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High-Pressure Synthesis and Structure of the New Spinel-Related Series $LnCu_2O_4$ (Ln = Nd, Gd, Er, Lu, Y)

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The new spinel-related series $LnCu_2O_4$ (Ln = Nd, Gd, Er, Lu, Y) has been prepared at pressures of 40−100 kbar using a multianvil apparatus. The structure of these phases was determined for the case of $NdCu_2O_4$ by Rietveld profile analysis of X-ray powder diffraction data. $NdCu_2O_4$ is monoclinic, $I2/a$, $a = 5.822(2)$ Å, $b = 9.695(3)$ Å, $c = 5.748(2)$ Å, $\beta = 92.34(2)°$, and $Z = 4$. The $NdCu_2O_4$ structure can be derived from that of spinel, as the cations in both have the Cu_2Mg-type arrangement. However, the metal coordination by oxygen in $NdCu_2O_4$ is unlike that in spinel, consisting of NdO_8 polyhedra and square-coplanar CuO_4. The structure is comprised of $Cu^{II}O_4$ chains along ⟨100⟩ and $Cu^{III}O_4$ chains along ⟨001⟩. These are linked perpendicularly through the corners of CuO_4 square planes, leading to an array of parallel pseudotetragonal tunnels in which the Nd cations reside. Superconductivity was not observed in any of the new $LnCu_2O_4$ phases to 4 K.

Introduction

Ternary oxides with the general formula AB_2O_4 display several structures. Kugimiya and Steinfink[1] have grouped the known structures of the AB_2O_4 compounds by plotting the ratio r_a/r_b versus the force constant K_{ab} which was defined as

$$K_{ab} = X_aX_b/r_e^2$$

where $r_e^2 = (r_a + r_o)^2 + (r_b + r_o)^2 + 1.155(r_a + r_o)(r_b + r_o)$, r_a, r_b, and r_o are the radii of the A, B, and O ions, and X_a and X_b are the electronegativities of the A and B ions, respectively. This relationship provides a valuable map for predicting the structural types of unknown AB_2O_4 phases. Other correlations have been reported in which the influence of cation radii is considered in determining the crystal type.[2,3] In the Kugimiya−Steinfink mapping,[1] the normal spinel, $BaAl_2O_4$, or $CaFe_2O_4$-type structures occur for $r_a/r_b > 1$. If $r_a/r_b < 1$, the compounds exhibit inverse spinel, K_2MgF_4, K_2SO_4, or olivine-type structures. Within each of these regimes, the specific structure will of course depend on the strength of the force constant K_{ab}.

A large majority of AB_2O_4 compounds are spinels. The structure of normal spinel consists of cubic close-packing of anions with the A atoms in tetrahedral sites and the B atoms in octahedral sites. Each AO_4 tetrahedron shares corners with four BO_6 octahedra, which are linked to each other through their edges. Spinel oxides exhibit interesting electric and magnetic properties, including superconductivity. The spinel $LiTi_2O_4$, comprising mixed valence Ti^{3+}/Ti^{4+}, has the highest T_c of the nonperovskite-related superconducting ternary oxides.[4] It is of interest to know whether a mixture of Cu^{2+} and Cu^{3+} in the spinel structure can play a role similar to mixed Cu^{2+} and Cu^{3+} in the superconducting cuprates or like Ti^{3+} and Ti^{4+} in the superconducting spinels. We report herein the synthesis and structure of a new $LnCu_2O_4$ series (Ln = Nd, Gd, Er, Lu, and Y), containing mixed valence Cu^{2+} and Cu^{3+}, whose structure can be derived from that of spinel. The compounds were prepared at high pressure, and their structures determined by Rietveld profile analysis.[5]

Experimental Section

A coprecipitation technique, similar to that employed in earlier work on the $LaCuO_{3-\delta}$ perovskites,[6] was used to synthesize precursors for the $LnCu_2O_4$ phases (Ln = La, Nd, Gd, Er, Lu, Y, Sc). Ln_2O_3 (0.001 mol) and CuO (0.004 mol) powders (Alfa) were dissolved with 1 M HNO_3 (40 mL) by gentle heating and stirring. The solution was diluted to 100 mL with H_2O and cooled in an ice bath to 5 °C. Aqueous NaOH (3 M) was then added with stirring until a blue precipitate appeared (pH ~ 9). The precipitate was filtered and washed with H_2O to remove sodium, placed in a platinum crucible, and heated at 800 °C for 20 h. The resulting product was diphasic with overall $Ln_2Cu_4O_7$ stoichiometry. The larger rare-earth cations gave precursors which were mixtures of CuO and T′−Ln_2CuO_4[7], while smaller rare earths formed mixtures of CuO- and $Ho_2Cu_2O_5$-type $Ln_2Cu_2O_5$.[8]

The precursors were mixed and thoroughly ground in a 3:1 ratio with the oxygen source $KClO_3$, packed into 2.5 mm i.d. × 6 mm long Al_2O_3 crucibles and loaded into a ceramic octahedron with a truncated edge length (TEL) of 8 mm. The assemblies were also fitted with $LaCrO_3$ sleeves, which

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Table 1. Lattice Parameters r_a/r_b and K_{ab} for $LnCu_2O_4$ (Ln = Nd, Gd, Y, Er, Lu)

	a (Å)	*b* (Å)	*c* (Å)	*β* (deg)	r_a/r_b	K_{ab}
$NdCu_2O_4$	5.822(2)	9.695(3)	5.748(2)	92.34(2)	1.55	0.12
$GdCu_2O_4$	5.742(2)	9.628(3)	5.663(2)	92.40(2)	1.45	0.13
YCu_2O_4	5.695(2)	9.569(3)	5.611(2)	92.56(2)	1.37	0.13
$ErCu_2O_4$	5.668(2)	9.548(3)	5.590(2)	92.48(2)	1.33	0.13
$LuCu_2O_4$	5.624(2)	9.507(3)	5.545(2)	92.51(2)	1.27	0.14

functioned as heaters, and W 3% Re/W 25% Re thermocouples. A full description of the multianvil apparatus and the high-pressure experimental procedures has been published previously.[9] The final products were obtained by processing the reactants at 1000−1200 °C and 40−100 kbar for 20−30 h. $LnCu_2O_4$ phase compositions were determined by electron microprobe using $Ln_2Cu_2O_5$ standards.

Samples were characterized with a Siemens D-500 X-ray powder diffractometer using Cu Kα radiation. The X-ray powder data were obtained in the range $15° < 2\theta < 70°$ using a 0.02° step width and a counting period of 20 s. The reflection conditions, *hkl*: $h + k + l = 2n$, and *h*0*l*: $h, l = 2n$ indicated the possible space group *I*2/*a* (*C*2/*c*). The structure parameters for $NdCu_2O_4$ were refined by the FullProf program[10] in space group *I*2/*a* using a pseudo-Voigt peak-shape function. The refined parameters include atom positions, lattice parameters, a zero point error, isotropic temperature factors, overall scale factor, peak-shape parameter, full-width parameters and background parameters. Lattice constants for the remaining $LnCu_2O_4$ phases were also refined by FullProf using the refined $NdCu_2O_4$ coordinates. The compounds were tested for superconductivity down to 4 K using a conventional ac mutual inductance technique to search for diamagnetic transitions.

Results and Discussion

The new $LnCu_2O_4$ series (Ln = Nd, Gd, Er, Lu, and Y) was obtained from the precursor/$KClO_3$ mixtures at temperatures between 1000 and 1200 °C and pressures of 40−100 kbar. The samples prepared at 40 kbar were single phase except for the presence of KCl from the decomposition of the buffer. On the other hand, those obtained at 100 kbar contained $LnCu_2O_4$ product mixed with CuO, KCl, and various rare earth copper oxides, suggesting that the new phases do not actually require very high pressures to stabilize them. Attempts to synthesize $LaCu_2O_4$ and $ScCu_2O_4$ failed. No superconductivity was found in any of the samples to 4 K.

All the $LnCu_2O_4$ compounds prepared at high pressure were found to crystallize with monoclinic symmetry. The lattice parameters *a*, *b*, *c*, and *β*, listed in Table 1, decrease with decreasing the size of the Ln cation. To develop an initial structural model for these $LnCu_2O_4$ phases, r_a/r_b and K_{ab} for $LnCu_2O_4$ were calculated using Ahrens' electronegativities and radii[11] and $r_b(Cu^{3+}) = 0.67$ Å. The values of these parameters are also shown in Table 1. The phases all fall in the spinel region of the Kugimiya−Steinfink AB_2O_4 correlation diagram. Moreover, their X-ray patterns and unit-cell dimensions in space group *I*2/*a* are similar to those of Mn_3O_4, a tetragonal spinel with space group $I4_1/amd$, $a = 5.7621$ Å, and $c = 9.4696$ Å.[12] Therefore, a spinel-related structure for these compounds might be expected, and spinel became the starting model for the subsequent calculations.

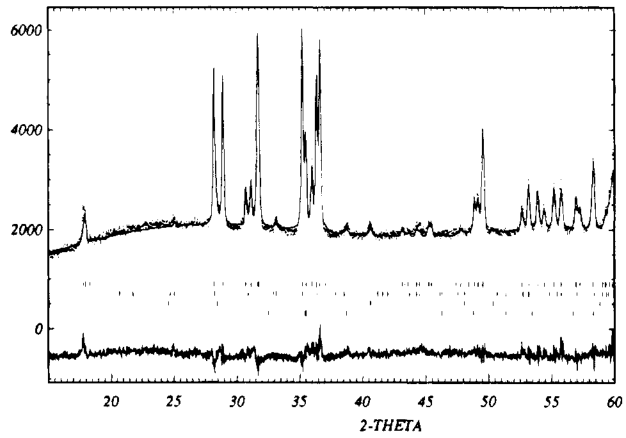

Figure 1. Comparison of calculated and observed X-ray patterns for $NdCu_2O_4$. The impurity phases visible in the pattern, $NdCuO_{2.93}$, CuO, and KCl, have been included in the refinement.

Table 2. Crystallographic Data for $NdCu_2O_4$

formula	$NdCu_2O_4$
color	black
crystal system	monoclinic
space group	*I*2/*a* (No. 15)
a (Å)	5.822(2)
b (Å)	9.695(3)
c (Å)	5.748(2)
β (deg)	92.34(2)
V (Å³)	324.2(1)
Z	4
D_{calc} (g/cm³)	6.871
R_{wp} (%)	15.7
R_I (%)	6.34

[a] $R_{wp} = [\Sigma w(Y_{obs} - Y_{cal})^2/\Sigma(Y_{obs})^2]^{1/2}$. [b] $R_I = \Sigma|I_{obs} - I_{cal}|/\Sigma I_{obs}$.

Table 3. Positional Parameters for $NdCu_2O_4$

atom	site	*x*	*y*	*z*	*B* (Å²)[a]
Nd	4e	1/4	0.875	0	0.69
Cu(1)	4b	0	1/2	0	0.37
Cu(2)	4d	1/4	1/4	1/4	0.48
O(1)	8f	0.617(1)	−0.074(1)	0.800(1)	0.23
O(2)	8f	−0.011(1)	0.826(1)	0.622(1)	0.96

[a] Isotropic temperature factors.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $NdCu_2O_4$

Nd−O(1)	2.513(8) [2×]	Cu(1)−O(1)	1.964(5) [2×]
Nd−O(1)	2.365(8) [2×]	Cu(1)−O(2)	1.830(5) [2×]
Nd−O(2)	2.644(8) [2×]	Cu(2)−O(1)	1.897(5) [2×]
Nd−O(2)	2.583(8) [2×]	Cu(2)−O(2)	1.763(5) [2×]
Cu(1)−Cu(1)	2.911(1)	Cu(2)−Cu(2)	2.874(1)
O(1)−Cu(1)−O(2)	91.2(2)	O(1)−Cu(2)−O(2)	91.4(2)
O(1)−Cu(1)−O(2)	88.9(2)	O(1)−Cu(2)−O(2)	88.6(2)

A full Rietveld refinement using X-ray powder data was carried out for $NdCu_2O_4$ synthesized at 1000 °C and 100 kbar for 20 h. This preparation also contained small amounts of CuO, KCl, and $NdCuO_{2.93}$,[13] which were also included in the refinement. Although the space group *C*2/*c* with $a = 8.012$ Å, $b = 9.695$ Å, $c = 5.822$ Å, and $\beta = 134.2°$ for $NdCu_2O_4$ should be chosen in a more standard setting, the space group *I*2/*a* was used for the refinement in order to underline the structural relationship between the new phase and spinel. A comparison of the calculated and observed X-ray pattern is shown in Figure 1. Crystallographic data, positional parameters, and selected bond distances

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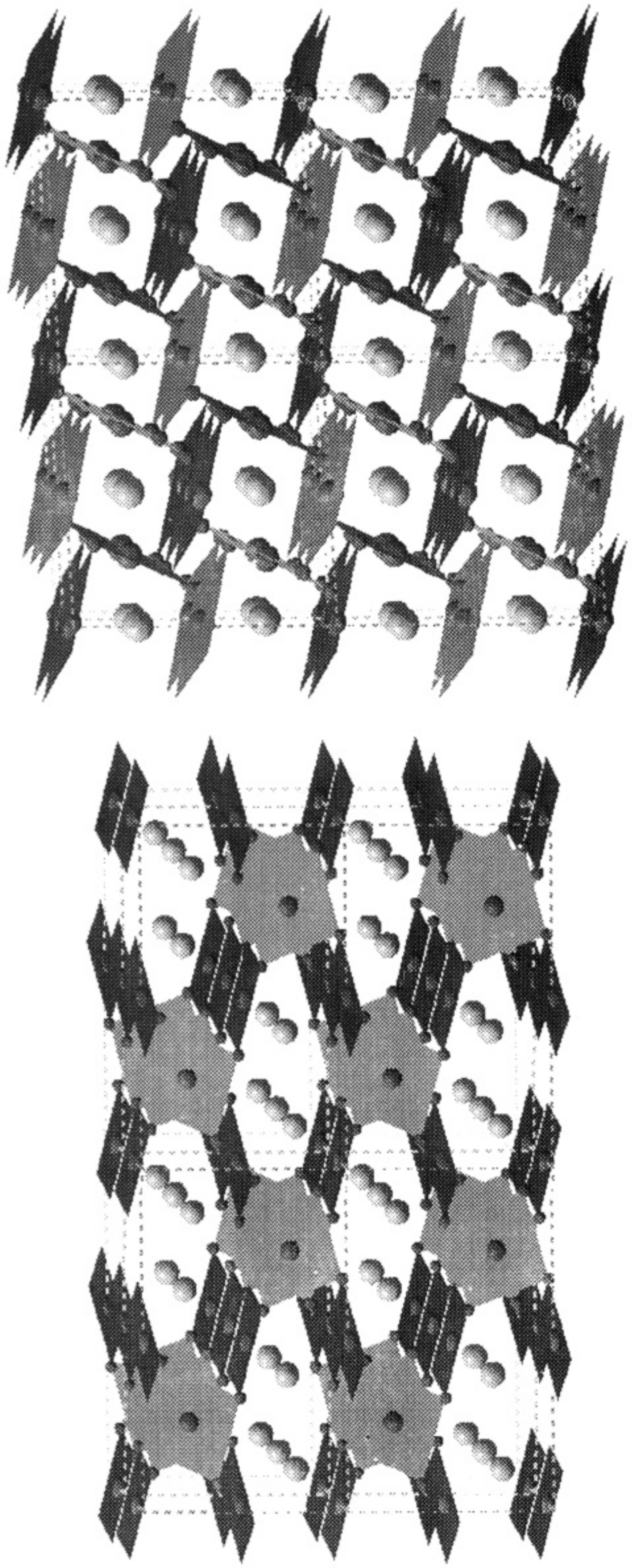

Figure 2. Structure for $NdCu_2O_4$ projected on [010] (a, top) and [001] (b, bottom).

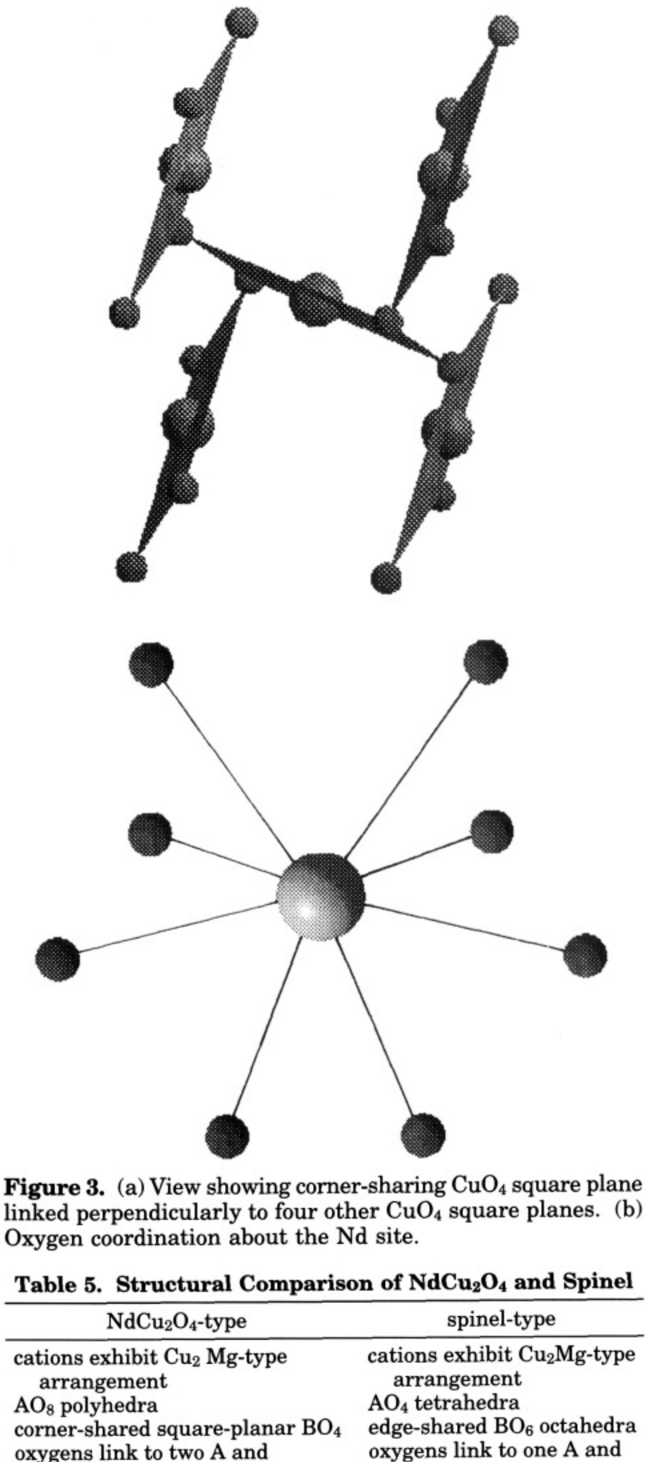

Figure 3. (a) View showing corner-sharing CuO_4 square plane linked perpendicularly to four other CuO_4 square planes. (b) Oxygen coordination about the Nd site.

Table 5. Structural Comparison of $NdCu_2O_4$ and Spinel

$NdCu_2O_4$-type	spinel-type
cations exhibit Cu_2 Mg-type arrangement	cations exhibit Cu_2Mg-type arrangement
AO_8 polyhedra	AO_4 tetrahedra
corner-shared square-planar BO_4	edge-shared BO_6 octahedra
oxygens link to two A and two B atoms	oxygens link to one A and three B atoms

and angles for $NdCu_2O_4$ are given in Tables 2–4, respectively. The structure for $NdCu_2O_4$ is shown in Figure 2. It is similar to spinel in that the cations in both have the Cu_2Mg-type arrangement. However, the coordination of oxygen about the cations is very different in the two structure types. Eight-fold coordination of the A-sites and four-fold coordination of the B-sites by oxygen are found in $NdCu_2O_4$, similar to that observed in Nd_2CuO_4.[7] $NdCu_2O_4$ consists of corner-sharing CuO_4 square planes perpendicular to one another (Figure 3a), leading to an array of parallel pseudo-tetragonal tunnels along ⟨010⟩. The Nd atoms reside in the tunnels surrounded by eight oxide anions (Figure 3b). A comparison of the structures of $NdCu_2O_4$ and spinel is given in Table 5.

Nd–O distances between 2.37 and 2.64 Å in $NdCu_2O_4$ are similar to those found in the perovskite $NdCuO_{2.93}$, where Nd is coordinated by eight oxygens at distances between 2.29 and 2.59 Å.[13] Since the average Cu(1)–O distance of 1.90 Å is larger than the average Cu(2)–O spacing of 1.83 Å, the Cu(1) and Cu(2) positions are expected to be occupied by Cu^{2+} and Cu^{3+}, respectively. Parallel $Cu^{II}O_4$ square coplanar units form chains along

⟨100⟩. In the same way, $Cu^{III}O_4$ planes form chains along ⟨001⟩. One possible reason for the fact that the *a* parameter of the unit cell is somewhat larger than the *c* parameter might be stronger electrostatic repulsion of the oxygens between the $[Cu^{II}O_4]^{6-}$ planes compared to the $[Cu^{III}O_4]^{5-}$ planes.

In summary, a new series of mixed valence $LnCu_2O_4$ phases with Ln = Nd, Gd, Er, Lu, and Y have been prepared at high pressures. These compounds map into the normal spinel region of the Kugimiya–Steinfink's AB_2O_4 correlation diagram, where very few compounds fall, suggesting that this region belongs to a new AB_2O_4 group—the $NdCu_2O_4$-type phases. Because of the relationship between the $LnCu_2O_4$ and spinel structure types, it is possible that the new materials might become superconducting with appropriate doping. While an investigation of the synthesis and physical properties of the doped materials is underway, preliminary results have not been encouraging. Finally, as this manuscript was being completed, we learned that the new $LnCu_2O_4$ series has also been prepared using a low-temperature flux method.[14] This suggests that oxygen fugacity, and not pressure, is the key to the synthesis of these phases, a result consistent with our findings.

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