

Structure and Oxygen Stoichiometry in $\text{Ln}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6-y}$ (Ln = La, Nd, Sm) Phases

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The structures of two new complex copper oxide phases refined from powder neutron diffraction data are reported. $\text{LaNdSrCu}_2\text{O}_6$ is isostructural with $\text{La}_2\text{SrCu}_2\text{O}_6$ but shows an unusual ordering of Nd and La over the perovskite-type A sites. $\text{Nd}_{1.4}\text{Sr}_{1.6}\text{Cu}_2\text{O}_{5.79}$ has a structure based on a tripled ($a \times 3a \times c$) $\text{La}_2\text{SrCu}_2\text{O}_6$ unit cell. The oxygen vacancy order gives rise to a unique pseudo one-dimensional tunneled copper-oxygen sublattice built from vertex-linked CuO_3 square pyramids. The cation ordering in this material has been resolved. The lattice parameters and oxygen stoichiometries of a number of new phases of both structure types are presented. © 1990 Academic Press, Inc.

1. Introduction

The structural chemistry of mixed-valence copper oxides has recently received much attention since the discovery of high temperature superconductivity in some of these materials (1-9). In such compounds, the partial oxidation of copper beyond Cu(II) is achieved either by an annealing treatment in an oxygen atmosphere or by a variation of the trivalent:divalent cation ratio of the other metallic elements present. Work on the structural chemistry of other complex copper oxide phases has been largely restricted to isostructural compounds, closely related to the superconducting materials, derived from solid solution work (10) and studies of common impurity phases (11, 12). The occurrence of a number of other complex copper oxide

phases has been reported with details of the mixed-valence nature of the copper, oxygen stoichiometry, and electrical and magnetic properties (13-17). In view of the intimate relationship between crystal structure, copper valence, and superconductivity in the recently discovered materials it is worthwhile investigating the structures of these related nonisomorphous compounds in detail and extending the range of materials in such systems in order to clarify the structural features necessary for high temperature superconductivity.

This paper reports a number of new complex copper oxides which are based on the semimetallic-semiconducting $\text{La}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6\pm y}$ (La212) solid solution discovered by Nguyen *et al.* (13). Powder XRD showed that this system has a structure derived from $\text{Sr}_3\text{Ti}_2\text{O}_7$; it is of particular interest because of the square-pyramidal copper coordination which has four short basal

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Cu–O bonds and one long apical Cu–O distance. There is a strong structural similarity of the central region of the unit cell in this system (13) and YBCO (18) with an oxygen deficient perovskite layer giving rise to extended two-dimensional Cu–O₂ planes in both materials. Furthermore, it is possible to introduce some Cu(III) into this system by an increase in x and/or y (14) which creates a further resemblance with YBCO.

Some later work by Nguyen *et al.* on the $\text{Ln}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6\pm y}$ solid solution (15) showed that materials with $\text{Ln} = \text{Sm}, \text{Gd}$ ($0.7 \leq x \leq 0.9$) and Eu ($0.6 \leq x \leq 0.9$) are semiconducting possessing a complex La212-type unit cell with a threefold superstructure along the b axis (Ln636), apparently caused by both cation and oxygen vacancy ordering. A significantly reduced oxygen stoichiometry ($-0.45 \leq y \leq 0.3$) was also reported, suggesting no oxidation of copper beyond Cu(II). A structural model from powder XRD data was proposed although, with the limited amount of data available and the complexity of the unit cell, a high level of uncertainty in the oxygen positions and occupation factors cannot be discounted. It was therefore decided to study this structure by powder neutron diffraction (PND) to resolve the cation and oxygen vacancy ordering. However, Sm, Gd, and Eu are all very efficient neutron-absorbing nuclei and it would be impractical to study phases containing quantities of these elements because of the extended collection times necessary to produce data of a satisfactory quality. In this paper, we describe the synthesis of a neodymium-doped analog of these tripled compounds and its structural characterization by PND.

2. Experimental

Samples of nominal composition $\text{La}_{2-x}\text{Nd}_x\text{SrCu}_2\text{O}_{6\pm y}$ ($x = 0.5, 1.0, 1.5, 2.0$)(series A) and $\text{Ln}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6\pm y}$ ($\text{Ln} = \text{Nd}, 0.2 \leq$

$x \leq 0.8; \text{Ln} = \text{Dy}, 0.4 \leq x \leq 1.6; \text{Ln} = \text{Sm}, x = 0.7$)(series B) were prepared by conventional solid state reaction for 72 hr with frequent regrinding ($\text{La}_2\text{O}_3, \text{SrCO}_3, \text{CuO}$, 99.99%, Berkshire Ores and Chemicals; $\text{Nd}_2\text{O}_3, \text{Sm}_2\text{O}_3, \text{Dy}_2\text{O}_3$, 99.9%, Johnson Matthey). The sintering temperatures used were 1030, 1020, and 1000°C for Nd-, Sm- and Dy-doped materials, respectively, as it was found that the melting point decreased with the diminishing size of the substituting lanthanide ion.

Subsequent powder XRD showed all the series A samples, with the exception of $x = 2.0$, to be single phase and isostructural with La212. Nd212 could not be prepared as a pure material by this method but showed a majority La212-type phase with lattice parameters very similar to the $x = 1.5$ material. A 15-g sample of the $x = 1.0$ compound, $\text{LaNdSrCu}_2\text{O}_{6\pm y}$, was prepared for PND experiments.

The series B compounds were all multiphase with a majority of the Ln636 structure. The impurity levels of the $x = 0.4$ and $x = 0.6$ samples were only very slight, with only a few weak nonindexable peaks below $2\theta = 35^\circ$. It was considered that the intrinsic inhomogeneity of the oxide/carbonate precursor mixture may be a contributory factor causing the impure products and that this could be removed by adopting a solution-based citrate gel preparation technique.

A pure 15-g sample of $\text{Nd}_{1.4}\text{Sr}_{1.6}\text{Cu}_2\text{O}_6$ was subsequently prepared using the procedure of Wang *et al.* (19) in which the correct metal stoichiometry is suspended in a viscous gel and thermally decomposed, ensuring all the ions originally in solution are transferred to the solid phase. The preparation of Dy-doped materials also using this method was attempted for the $x = 1.0$ composition: the purity of the product was much improved but a single phase material was not obtained, although it was possible to index most XRD peaks to the Ln636 unit

TABLE I
RESULTS OF XRD AND TGA MEASUREMENTS

Sample	Cell dimensions (Å)			Oxygen content	m in Cu^{m+}
	a	b	c		
$\text{La}_2\text{SrCu}_2\text{O}_y$	3.853(1)	—	19.869(6)	6.00(1)	2.00(1)
$\text{La}_{1.5}\text{Nd}_{0.5}\text{SrCu}_2\text{O}_y$	3.856(1)	—	19.833(4)	6.03(2)	2.03(2)
$\text{LaNdSrCu}_2\text{O}_y$	3.854(1)	—	19.769(1)	5.99(2)	1.99(2)
$\text{La}_{0.5}\text{Nd}_{1.5}\text{SrCu}_2\text{O}_y$	3.834(1)	—	19.634(5)	6.00(2)	2.00(2)
$\text{Sm}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_y$	3.740(1)	11.293(2)	19.958(5)	5.78(1)	2.13(1)
$\text{Nd}_{1.4}\text{Sr}_{1.6}\text{Cu}_2\text{O}_y$	3.778(1)	11.371(1)	20.132(2)	5.79(2)	2.09(2)
$\text{SmLa}_{0.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_y$	3.765(1)	11.335(3)	20.066(3)	5.86(2)	2.21(2)
$\text{Sm}_{0.7}\text{La}_{0.6}\text{Sr}_{1.7}\text{Cu}_2\text{O}_y$	3.767(1)	11.402(2)	20.081(3)	5.83(2)	2.18(2)
$\text{Sm}_{0.4}\text{La}_{0.9}\text{Sr}_{1.7}\text{Cu}_2\text{O}_y^a$	3.769(2)	11.409(4)	20.095(6)	—	—
$\text{DySr}_2\text{Cu}_2\text{O}_y^a$	3.774(1)	11.195(2)	19.996(3)	—	—

^a Majority Ln636 phase in multicomponent sample. Nominal composition only.

cell. Pure samples of $\text{Sm}_{1.3-x}\text{La}_x\text{Sr}_{1.7}\text{Cu}_2\text{O}_{6\pm y}$ ($x = 0.3, 0.6, 0.9, 1.2$) were also synthesized by the citrate gel method in order to investigate the possibility of forming a lanthanum-containing Ln636 phase and to determine whether a smooth transition to an La212 phase would be observed as x was increased.

Cell parameters for all samples of sufficient quality were refined using a least-squares method on the powder XRD data which was collected on the INEL CPS-120 system, fitted with a primary monochromator giving exclusively $\text{CuK}\alpha_1$ radiation. Oxygen stoichiometries were determined from the weight change on reduction of a 30- to 50-mg sample of each material heated to 950°C in flowing 5% H_2 in N_2 using a Stanton Redcroft TG1000 series thermobalance. Electrical properties were measured using a standard four probe DC resistivity and AC susceptibility techniques between 6 and 300 K, as described elsewhere (20). PND data were collected for samples of air-quenched $\text{LaNdSrCu}_2\text{O}_{6\pm y}$ and $\text{Nd}_{1.4}\text{Sr}_{1.6}\text{Cu}_2\text{O}_{6\pm y}$ on the diffractometer D1A (21) at the ILL-HFR in Grenoble and refined using a full profile Rietveld method (22–24).

3. Results

The results of XRD and TGA measurements are summarized in Table I. All materials studied were semiconducting down to 6 K, with no evidence of a Meissner signal in the AC susceptibilities.

The Dy122 composition was not analyzed thermogravimetrically as the impurities observed in the XRD pattern of this sample would obviously influence the results and yield an oxygen stoichiometry and copper oxidation state which would not accurately apply to the majority phase. Indeed, the presence of impurities suggest that the Ln636 phase present in this mixture is unlikely to correspond to the overall $\text{DySr}_2\text{Cu}_2\text{O}_{6\pm y}$ composition.

The majority of the lanthanum-containing samples are isomorphous with the La212 compound; the exception is the $\text{Sm}_{1.3-x}\text{La}_x\text{Sr}_{1.7}\text{Cu}_2\text{O}_{6\pm y}$ solid solution which shows a unit cell tripling. It is evident from the lattice parameters that lanthanum is genuinely incorporated into the structure as a comparison with the lanthanum-free material indicating that there is a substantial lattice expansion when the dopant is intro-

duced. Attempting to replace more samarium in this material by lanthanum resulted in a continuing increase in the unit cell volumes and a retention of the Ln636 structure to $x = 1.2$, although samples with $x \geq 0.9$ showed evidence of increasing proportions of impurity phases.

4. Powder Neutron Diffraction Refinements

4.1. $\text{LaNdSrCu}_2\text{O}_{6\pm y}$

The refinement was based on the structural model of Nguyen *et al.* (13) in the space group $I4/mmm$ (No. 139) (25). The difference in the scattering lengths of lanthanum, neodymium, and strontium (8.27, 7.80, and 6.90 fm, respectively) would enable any systematic ordering of the A -site cations to be observed. Initially, lanthanum, neodymium, and strontium were statistically distributed over the A_1 (0, 0, 0) and A_2 (0, 0, 0.18) sites and the three distinct oxygen sites were fully occupied, as in $\text{Sr}_3\text{Ti}_2\text{O}_7$. The refinement indicated that the O(3) position at (0, 0, $\frac{1}{2}$) was vacant, in agreement with the previous work, with the remaining oxygen positions fully occupied, corresponding to six oxygens per formula unit, in excellent agreement with the TGA results (Table I). The large cation site occupancies were refined and it was found that A_1 was occupied by neodymium and the A_2 site contained lanthanum and strontium in a 1:1 ratio. Full details of the refinement are given in Table II with a difference plot in Fig. 1 and an ORTEPII (26) representation of the unit cell and copper–oxygen coordination in Fig. 2.

4.2. $\text{Nd}_{1.4}\text{Sr}_{1.6}\text{Cu}_2\text{O}_{6\pm y}$

Full results of this refinement are given in Table III: for clarity the atom numbering scheme of the previous work was adopted. The initial model was based on the structure of $\text{Eu}_{1.3}\text{Sr}_{1.7}\text{Cu}_2\text{O}_{5.65}$ determined by

Nguyen *et al.* (15) in the orthorhombic space group $Immm$ (No. 71) (25). The four A sites were filled with a statistical distribution of neodymium and strontium reflecting the overall stoichiometry and all eight oxygen sites were fully occupied, corresponding to seven oxygens per formula unit. The oxygen occupancies refined rapidly and it was found that O(3) was vacant and O(4) and O(7) were partially occupied at approximately 60 and 18%, respectively. Indeed,

TABLE II
FINAL CRYSTALLOGRAPHIC RESULTS FOR
 $\text{LaNdSrCu}_2\text{O}_6$

Tetragonal, space group $I4/mmm$ (No. 139) $a = 3.8540(1) \text{ \AA}$; $c = 19.7688(6) \text{ \AA}$					
Atom	Wyckoff symbol	x/a	y/b	z/c	Site occupancy
A(1)	$2a$	0	0	0	1.0 Nd
A(2)	$4e$	0	0	0.1790(1)	0.5 La, 0.5 Sr
Cu(1)	$4e$	0	0	0.5913(1)	
O(1)	$8g$	0	$\frac{1}{2}$	0.0814(1)	
O(2)	$4e$	0	0	0.7025(1)	
Temperature factors (\AA^2)					
Atom	B_{11}	B_{22}	B_{33}		
A(1)	0.78(6)	0.78	1.28(12)		
A(2)	1.32(5)	1.32	1.35(9)		
Cu(1)	0.60(4)	0.60	1.69(9)		
O(1)	0.57(5)	1.18(6)	2.40(9)		
O(2)	3.88(7)	3.88	1.22(13)		
$R_n = 2.8\%$					
$R_e = 4.1\%$					
$R_p = 7.8\%$					
$R_{wp} = 8.5\%$					
N–P + C = 1567					
Anisotropic temperature factors are defined as $\exp[-(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33})]$					
Bond lengths (\AA ($\pm 0.001 \text{ \AA}$))					
A(1)–O(1)		2.511	$\times 8$		
A(2)–O(1)		2.727	$\times 4$		
–O(2)		2.764	$\times 4$		
Cu(1)–O(1)		1.937	$\times 4$		
–O(2)		2.199	$\times 1$		

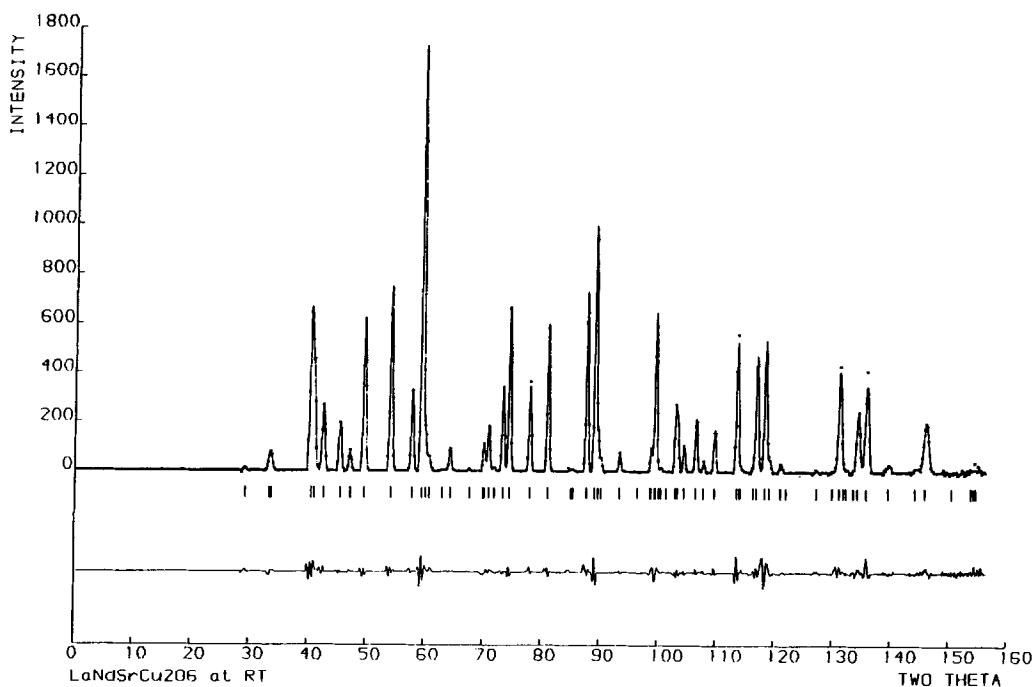


FIG. 1. Powder neutron diffraction data for $\text{LaNdSrCu}_2\text{O}_6$. Dots, observed profile; solid line, calculated profile and fit.

attempts to place oxygen on the O(3) at $(\frac{1}{2}, 0, z)$ site with subsequent refinement showed an occupancy which oscillated around zero, with an unstable temperature factor, and a z ordinate which gradually approached that of A_3 . This may be rationalized by the observation that it is not possible to find a value of z which produces reasonable A_1 -O(3), A_2 -O(3), and Cu(2)-O(3), distances simultaneously. It was not possible to refine anisotropic temperature factors for O(7) because of the low refined occupancy on this site. All other oxygen positions had refined occupancies which were consistent, within the error limits, with full population at each site and were therefore fixed as such during the latter stages of the refinement. Attempts to refine the data in the lower symmetry space group I222 (No. 23) which allows displacement of A_4 , Cu(2), O(1), O(2), and O(6) from $(0, y, z)$ to (x, y, z) produced no signifi-

cant improvement to the refinement with the x ordinates oscillating around zero and highly correlated with each other.

The PND refinement also revealed some differences in the distribution of cations on the A sites. In common with previous work, it was found that the A_1 and A_4 sites were fully occupied by rare earth (Nd) and strontium, respectively. However, the A_2 and A_3 site populations are markedly different to the previous study: the latter is fully occupied by neodymium only and it is the A_2 site which contains a mixture of 60% Nd and 40% Sr. A difference plot is shown in Fig. 3 and an ORTEPII (26) diagram of the structure is shown in Fig. 4.

5. Discussion

5.1. $\text{LaNdSrCu}_2\text{O}_6$

The results confirm the oxygen vacancy order reported by Nguyen *et al.* with the

TABLE IIIa
FINAL CRYSTALLOGRAPHIC RESULTS FOR
Nd_{1.4}Sr_{1.6}Cu₂O_{5.79}

Orthorhombic, space group <i>Immm</i> (No. 71)				
$a = 3.7780(3) \text{ \AA}; b = 11.3712(8) \text{ \AA};$				
$c = 20.1315(14) \text{ \AA}$				
Atom	Wyckoff symbol	x/a	y/b	Site occupancy
A(1)	$2a$	0	0	Nd 1.0
A(2)	$4g$	0	0.3073(6)	Nd 0.6; Sr 0.4
A(3)	$4i$	0	0	Nd 1.0
A(4)	$8l$	0	0.3256(5)	Sr 1.0
Cu(1)	$4i$	0	0	0.5873(3)
Cu(2)	$8l$	0	0.3524(3)	0.6013(2)
O(1)	$8l$	0	0.1621(5)	0.4163(3)
O(2)	$8l$	0	0.1356(5)	0.0955(4)
O(4)	$4j$	$\frac{1}{2}$	0	0.4242(10)
O(5)	$4i$	0	0	0.6940(5)
O(6)	$8l$	0	0.3451(6)	0.6989(2)
O(7)	$2c$	$\frac{1}{2}$	$\frac{1}{2}$	0
O(8)	$4h$	0	0.3732(7)	$\frac{1}{2}$

O(3) site used by Nguyen is unoccupied

Temperature factors (\AA^2)

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
A(1)	0.2(4)	0.3(1)	0.3(4)	0	0	0
A(2)	2.2(4)	3.8(5)	1.3(3)	0	0	0
A(3)	0.9(4)	1.9(3)	1.1(3)	0	0	0
A(4)	1.6(3)	1.7(3)	0.6(2)	0	0	-0.6(2)
Cu(1)	3.2(4)	0.3(2)	1.4(3)	0	0	0
Cu(2)	0.4(1)	1.5(2)	0.4(1)	0	0	0.7(2)
O(1)	4.2(3)	1.8(3)	0.7(4)	0	0	-0.3(2)
O(2)	0.3(2)	2.0(3)	2.8(3)	0	0	-0.7(2)
O(3)	—	—	—	—	—	—
O(4)	1.2(9)	3.0(7)	6.7(12)	0	0	0
O(5)	6.3(9)	3.1(5)	4.3(5)	0	0	0
O(6)	1.7(3)	1.1(3)	0.1(1)	0	0	0.2(2)
O(7)	$B_{\text{iso}} = 7.1(12)$					
O(8)	1.1(4)	0.9(4)	0.4(3)	0	0	0

$$R_n = 4.1\%$$

$$R_e = 5.3\%$$

$$R_p = 10.4\%$$

$$R_{\text{wp}} = 11.4\%$$

$$N-P + C = 2201$$

(No absorption correction applied to Nd)

TABLE IIIb
SELECTED INTERATOMIC DISTANCES AND COPPER
COORDINATION IN Nd_{1.4}Sr_{1.6}Cu₂O_{5.79}

A(1)-O(2)	2.465	×4	Cu(1)-O(1)	1.844	×2
-O(8)	2.376	×4	-O(4)	1.903	×1.21
A(2)-O(1)	2.555	×4	-O(5)	2.147	×1
-O(2)	2.741	×2	-O(7)	1.758	×0.17
-O(4)	2.670	×1.21	Cu(2)-O(1)	2.193	×1
-O(7)	2.893	×0.35	-O(2)	1.897	×2
-O(8)	2.790	×2	-O(6)	1.967	×1
			-O(8)	2.052	×1
A(3)-O(2)	2.524	×2	O(1)-Cu(1)-O(1)	175.5°	
-O(5)	2.239	×1	O(1)-Cu(1)-O(4)	89.7°	
-O(6)	2.584	×4	O(1)-Cu(1)-O(5)	92.3°	
A(4)-O(1)	2.658	×2	O(1)-Cu(1)-O(7)	87.7°	
-O(2)	2.704	×1	O(4)-Cu(1)-O(5)	97.0°	
-O(4)	2.833	×0.60	O(4)-Cu(1)-O(7)	83.0°	
			O(5)-Cu(1)-O(7)	180.0°	
			O(1)-Cu(2)-O(2)	93.5°	
			O(1)-Cu(2)-O(6)	96.9°	
			O(1)-Cu(2)-O(8)	87.4°	
			O(2)-Cu(2)-O(6)	93.7°	
			O(2)-Cu(2)-O(8)	86.1°	
			O(6)-Cu(2)-O(8)	175.8°	

Note. Bond distances to $\pm 0.001 \text{ \AA}$. Angles to $\pm 0.3^\circ$.

copper-oxygen coordination showing an extended two-dimensional arrangement of Cu-O₅ pyramids similar to those seen in YBCO (18). However, this refinement reveals a large-cation distribution which is significantly different from the results of previous work in which X-ray studies had indicated a strontium occupancy of the A₁ and A₂ sites of 50 and 25%, respectively (13). A low resolution PND study of La₂₁₂ on the liquids and amorphous materials diffractometer (LAD) at ISIS confirms the result of the present study in that strontium is isolated on the A₂ site (27). Perhaps the most unusual feature of the cation distribution of LaNdSrCu₂O₆ is the preferential ordering of neodymium on the A₁ site despite its close similarity to lanthanum: this must be attributable to the slightly different sizes of the cations, 1.18 and 1.12 for La and Nd in 8-coordination, respectively (28). Indeed, attempts to constrain a statistical distribution of lanthanum and neodymium over the A sites, given that strontium occu-

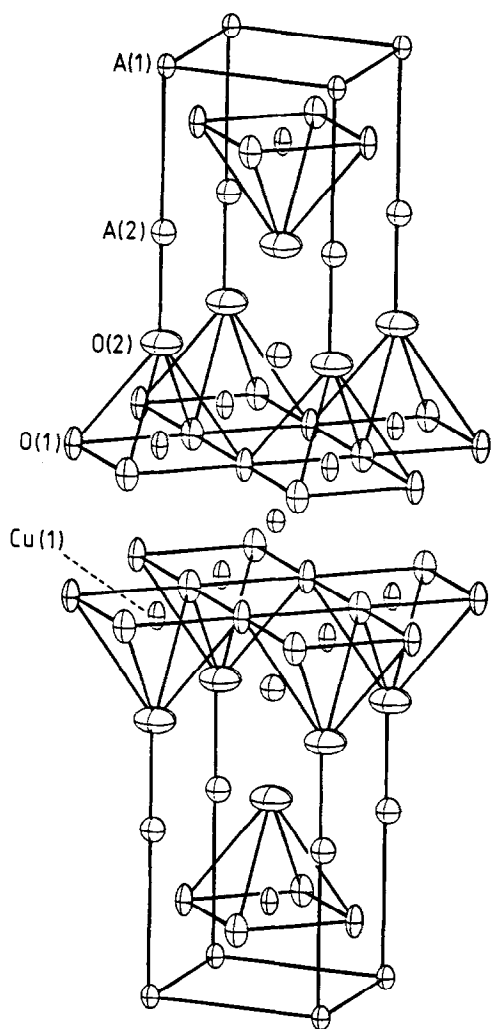


FIG. 2. ORTEP (26) diagram of a unit cell of $\text{LaNdSrCu}_2\text{O}_6$.

pies A_2 , resulted in R factors about 2% larger.

The use of the bond valence theory (29, 30) of Brown provides a reasonable explanation for the observed cation ordering. The formula

$$V_i = \sum \exp[(R_0 - R_{ij})/B],$$

with $B = 0.37$ and the R_0 values of Brown and Aldermatt (31) for La (2.172 Å), Nd (2.105 Å), and Sr (2.118 Å) for the A sites,

and the R_0 values and method for the copper site as described elsewhere (29) were used. Results are given in Table IV for (a) the refined cation distribution and (b) Sr on A_2 plus random La/Nd distribution. Both sets of results indicate that the A sites are underbonded; that is, the valence sums are somewhat lower than their expected values. This is compensated for by an overbonded copper environment which, of course, remains unchanged throughout. Thus the copper–oxygen framework is in compression and the A sites are in tension as the calculated valences indicate the latter to have smaller radii than is ideal for this position. Considering the differences between the observed and the calculated values, it is apparent that the refined cation distribution is the most energetically favorable arrangement because the degree of underbonding is evenly distributed over the A_1 and A_2 sites and hence over the entire structure. In model (b), however, the internal stresses lack this even distribution and appear more highly localized at the A_2 position.

5.2. $\text{Nd}_{1.4}\text{Sr}_{1.6}\text{Cu}_2\text{O}_{5.79}$

The unit cell tripling observed by Nguyen *et al.* has been confirmed although there are a number of important additional features which have been resolved from this refinement, which complicate the structural rela-

TABLE IV
BOND VALENCE CALCULATIONS FOR $\text{LaNdSrCu}_2\text{O}_6$

	Calculated	Observed	Difference (obsd - calcd)
(a)			
A_1 (Nd)	2.67	3.00	0.33
A_2 (La/Sr) (1:1)	2.17	2.50	0.33
(b)			
A_1 (La/Nd) (1:1)	2.92	3.00	0.08
A_2 (La/Nd/Sr) (1:1:2)	2.07	2.50	0.43
Cu(1)	2.36	1.99	-0.37

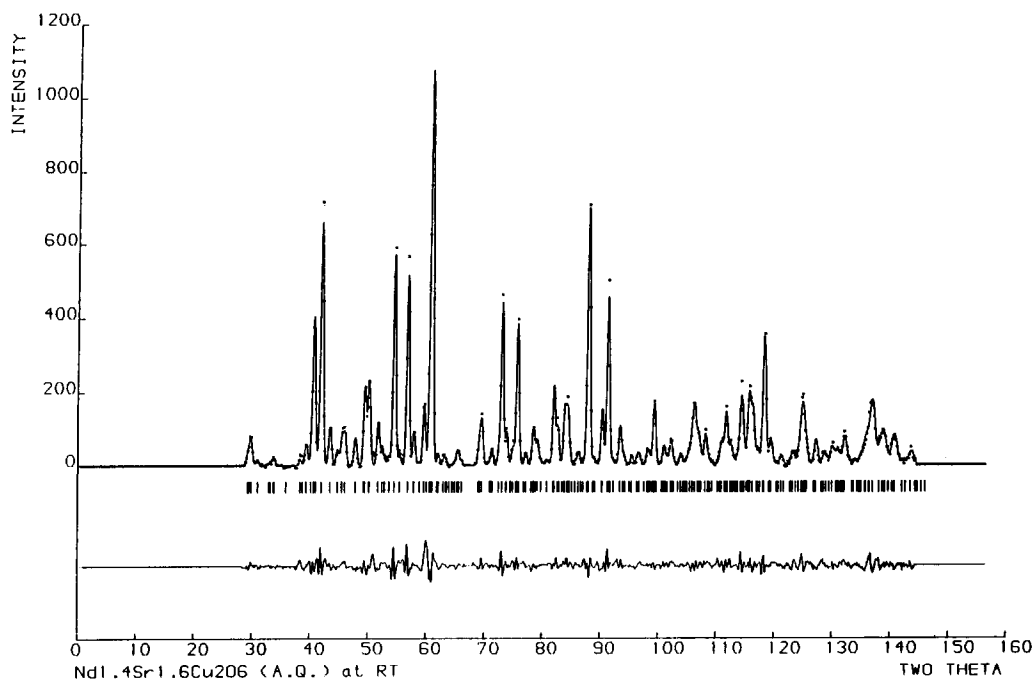


FIG. 3. Powder neutron diffraction data for Nd_{1.4}Sr_{1.6}Cu₂O_{5.79}. Dots, observed profile; solid line, calculated profile and fit.

tionship between La212 and Ln636. The Ln636 structure may be viewed initially as a La212 unit cell, tripled in the *b* direction. The three *A*₁ sites become *A*₁ + 2*A*₂ and, similarly, *A*₂ → *A*₃ + 2*A*₄. The copper–oxygen coordination of the central Cu(1)–O₅ pyramid is then largely unchanged, although there is the possibility of occasional Cu(1)–O₆ octahedra formation with the partial occupancy of O(7). The outer two Cu(1)–O₅ pyramids (i.e., the Cu(2)-centered polyhedra of Ln636) are reoriented, becoming apex-linked with the central pyramid, with the body-centered condition similarly modifying the central region of the basic tripled La212.

With regard to the large cation distribution, this work shows that neodymium occupies the *A*₃ site and that there is a mixed Nd/Sr *A*₂ site occupancy, contrary to the earlier study. At first sight, the refined oc-

cupancies presented here appear unusual in view of the refinement of LaNdSrCu₂O₆ where no strontium was observed in the 001 planes. However, a detailed analysis of all four *A* sites with bond valence calculations (29, 30) show that this arrangement satisfies the bond valence requirements of both the cations and anions in the structure. The calculations confirm that the *A*₁ and *A*₃ sites have the highest valences, with *A*₄ the lowest, and an intermediate value for *A*₂, consistent with the refined distribution of Nd³⁺ on *A*₁ and *A*₃, Sr²⁺ on *A*₄ and a mixed *A*₂ site.

The oxygen vacancy order is also different from the earlier X-ray study where it was thought that there were alternating *A*₁Cu(2)O₃ perovskite and *A*₂Cu(1)O₂ oxygen-deficient perovskite blocks (the latter as seen in LaNdSrCu₂O₆). This refinement, however, reveals a more complicated and

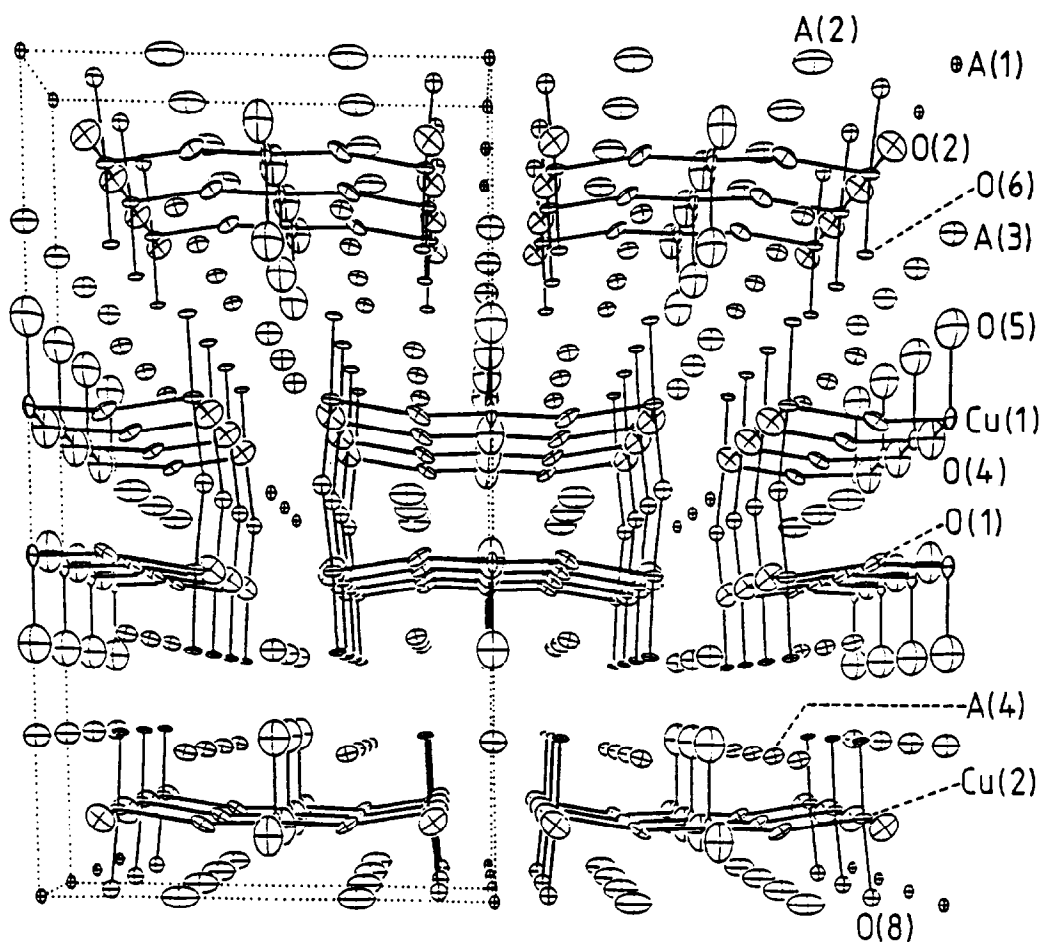


FIG. 4. ORTEP(26) diagram of $\text{Nd}_{1.4}\text{Sr}_{1.6}\text{Cu}_2\text{O}_{3.75}$ structure looking into a axis. Partially occupied O(7) site omitted for clarity. Boundary of unit cell is shown dotted.

disordered arrangement of oxygen vacancies. The most notable feature of this structure is the lack of continuity within the copper-oxygen sublattice in the b direction which is caused by the vacant sites at O(3): unlike $\text{LaNdSRCu}_2\text{O}_6$ and YBCO, there is no extended array of Cu-O_2 layers in any a - b plane as can be clearly seen in Fig. 4. Instead, there are six-membered rings of vertex-linked Cu-O_5 square pyramids which are corner-sharing with similar rings and form an extended irregular rectangular tunnel containing the A_2 cations running

parallel to the a direction. The tunnels are occasionally further blocked by the presence of Cu(1)-O(7)-Cu(1) bridges and this, in combination with the 60% occupancy of the O(4) position, may give rise to local reorientation of the Cu(1)-centered pyramids across the tunnel; both these defects are shown in Fig. 5. The formation of Cu(1)-O_6 octahedra is also probable and likely to be associated with the presence of neodymium on the A_2 site, increasing the local A_2 site valence to accommodate the higher charge: radius ratio of this ion. In fact, the

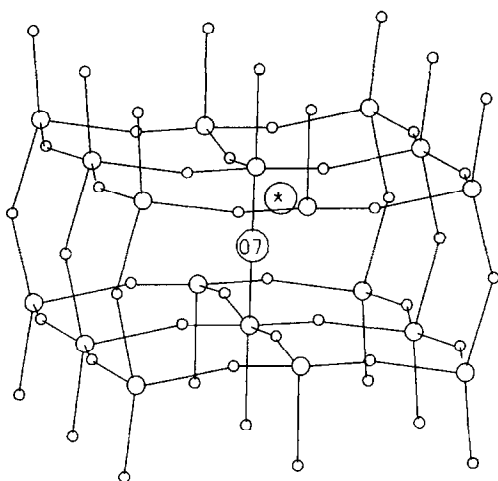


FIG. 5. Portion of the structure around $(0, \frac{1}{2}, 0)$ showing the position of O7 forming a CuO_6 octahedron and an oxygen vacancy on an adjacent O4 site (*).

refinement suggests that filling the O(7) site is unfavorable because of the observed partial occupancy and short average Cu(1)–O(7) bond length and may have to be encouraged by the presence of a tripositive A_2 ion in the vicinity combined with a local distortion of the structure. The latter effect is not observable by powder neutron diffraction but may account for the difficulty experienced in refining anisotropic temperature factors for O(7) and also the large observed isotropic temperature factor at this position. Despite these problems in refining the O(7) position there is strong evidence that a small amount of oxygen resides here in terms of lower R factors ($R_p = 10.4\%$ with O(7) and 11.1% without) and improved agreement between refined occupancies and analyzed stoichiometry. The result of this refinement therefore shows an unusual copper–oxygen sublattice with a pseudo one-dimensional tunnel structure which could be expected to show interesting anisotropic electrical properties.

The La212 compound with its limited solid solution has been studied in terms of its electrical properties and Cu(III) con-

tent previously (14). The sample of La212 prepared as the $x = 0$ member of the $\text{La}_{2-x}\text{Nd}_x\text{SrCu}_2\text{O}_{6\pm y}$ solid solution here is consistent with the previous work. As lanthanum is replaced by other rare earth cations, a gradual decrease in cell parameters is seen, consistent with the reduction in average ionic radius of the A sites. The neodymium-doped samples show very similar oxygen stoichiometries and, with experimental error, only the presence of Cu(II). A contraction of the cell parameters is observed as the neodymium level increases. Of note, however, is a larger contraction of the unit cell in $\text{La}_{0.5}\text{Nd}_{1.5}\text{SrCu}_2\text{O}_6$ which, from the PND study of the $x = 1.0$ material, is likely to be caused by the first substitution of neodymium for lanthanum on the A_2 site. For La212-type materials where the A_2 site is identical with La212, (i.e., in $\text{La}_{2-x}\text{Nd}_x\text{SrCu}_2\text{O}_{6\pm y}$ when $x \leq 1.0$) the a parameter is invariant with the size of the dopant cation: it is the c axis which responds to the introduction of the doping lanthanide. It was not possible to prepare a sample of the Nd212 compound in single phase using the stated conditions—there is only one assignment of an Nd212 phase in the literature, but only as an impurity in the preparation of the $\text{Nd}_{2-x}\text{Sr}_x\text{CuO}_4$ solid solution (32). The nonexistence of Nd212 is probably related to the degree of underbonding on the A sites, particularly the A_2 position: replacing La^{3+} wholly by the smaller Nd^{3+} would further decrease the calculated bond valence below 2.17.

Turning now to the materials with the Ln636 structure, it is immediately noticeable that lower oxygen stoichiometries are measured. However, the presence of a larger proportion of strontium on the A sites results in consistently higher average copper oxidation states than in the La212-based phases: all the measured oxygen stoichiometries of Ln636-type compounds in this study suggest the presence of some Cu(III) in contrast to the earlier work (15).

It is also clear from these results that the formation of an Ln636 phase is not related to the average ionic radius of the A sites: the range of materials encompassed in this study shows that both La212- and Ln636-type phases form when the average A site radius lies between 1.17 and 1.21 Å. The factor which appears to encourage the formation of the Ln636 structure in an $\text{Ln}_{2-x}\text{Sr}_{1+x}\text{Cu}_2\text{O}_{6\pm y}$ solid solution is primarily a high strontium level ($x \geq 0.6$), with the presence of a lanthanide ion of intermediate size of secondary importance. This suggests that a reasonable difference in ionic size between strontium and rare earth ion is important in order to provide suitable combinations of both which offer the correct average valences for the variety of cation sites available in the structure.

In view of the structure refinement of $\text{Nd}_{1.4}\text{Sr}_{1.6}\text{Cu}_2\text{O}_{5.79}$, the ability of the Ln636 structure to tolerate substantial levels of lanthanum substituting for samarium is not entirely unexpected given the variety of the A site valences, although from lattice parameter considerations it appears that a maximum is reached close to the $x = 0.6$ level. For $x > 0.6$, impurity phases are observed in the XRD patterns and the lattice parameters of the Ln636 majority phases do not continue to increase significantly.

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References

1. J. G. BEDNORZ AND K. A. MÜLLER, *Z. Phys. B* **64**, 189 (1986).
2. P. H. HOR, R. L. MENG, Y. Q. WANG, L. GAO, Z. J. HUANG, J. BECHTOLD, K. FORSTER, AND C. W. CHU, *Phys. Rev. Lett* **58**, 1891 (1987).
3. C. MICHEL, M. HERVIEU, M. M. BOREL, A. GRANDIN, F. DESLANDES, J. PROVOST, AND B. RAVEAU, *Z. Phys. B* **68**, 421 (1987).
4. H. MAEDA, Y. TANAKA, M. FUKUTOMI, AND T. ASANO, *Japan. J. Appl. Phys.* **27**, L209 (1988).
5. Z. Z. SHENG AND A. M. HERMANN, *Nature (London)* **332**, 55 (1988).
6. R. M. HAZEN, L. W. FINGER, R. J. ANGEL, C. T. PREWITT, N. L. ROSS, C. G. HADIDIACOS, P. J. HEANEY, D. R. VEBLEN, Z. Z. SHENG, A. EL ALI, AND A. M. HERMANN, *Phys. Rev. Lett* **60**, 1657 (1988).
7. M. TAKANO, *Nature (London)* **333**, 200 (1988).
8. S. M. GREEN, C. JIANG, Y. MEI, H. L. LUO, AND C. POLITIS, *Phys. Rev. B* **38**, 5016 (1988).
9. B. JAYARAM, P. C. LANCHESTER, M. T. WELLER, J. R. GRASMEDER, P. A. J. DE GROOT, AND G. P. RAPSON, *J. Phys.: Condens. Matter* **1**, 477 (1989).
10. J. R. GRASMEDER, M. T. WELLER, P. C. LANCHESTER, AND C. E. MEATS, *Solid State Ionics* **32/33**, 1115 (1989).
11. M. T. WELLER AND D. R. LINES, *J. Chem. Soc., Chem. Commun.* **484** (1989).
12. H. FELLVÅG, P. KAREN, AND A. KJEKSHUS, *Acta Chem. Scand. A* **41**, 283 (1987).
13. N. NGUYEN, L. ER-RAKHO, C. MICHEL, J. CHOISNET, AND B. RAVEAU, *Mater. Res. Bull.* **15**, 891 (1980).
14. N. NGUYEN, C. MICHEL, F. STUDER, AND B. RAVEAU, *Mater. Chem.* **7**, 413 (1982).
15. N. NGUYEN, J. CHOISNET, AND B. RAVEAU, *Mater. Res. Bull.* **17**, 567 (1982).
16. C. MICHEL AND B. RAVEAU, *Rev. Chim. Miner.* **21**, 407 (1984).
17. M. ARJOMAND AND D. J. MACHIN, *J. Chem. Soc. Dalton Trans.* 1061 (1975).
18. W. I. F. DAVID, W. T. A. HARRISON, J. M. F. GUNN, O. MOZE, A. K. SOPER, P. DAY, J. D. JORGENSEN, D. G. HINKS, M. A. BENO, L. SODERHOLM, D. W. CAPONE II, I. K. SCHULLER, C. U. SEGRE, K. ZHANG, AND J. D. GRACE, *Nature (London)* **327**, 310 (1987).
19. H. H. WANG, K. D. CARLSON, U. GEISER, R. J. THORN, H. C. I. KAO, M. A. BENO, M. R. MONAGHAN, T. J. ALLEN, R. B. PROKSCH, D. L. STUPKA, J. M. WILLIAMS, B. K. FLANDERMEYER, AND R. B. POEPEL, *Inorg. Chem.* **26**, 1474 (1987).
20. M. T. WELLER, J. R. GRASMEDER, AND P. C. LANCHESTER, *J. Phys. C* **21**, 411 (1988).
21. A. W. HEWAT AND I. BAILEY, *Nucl. Instrum. Methods* **137**, 463 (1976).
22. H. M. RIETVELD, *J. Appl. Crystallogr.* **2**, 65 (1969).
23. A. W. HEWAT, "Harwell Report AERE-R7350." (1973).
24. C. J. HOWARD, *J. Appl. Crystallogr.* **15**, 615 (1982).
25. "International Tables for Crystallography," Vol. A, D. Reidel Publishing Company, Dordrecht (1983).

26. C. K. JOHNSON, "Oak Ridge National Laboratory Report ORNL-5158." (1976).
27. W. I. F. DAVID, D. E. AKPORIAYE, R. M. IBBERTSON, AND C. C. WILSON, $\text{La}_2\text{SrCu}_2\text{O}_6$ —A WORKED EXAMPLE in "The HRPD at ISIS—An Introductory Users Guide," Version 1.0, Rutherford Appleton Laboratory, NJ (1988).
28. R. D. SHANNON AND C. T. PREWITT, *Acta Crystallogr. B* **25**, 925 (1969).
29. I. D. BROWN, *J. Solid State Chem.*, to be published.
30. I. D. BROWN, *Chem. Soc. Rev.* **7**, 359 (1978).
31. I. D. BROWN AND D. ALDERMATT, *Acta Crystallogr. B* **41**, 244 (1985).
32. J. GOPALAKRISHNAN, M. A. SUBRAMANIAN, C. C. TORARDI, J. P. ATTFIELD, AND A. W. SLEIGHT, *Mater. Res. Bull.* **24**, 321 (1989).