enthalpy interaction parameter of +51.8 kJ per mole of $(La_{1-x}Nd_x)_2CuO_4$, that is, per 2 mol of cations being mixed.

It has been suggested that $(La_{0.75}Nd_{0.25})_2CuO_4$ forms a tetragonal T″ structure related to T′, but with ordering of $La^{3+}$ and $Nd^{3+}$ cations within the (La, Nd)$O_2$ layers (*15*). Neutron diffraction experiments, however, did not reveal such intralayer ordering (*16*). Similarly, we have found no evidence of intralayer ordering from both X-ray and electron diffraction studies of our $(La_{0.75}Nd_{0.25})_2CuO_4$ samples. Electron diffraction patterns from crystallites in our calorimetric samples (see Table I for preparation conditions) typically gave the results shown in Fig. 3. The absence of superlattice

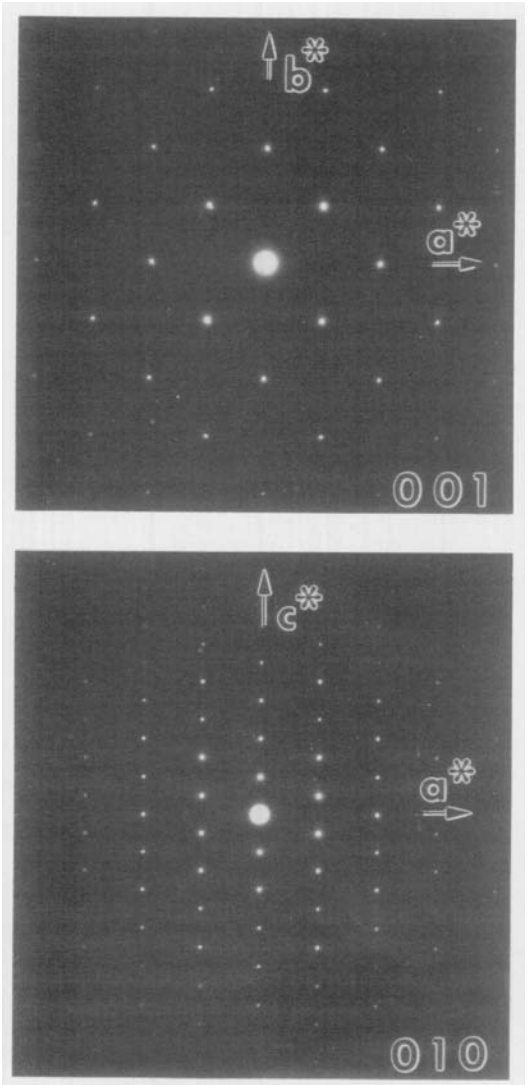


FIG. 3. Typical electron diffraction patterns for $(La_{0.75}Nd_{0.25})_2CuO_4$ samples.

reflections and $c/a = 1.106$ is completely consistent with a simple T′ structure with a disordered distribution of $La^{3+}$ and $Nd^{3+}$ cations in the rock-salt layers. Furthermore, the positive enthalpies of mixing seen do not support cation ordering, which would generally be expected to manifest itself in negative enthalpies of mixing. Thus if any La, Nd ordering occurs, its structural effects are very subtle and its stabilizing energetics must be masked by other factors. The observed positive enthalpy of mixing in the T′ phase argues against cation ordering being thermodynamically important.

The data may be used to calculate directly the enthalpy of transformation between T and T′ structures in $(La_{0.75}Nd_{0.25})_2CuO_4$ since both phases were synthesized and solution calorimetry was performed. The enthalpy of the transition

$$T' - (La_{0.75}Nd_{0.25})_2CuO_4 \Rightarrow T - (La_{0.75}Nd_{0.25})_2CuO_4 \quad (5)$$

is 6.3 ± 2.8 kJ/mol at 704°C.

The calorimetric data may also be used to estimate enthalpy differences between T and T′ structures for other compositions as follows.

A linear extrapolation of the enthalpy of solution data for the T structure gives $\Delta H_{sol}(T - Nd_2CuO_4) = 70.1$ kJ mol$^{-1}$, for pure $Nd_2CuO_4$. Therefore, for

$$T' - Nd_2CuO_4 \Rightarrow T - Nd_2CuO_4, \quad (6)$$

$\Delta H = 28.6$ kJ mol$^{-1}$. We estimate the uncertainty in this extrapolation to be ±10 kJ mol$^{-1}$ because of the small range of solid solubility. This endothermic value is consistent with the nonexistence of the T phase under atmospheric pressure conditions.

For $La_2CuO_4$, the data point to a more complex interpretation. Extrapolation of Eq. (4) to $x = 0$ gives an enthalpy of solution of −60.3 kJ mol$^{-1}$ for T′ − $La_2CuO_4$ and, for the reaction

$$T - La_2CuO_4 \Rightarrow T' - La_2CuO_4, \quad (7)$$

$\Delta H = -13.0$ kJ mol$^{-1}$. This exothermic enthalpy would imply that the T′ structure is thermodynamically stable at low temperature for $La_2CuO_4$.

The regular solution approximation may overestimate the curvature of the heat of solution data in the T′ phase (see Fig. 2). The form of the heat of solution curve may

depend in a complex manner on composition and not be properly represented by any simple polynomial, especially if there is any tendency toward cation ordering, as discussed above. For illustrative purposes, the dashed curve in Fig. 2 represents a (hand-drawn) smooth curve with the least curvature required by the data. It implies an enthalpy of transition (Eq. (7)) of about $-3$ kJ mol$^{-1}$. This would still suggest that T′ − $La_2CuO_4$ could be a stable phase at low temperature.

T′ − $La_2CuO_{4+\delta}$ can be obtained when reduced lanthanum cuprate of $Sr_2CuO_3$-type structure (so-called S structure) is slowly oxidized in oxygen at temperatures below 500°C (*17*). We have obtained two T′ − $La_2CuO_4$ samples (A and B) using this procedure and used transposed temperature drop calorimetry to obtain the enthalpy of transition (see Table III). However, both samples showed significant weight loss (0.4% and 0.9% respectively) during the first drop, implying loss of volatiles. They showed no further weight change in subsequent drops. If all weight loss was due to oxygen evolution, and if one assumed that the product, T − $La_2CuO_4$, was stoichiometric, then the two initial samples would be significantly oxygen-rich, namely T′ − $La_2CuO_{4.10}$ and T′ − $La_2CuO_{4.25}$. To check this assumption, we performed thermal programmed desorption (TPD) measurements with analysis of evolved gases by Knudsen effusion mass spectrometry (KEMS). The results (see Table IV) show that oxygen was only a minor component of the volatiles evolved, which were mainly water and carbon dioxide. We use these data to correct for the enthalpy of volatile evolution in the first drop. We assume, as a starting point, that the $H_2O$, $CO_2$, and $O_2$ are adsorbed on the sample surface and have the thermochemical properties of pure liquid water, gaseous carbon dioxide, and gaseous oxygen, respectively. The observed enthalpy, in J/g, on the first drop, is then

$$\Delta H_{obs} = (\text{weight fraction } La_2CuO_4)\,\Delta H(La_2CuO_4) + (\text{weight fraction volatiles})\,\Delta H(\text{volatiles}), \quad (8)$$

where $\Delta H$ (volatiles) is the heat content (in J/g) of a mixture of $H_2O$, $CO_2$, and $O_2$ in the proportions obtained from the KEMS measurements. From this $\Delta H(La_2CuO_4)$ in J/g and in kJ mol$^{-1}$ can be obtained (see Table III). The correction is significant. Furthermore, it brings the results for sample A and B, which have different volatile contents and different proportions of $H_2O$, $CO_2$, and $O_2$, into better agreement with each other, giving values near 114 kJ mol$^{-1}$. Alternatively, the calculation may be repeated using gaseous water as the reference state; that is, assuming the $H_2O$ in the sample has properties more like loosely adsorbed water vapor then like liquid. This gives (see Table III) 115 kJ mol$^{-1}$ for sample A and 118 kJ mol$^{-1}$ for sample B.

If the oxygen desorbed from the sample were initially chemically bound, then $\Delta H(La_2CuO_4)$ would be more exothermic. Rapp *et al.* (*27*) have found that excess oxygen in $La_2CuO_{4+y}$ has an almost zero enthalpy of incorporation (oxidation enthalpy) for values of $y$ near zero. This, coupled with the small proportion of $O_2$ seen in KEMS, makes any correction for the nature of the adsorbed oxygen unimportant.

We conclude that the enthalpy change associated with T′ − $La_2CuO_4$ on the first drop is in the range 114–118 kJ mol$^{-1}$. The uncertainty is hard to judge because it arises both from uncertainties in the evolved gas analyses and in assumptions about the state of water discussed above.

Subsequent drops (with no further weight change) gave 113.8 ± 1.4 kJ mol$^{-1}$ for sample A and 116.7 ± 0.7 kJ mol$^{-1}$ for sample B. Both had transformed to the T structure during the first drop and thus the enthalpy measured was simply the heat content of T − $La_2CuO_4$. This value, measured on T −

TABLE III

RESULTS OF TRANSPOSED TEMPERATURE DROP CALORIMETRY FOR T' $La_2CuO_4$

| Sample and conditions | $\Delta H$ observed (J/g) | $\Delta H$ calculated (kJ/mol) |
|---|---|---|
| T' (A), first drop | 287.2 ± 0.2 (6)[a] | 116.4[b,c]<br>113.7[d,c]<br>115.3[e,c] |
| T (A), second and third drops on transformed sample | 280.3 ± 3.5 (5)[a] | 113.8 ± 1.4[f] |
| T' (B), first drop | 299.7 ± 3.8 (5)[a] | 121.5[b,c]<br>113.8[d,c]<br>118.1[e,c] |
| T (B), second and third drops on transformed sample | 287.9 ± 1.7 (5)[a] | 116.7 ± 0.7[f] |
| T, normal high temperature preparation | 285.7 ± 3.0 (6)[a] | 115.8 ± 1.2[g] |

[a] Uncertainty is two standard deviations of the mean, value in ( ) is number of experiments performed.

[b] Uncorrected for volatile impurities lost during first drop.

[c] Uncertainty hard to judge because it arises from uncertainty in impurity correction as well as propagation of error in observed $\Delta H$, which, alone, gives ±1 to ±1.5 kJ/mol.

[d] Corrected for volatile impurities ($H_2O$, $CO_2$, $O_2$) based on analysis in Table IV. $H_2O$ assumed to be liquid-like, see text.

[e] Corrected as in [d] but $H_2O$ assumed to be gas-like.

[f] No further weight loss, no correction needed.

[g] No weight loss, no correction. From Bularzik and Navrotsky (*28*).

$La_2CuO_4$ prepared by normal high temperature synthesis, was previously measured in this laboratory as 115.8 ± 1.2 kJ $mol^{-1}$.

Thus the first drop gave values in a range overlapped by data for T − $La_2CuO_4$. We cannot say from these data whether T or T' is energetically more stable, but both these direct experiments and the extrapolation from the solid solutions point to the enthalpy

TABLE IV

GAS ANALYSIS OF VOLATILES IN T'-$La_2CuO_4$ AS FOUND BY MASS SPECTROSCOPY DURING TPD EXPERIMENTS

| Gas | mol fraction of total volatiles | |
|---|---|---|
| | Sample A[a] | Sample B[b] |
| $O_2$ | 0.14 | 0.07 |
| $CO_2$ | 0.26 | 0.14 |
| $H_2O$ | 0.60 | 0.79 |

[a] Contains total 0.4 wht% volatiles.

[b] Contains total 0.9 wht% volatiles.

TABLE V

ENTHALPY OF SOLUTION OF $(La_{0.6}Dy_{0.35}Ce_{0.05})_2CuO_4$ AND $(La_{0.6}Dy_{0.35}Th_{0.05})_2CuO_4$ IN $2PbO \cdot B_2O_3$ AT 704°C

| | Structure type | $\Delta H_{sol}$ (kJ $mol^{-1}$) |
|---|---|---|
| $(La_{0.6}Dy_{0.35}Ce_{0.05})_2CuO_4$ | T* | −48.5 ± 1.7[a] (7)[b] |
| | T' | −105.2 ± 5.0 (6) |
| $(La_{0.6}Dy_{0.35}Th_{0.05})_2CuO_4$ | T* | −56.0 ± 3.1 (5) |
| | T' | −94.3 ± 4.2 (6) |

[a] Two standard deviations of mean.

[b] Number of experiments performed.

of the T′ to T transition in $La_2CuO_4$ being small and probably positive, and we choose 3 ± 8 kJ/mol as its best estimate.

### *T* to T Transition*

We studied the energetics of T* to T′ transition in two systems, $(La_{0.6}Dy_{0.35}Ce_{0.05})_2CuO_4$ and $(La_{0.6}Dy_{0.35}Th_{0.05})_2CuO_4$, using solution calorimetry. In each case, samples could be made in both structures by varying preparation conditions, see Table I. Calorimetric results are presented in Table IV. The (T′ − $La_{0.6}Dy_{0.35}Ce_{0.05})_2CuO_4$ sample showed a significant (~5%) amount of an unknown phase by X-ray diffraction (weak line around 3.09 Å). Therefore the numerical data for enthalpy of solution of T′ phase and enthalpy of transition for the Ce doped system have to be considered as somewhat approximate.

The enthalpy of the T* to T′ transition is 56.7 ± 5.3 kJ $mol^{-1}$ in the cerium doped system and +38.3 ± 5.2 kJ $mol^{-1}$ in the thorium doped system. Both values indicate that the T* structures are much more energetically stable than T′. These numbers are several times larger than +6.3 ± 2.8 kJ $mol^{-1}$ found for T′ to T transition in $(La_{0.75}Nd_{0.25})_2CuO_4$. This might be considered somewhat surprising since the T* structure is a hybrid between T and T′ and might be expected to be intermediate in energy as well. However, the systems compared are not isocompositional, and the effect of differing ionic radii must be taken into account, see below. Nevertheless, it is possible that the T* structure can derive energetic stability relative to T or T′ by more relaxation of mismatch in bond lengths in the copper and rare earth layers. (See Table V).

Figure 4 shows that the enthalpy of transition (T′ to T and T* to T) depends approximately linearly on the volume of transformation (obtained from measured lattice parameters at room temperature), namely

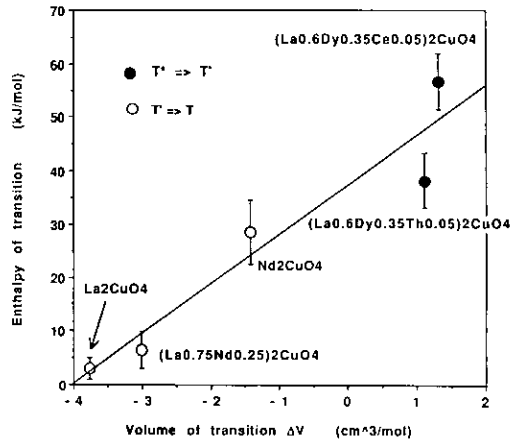


FIG. 4. The dependence of enthalpy of transition (T′ ⇒ T, open circles and T* ⇒ T′, solid circles) on volume of transition measured at room temperature (*1*, *14*) $\Delta H$ (kJ $mol^{-1}$) = 37.4 + 9.27 $\Delta V$ ($cm^3$ $mol^{-1}$).

$$\Delta H(\text{kJ/mol}) = 37.4 + 9.27\ \Delta V(\text{cm}^3/\text{mol}). \quad (9)$$

This is not accounted for by a $P\Delta V$ work term for the transition, which is three orders of magnitude smaller than the observed enthalpies and would always be negative for transitions to the denser T structure. Rather it reflects the changing chemistry and bond lengths within this series of perovskite-related structures. The above linear relation may be useful for estimating how energetically unstable possible new phases in the T, T′, and T* structures might be, since their volumes can be estimated from crystal systematics such as tolerance factor arguments (*1*).

The question of stability of T, T′, and T* phases, both at atmospheric and high pressure, involves enthalpy, entropy, and volume terms. One might expect such a transition to occur at high pressure if the $\Delta H$ term is not too prohibitive and $\Delta V$ is negative and reasonably large. From Fig. 4 it is clear that $Nd_2CuO_4$ and its solid solutions are good candidtes to transform from the T′ to the T structure at high pressure. Our synthesis of $(La_{0.7}Nd_{0.3})_2CuO_4$ in the T

structure at 400 bar oxygen pressure may have been aided by the pressure itself, as well as the high oxygen fugacity. Recently we also partially transformed T′ – $(La_{0.6}Nd_{0.4)2}CuO_4$ to the T structure by a 4-h anneal at 20 kbar and 700°C. The nature of this transformation and the composition of the products are receiving further study. It does appear that the T structure, being denser, should be more prevalent at high pressure.

The entropy systematics for the transition are harder to evaluate. If T′ $La_2CuO_4$ is indeed a stable low temperature phase, as our results suggest, then $\Delta S$ (T′ to T) is positive. With a negative $\Delta V$, this would imply a negative $P$–$T$ slope for the T′ ⇒ T transition in $La_2CuO_4$ since $dP/dT = \Delta S/\Delta V$. Although for most phase transitions $dP/dT$ is positive, instances of negative $dP/dT$ ($\Delta S$ and $\Delta V$ having opposite signs) are known, especially when the phase change involves increasing the cation coordination number (*21, 26*). The overall increase in density is achieved by a denser and more symmetrical packing of polyhedra, but is accompanied by an increase in bond distances for the cations occupying sites of high coordination number. Therefore with increasing coordination number and bond length, the individual bonds are weaker. These changes lead to a higher entropy for the denser polymorph (*21*). Example of such behavior include the following. An anomolously large entropy found for pyrope garnet, related apparently, to the vibration of Mg in 8-coordinated sites (*22*). The high entropy of $CdTiO_3$ and $CdSnO_3$ perovskites, resulting in a negative $dP/dT$ for the ilmenite–perovskite transition, may arise from the vibrations of the rather small $Cd^{2+}$ ion in the large central site of perovskite (*23*). Negative slopes for perovskite-forming reactions have also been confirmed for $CaGeO_3$ (*24*) and $MgSiO_3$(*25*). In the transtition T′ ⇒ T, densification occurs by increasing the coordination number of rare earth cations from 8 to 9 and copper cations from 4 to 6. Simultaneously, rare earth–oxygen bond lengths increase in the T structure. These longer (and weaker) bonds may lead to higher entropy for the T phase and a positive entropy change for the T′ to T transition.

However, it is not clear whether the T structure would be of higher entropy than the T′ (or T*) for all possible compositions. In the transition from rocksalt-type to cesium chloride-type, which involves an increase in density and an increase in coordination number, $\Delta S$ and $\Delta V$ are roughly linearly related, and $\Delta S$ is positive for the more negative volume changes but negative for other $\Delta V$(*26*). This general problem deserves further study by high pressure synthesis, phase equilibria, calorimetry, and modeling of lattice dynamics.

## Conclusions

The enthalpy of formation from oxides at 700°C of $(La_{1-x}Nd_x)CuO_4$ ($0 \leq x \leq 1$) varies from −20 to −7 kJ mol$^{-1}$ depending on composition. The enthalpy of the T′ to T transition in $(La_{0.75}Nd_{0.25})_2CuO_4$ is 6.3 ± 2.8 kJ mol$^{-1}$, indicating that the T′ phase of this composition is energetically more stable than T. Extrapolated enthalpies of transition from T′ to T are 3 ± 8 kJ mol for $La_2CuO_4$ and 28 ± 10 kJ mol$^{-1}$ for $Na_2CuO_4$, indicating that the T′ structure is more energetically stable than the T structure for both compounds. The positive enthalpy of mixing (regular solution parameter of +51.8 kJ mol$^{-1}$) in the T′ phase of $(La_{1-x}Nd_x)_2CuO_4$ argues against cation ordering being important in this system. Enthalpies of the T* to T″ transition in $(La_{0.60}Dy_{0.35}Th_{0.05})_2CuO_4$ and $(La_{0.60}Dy_{0.35}Ce_{0.05})_2CuO_4$ are 38 ± 5 and 51 ± 6 kJ mol$^{-1}$, indicating that the T* structure is more stable than the T′ structure for these compounds. Our structural and calorimetric measurements provide no indication of the existence of the T″ structure in the $(La_{1-x}Nd_x)_2CuO_4$ system.

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