JOURNAL OF SOLID STATE CHEMISTRY **80**, 112–119 (1989)

Preparation and Crystal Structures of $La_2Cu_{1-x}Li_xO_4$ Solid Solutions and Evidence for a New Oxide with a Defect K_2NiF_4 Structure: $La_4Li_2O_7$

J. PAUL ATTFIELD*,† AND GÉRARD FÉREY

Laboratoire des Fluorures, UA CNRS 449, Faculté des Sciences, Université du Maine, Route de Laval, 72017 Le Mans Cédex, France

Received October 3, 1988; in revised form January 24, 1989

$La_2Cu_{1-x}Li_xO_4$ ($0 < x < 0.50$) solid solutions have been prepared and characterized by powder neutron diffraction at 5 K. They possess the orthorhombic La_2CuO_4 structure up to $x = 0.10$ at room temperature and to above $x = 0.25$ at 5 K. An ordering of copper and lithium cations is observed close to $x = 0.5$ and anisotropic broadening of the superstructure peaks indicates that the ordering is of long range in the xy plane, but is of much shorter range between planes due to stacking faults. Partial refinements of ordered structures with $x = 0.46$ and 0.50 are presented. No significant evidence for oxygen vacancies is apparent from any of the refinements or analytical results. Hence these materials are remarkable for their Cu(III) contents (98(5)% at $x = 0.50$ from iodometric titrations) in view of their preparation in air at 900–950°C followed by quenching to room temperature. A new phase with a defect K_2NiF_4 structure has been identified as $La_4Li_2O_7$ ($a = 3.659(2)$ Å, $c = 13.232(8)$ Å). A structure refinement shows that the oxygen vacancies are in the $z = 0$ plane.

Introduction

Following the discovery of superconductivity in $La_{2-x}A_xCuO_{4-y}$ solid solutions (*1*, *2*) there has been much interest in the physical and chemical properties of metal cuprates in the search for new high-temperature superconductors. In most of the superconducting materials, an average Cu oxidation state of between 2.0 and 2.3 is achieved by varying the proportions of basic metal cations, e.g., substituting Sr^{2+} for La^{3+} in La_2CuO_4, and annealing under oxygen to fill the anion vacancies and oxidize Cu^{2+} to Cu^{3+}.

An alternative strategy for producing high oxidation states in metal oxides is the direct substitution of Li^+ for the transition metal cation, and $La_2M_{0.5}Li_{0.5}O_4$ compounds have been reported for M = Co (*3*, *4*), Ni (*3*), Cu (*5*), and Au (*6*). The only structure that has been well-characterized is that of the gold compound: an ordering of Li^+ and Au^{3+} cations was observed (*6*). No cation ordering was reported in red-brown $La_2Cu_{0.5}Li_{0.5}O_4$, which was prepared at 870°C under 1600 atm oxygen pressure (*5*). There have been no systematic studies of possible $La_2M_{1-x}Li_xO_4$ solid solutions, and so we have undertaken a study of the M = Cu series in order to compare the structures and properties of these materials with those of the $La_{2-x}A_xCuO_4$ series. Here we report their preparation and crystal structures.

---

* On leave from the Chemical Crystallography Laboratory, University of Oxford, 9 Parks Road, Oxford OX1 3PD, UK.

† To whom correspondence should be addressed.

0022-4596/89 $3.00

Magnetic and electrical measurements will be reported later; preliminary measurements show that none of these materials are superconducting above 4 K.

Sample Preparation and Analysis

Our initial experiments showed that homogeneous, black $La_2Cu_{1-x}Li_xO_4$ compounds could be prepared for $0 < x < 0.5$ by heating well-ground mixtures of La_2O_3 + $(1 - x)CuO$ + $(x/2)Li_2CO_3$ in air at 900–950°C, and quenching to room temperature. The X-ray powder patterns of these materials, recorded on a Siemens D501 diffractometer using Cu$K\alpha$ radiation, showed that these K_2NiF_4-type solid solutions are orthorhombic for $x < 0.10$ and tetragonal above $x = 0.15$. Refined cell parameters are given in Table I. A weak (1/2 1/2 0) peak was observed in the $x = 0.50$ profile and so the pattern was indexed on a tetragonal $\sqrt{2}a \times \sqrt{2}a \times c$ unit cell. A sample of nominal composition $x = 0.70$ produced a red-brown mixture of three phases after sintering; an $La_2Cu_{1-x}Li_xO_4$ solid solution with very similar cell parameters to those of the $x = 0.50$ sample, La_2O_3, and another K_2NiF_4-type material. The presence of La_2O_3 suggested that some lithium oxide had been lost from the sample. Small amounts of the second K_2NiF_4-type phase were also formed when a 2 : 1 mixture of La_2O_3 and Li_2CO_3 was heated at 950°C. All of the diffraction peaks from this material were indexed on a tetragonal cell in $I4/mmm$ with $a = 3.659(2)$ Å and $c = 13.232(8)$ Å. Thus, a plausible formula for this new phase is $La_4Li_2O_7$.

TABLE I

REFINED CELL PARAMETERS FOR $La_2Cu_{1-x}Li_xO_4$ COMPOSITIONS AT 300 K WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Nominal x	Actual x^a	a (Å)	b (Å)	c (Å)	V (Å^3)
0^b		5.366(2)	5.402(2)	13.149(4)	381.15(3)
0.100	0.100(4)	5.351(1)	5.385(1)	13.156(3)	379.11(2)
0.150	0.145(4)	3.7815(8)		13.168(3)	188.30(1)
0.250	0.252(3)	3.767(1)		13.166(4)	186.84(2)
0.500	0.46(1)	5.280(1)		13.184(4)	367.48(2)
0.700	0.50	5.268(1)		13.188(3)	365.97(2)

[a] Values from the neutron analyses.

[b] Taken from Ref. (*16*).

To confirm the results of the neutron refinements of the nominal $x = 0.50$ and 0.70 samples, these materials were chemically analyzed. The $x = 0.50$ material was investigated by iodometric titrations (*7*) and thermogravimetry. The titrations enabled both the total Cu content and the Cu^{3+}/Cu^{2+} ratio to be determined, giving values of $x = 0.45(1)$ and $y = 0.38(1)$ for the stoichiometry $La_2Cu^{2+}_{1-x-y}Cu^{3+}_yLi_xO_{4-x/2+y/2}$. This corresponds to an average Cu oxidation state of +2.70(5) and an oxygen content of 3.97(1) per formula unit. A total weight loss of 3.19% occurred up to 620°C when the sample was heated at 10°C min^{-1} under flowing hydrogen, and the X-ray diffraction pattern of the products showed that all the copper had been reduced to the metal. This weight loss gives $y = 0.41(1)$, assuming the above value of x, and hence an average Cu oxidation state of +2.75(5) and an oxygen content of 3.98(1).

The average Cu oxidation state in the mixture of compounds with bulk composition $x = 0.70$ was found to be +2.98(5) by iodometric titrations.

Structure Refinements

Ten-gram samples of the $x = 0.10$, 0.15, 0.25, 0.50, and 0.70 compositions were prepared by sintering at 900–950°C for 4 days, with several regrinds during preparation, and quenched to room temperature. The neutron diffraction profiles of these samples were recorded on diffractometer D1a at the ILL, Grenoble. The patterns were recorded at 5 K in order to minimize the effects of thermal motion. Data were collected between 6° and 156° 2θ in 0.05° steps at a wavelength of 1.9107 Å.

The profiles were fitted by the Rietveld method (*8*) using modified versions of a standard program (*9*) and a multipattern program (*10*). Neutron scattering lengths were taken from Sears (*11*). Small contributions from La_2O_3 were observed in all the patterns and were fitted in the refinements. Other weak peaks from unknown impurities were excluded from the $x = 0.25$ and 0.50 fits. No magnetic diffraction was evident in any of the profiles.

Although the solid solutions are tetragonal for $x > 0.15$ at room temperature, orthorhombic splittings were observed in the 5 K, $x = 0.10$, 0.15, and 0.25 profiles, and so all three were fitted in space group *Abma* using the structure of La_2CuO_4 (*12*) as a starting model. Isotropic thermal parameters, the Cu/Li ratio, and the oxygen site occupancies were then varied. In all three structures, vacancies were observed only on the O(1) site. In order to obtain sensible results it was necessary to fix B(Cu/Li) at 0.2 $Å^2$ in the refinement of the $x = 0.25$ structure, but in the other two fits it was possible to refine the four thermal parameters and two occupancies simultaneously without excessively large correlations. No evidence for lanthanum deficiency was found in any of these structures. The results of these refinements are presented in Table II. (For distances and selected bond angles, see Table III).

TABLE II

RESULTS OF THE REFINEMENTS OF THE $x = 0.10$, 0.15, AND 0.25 $La_2Cu_{1-x}Li_xO_4$ STRUCTURES AT 5 K

Nominal x:	0.10	0.15	0.25
Cell parameters (Å)			
a	5.3813(1)	5.3617(1)	5.3177(1)
b	5.3192(1)	5.3147(1)	5.3032(1)
c	13.1028(1)	13.1066(1)	13.1218(2)
FWHM parameters[a]			
U ($°^2$)	0.155(3)	0.156(3)	0.160(5)
V ($°^2$)	−3.389(7)	−0.394(6)	−0.42(1)
W ($°^2$)	0.368(4)	0.372(3)	0.484(5)
e	0.118(5)	0.135(5)	0.143(7)
R factors[b] (%)			
R_{WP}	6.8	7.4	7.9
R_P	5.6	5.1	6.3
R_{NUC}	1.9	1.8	3.9
R_{EX}	4.1	3.4	4.8
Largest correlation for atomic parameters	78% *B*, Occ. for Cu/Li	79% *B*, Occ. for Cu/Li	69% *B*, Occ. for O(1)

	Fractional coordinates[c]				
Nominal x	x: La	z: La	z: O(1)	x: O(2)	z: O(2)
0.10	−0.0076(2)	0.3619(1)	−0.0070(1)	0.0348(2)	0.1830(1)
0.15	−0.0066(2)	0.3619(1)	−0.0062(1)	0.0304(2)	0.1827(1)
0.25	−0.0030(3)	0.3621(1)	−0.0025(3)	0.0168(4)	0.1819(1)

	Isotropic B factors ($Å^2$)				Refined occupancies	
Nominal x	La	Cu/Li	O(1)	O(2)	Li	O(1)
0.10	0.36(2)	0.16(4)	0.41(3)	0.69(3)	0.100(4)	0.983(7)
0.15	0.41(2)	0.22(4)	0.51(3)	0.72(3)	0.145(4)	0.987(6)
0.25	0.52(2)	0.20	0.64(4)	0.78(3)	0.252(3)	0.990(8)

Note. Estimated standard deviations are given in parentheses.

[a] e is the "mixing parameter" in the pseudo-Voigt peak shape function and U, V, and W describe the variation of the Gaussian part. See Ref. (*9*) for more details.

[b] The R factors are defined in Ref. (*8*).

[c] Positions in space group *Abma* (No. 54): La and O(2) on 8(f) (x, 0, z); Cu/Li on 4(a) (0, 0, 0); O(1) on 8(d) (1/4, 1/4, z).

No orthorhombic splittings were observed in the pattern of the nominal $x = 0.50$ material; however, several extra reflections were observed, all of which could be indexed on the tetragonal 300 K supercell. Only ($hk0$): $k = 2n$ reflections were seen, but close examination of the profile revealed extremely broad peaks at some of the expected (hkl): $k + l = 2n$ positions, as shown in Fig. 1. This suggested that cation ordering takes place in the same manner as that in $La_2Au_{0.5}Li_{0.5}O_4$ (*6*), which lowers the supercell symmetry from *Fmmm* to *Ammm*. The structure was refined using only the fundamental reflections and the ($hk0$) supercell reflections. This did not permit a full refinement in *Ammm*, as it was only possible to refine the parameters that describe the structure in *Fmmm*, plus the variables that contribute to the ($hk0$) superstructure reflections in *Ammm*, i.e., x, y, and the occupancy of O(1), and occupation factors for the Cu and Li or the O(2) and O(3) sites. The best fit obtained by assum-

TABLE III

DISTANCES (Å) AND SELECTED BOND ANGLES (°) IN THE x = 0.10, 0.15, AND 0.25 $La_2Cu_{1-x}Li_xO_4$ STRUCTURES AT 5 K, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Nominal x:		0.10	0.15	0.25
La-O(2)	(×1)	2.355(2)	2.357(2)	2.367(2)
La-O(2)′	(×1)	2.532(2)	2.550(2)	2.618(3)
La-O(1)	(×2)	2.577(1)	2.578(1)	2.593(3)
La-O(1)′	(×2)	2.662(1)	2.654(1)	2.622(3)
La-O(2)″	(×2)	2.728(1)	2.724(1)	2.715(1)
La-O(2)″	(×1)	2.978(2)	2.938(2)	2.824(3)
Mean La-O distance		2.644	2.640	2.630
Cu/Li-O(1)	(×4)	1.894(1)	1.889(1)	1.878(3)
Cu/Li-O(2)	(×2)	2.405(1)	2.400(1)	2.389(1)
Mean Cu/Li-O distance		2.064	2.059	2.048
O(1)-Cu/Li-O(1)		89.2(1)	89.4(1)	89.8(1)
O(1)-Cu/Li-O(1)′		90.8(1)	90.6(1)	90.2(1)
O(1)-Cu/Li-O(1)″		180	180	180
O(1)-Cu/Li-O(2)		89.6(1)	89.7(1)	89.5(1)
O(1)-Cu/Li-O(2)′		90.4(1)	90.3(1)	90.5(1)
O(2)-Cu/Li-O(2)′		180	180	180

ing an ideal x = 0.50 composition gave R_{WP} = 9.4%, R_{NUC} = 4.5% and a total oxygen content of 3.82(3) per formula unit. However, when the occupancies of the Cu and Li sites were varied independently, the fit was improved (R_{WP} = 8.6%, R_{NUC} = 3.0%) with 9(1)% copper on the Li site and no oxygen vacancies. In view of the better profile fit and the agreement with the analytical results, the latter model with a lithium content of x = 0.46(1) was taken to be the best description of the structure. The results are presented in Table IV and distances and angles are given in Table V. Observed, calculated, and difference profiles are shown in Fig. 2.

The same ($hk0$): $k = 2n$ superstructure peaks were observed in the profile of the x = 0.70 sample, and so the same procedure was used to fit the $La_2Cu_{1-x}Li_xO_4$ peaks. Neither oxygen vacancies nor cation disorder was found in this structure, and so the

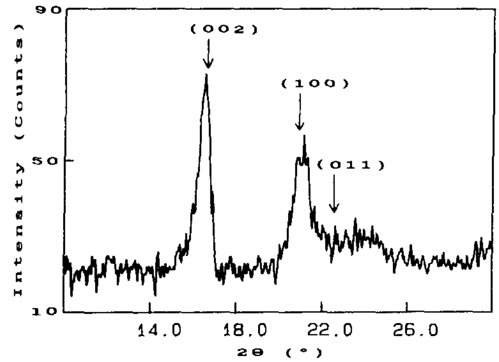

FIG. 1. Part of the x = 0.50 neutron diffraction profile showing the expected positions of the (002) and superstructure (100) and (011) reflections. The FWHM's of the (002) and (100) peaks are 0.6° and 0.8°, respectively, whereas the broad hump centered at the (011) position has a FWHM of approximately 5°.

TABLE IV

RESULTS OF THE REFINEMENTS OF THE CATION ORDERED $La_2Cu_{1-x}Li_xO_4$ STRUCTURES IN THE x = 0.50 AND 0.70 COMPOSITIONS AT 5 K

Nominal x:	0.50	0.70
Actual x:	0.46(1)	0.50
Cell parameters (Å)		
a	5.2636(2)	5.2517(9)
b	5.2580(2)	5.2510(10)
c	13.1460(2)	13.1539(3)
FWHM parameters (°²)		
U	0.169(6)	0.169(8)
V	−0.43(1)	−0.43(2)
W	0.416(6)	0.41(1)
R factors[a] (%)		
R_{WP}	8.6	8.0
R_P	8.6	8.3
R_{NUC}	3.0	2.8
R_{EX}	5.5	4.0
Largest correlation for atomic parameters	87%: y, B for O(1)	89% y, B for O(1)

Fractional coordinates[b]

x	z: La(1), La(2)	x: O(1)	y: O(1)	z: O(2), O(3)
0.50	0.3621(1)	0.249(1)	0.234(2)	0.1830(1)
0.70	0.3622(1)	0.248(2)	0.233(4)	0.1808(1)

	Isotropic B factors (Å²)				
x	La(1), La(2)	Cu, Li	O(1)	O(2), O(3)	Proportion of Cu on Li site
0.50	0.32(3)	0.1(1)	0.36(7)	0.62(3)	0.09(1)
0.70	−0.01(4)	0.3(1)	0.0(1)	0.32(6)	0

Note. Estimated Standard Deviations are given in parentheses

[a] The R factors are defined in Ref. (*8*).

[b] Positions in space group *Ammm* (No. 65): La(1) and O(2) on 4(i) (0, 0, z); La(2) and O(3) on 4(j) (1/2, 1/2, z); Cu on 2(a) (0, 0, 0); Li on 2(c) (1/2, 1/2, 0); O(1) on 8(O) (x, y, 0).

actual value of x for this phase is 0.50. In addition, the structure of La_2O_3 was refined in $P\bar{3}m1$ (*13*), and the contribution from $La_4Li_2O_7$ was fitted assuming $I4/mmm$ symmetry for this new phase. Variation of the occupation factors of the anion sites in this structure showed that all the vacancies are at the O(1) position. Results for $La_2Cu_{0.5}Li_{0.5}O_4$ are listed in Tables IV and V and a view of the structure is shown in Fig. 3. Final results for $La_4Li_2O_7$ are shown in Table VI and the parameters obtained for La_2O_3 are given in Table VII.

TABLE V

DISTANCES (Å) AND SELECTED BOND ANGLES (°) IN THE CATION ORDERED $La_2Cu_{0.54}Li_{0.46}O_4$ (i) AND $La_2Cu_{0.5}Li_{0.5}O_4$ (ii) STRUCTURES AT 5 K, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Sample		(i)	(ii)
La(1)–O(2)	(×1)	2.380(2)	2.387(3)
La(1)–O(1)	(×4)	2.638(7)	2.63(1)
La(1)–O(2)′	(×2)	2.690(1)	2.686(1)
La(1)–O(3)	(×2)	2.692(1)	2.686(1)
La(2)–O(3)	(×1)	2.380(2)	2.387(3)
La(2)–O(1)	(×4)	2.56(1)	2.56(2)
La(2)–O(3)′	(×2)	2.690(2)	2.686(3)
La(2)–O(2)	(×2)	2.692(1)	2.686(1)
Cu–O(1)	(×4)	1.795(9)	1.79(2)
Cu–O(2)	(×2)	2.380(1)	2.378(3)
Li–O(1)[a]	(×4)	1.926(9)	1.93(2)
Li–O(3)	(×2)	2.380(1)	2.378(3)
O(1)–Cu–O(1)		86(1)	86(2)
O(1)–Cu–O(1)′		94(1)	94(2)
O(1)–Cu–O(1)″		180	180
O(1)–Cu–O(2)		90	90
O(2)–Cu–O(2)′		180	180
O(1)–Li–O(1)		87(1)	87(2)
O(1)–Li–O(1)′		93(1)	93(2)
O(1)–Li–O(1)″		180	180
O(1)–Li–O(2)		90	90
O(2)–Li–O(2)′		180	180

[a] In structure (i) there is 9(1)% Cu on the Li site.

Discussion

The above results show that homogeneous $La_2Cu_{1-x}Li_xO_4$ solid solutions can be prepared for $0 < x < 0.50$ in air. Although the refined values of x in Table II are in excellent agreement with the starting compositions for the $x = 0.10$, 0.15, and 0.25 samples, the presence of traces of La_2O_3 suggests that lithium oxide may be lost by evaporation or through reaction with the alumina crucibles. In the $x = 0.50$ material some loss of lithium is evident, as the refined composition is $x = 0.46(1)$, but when excess lithium is present, as in the $x = 0.70$ sample, stoichiometric $La_2Cu_{0.5}Li_{0.5}O_4$ results. Thus, the upper limit of lithium substitution is $x = 0.50$.

When x is close to 0.50 we observe a cation ordering similar to that in $La_2Au_{0.5}Li_{0.5}O_4$ (*6*) in which every Au has four Li nearest-neighbors in the (001) plane and vice versa. The extremely anisotropic FWHM variation of the superstructure peaks (see Fig. 1) indicates that long-range cation order takes place within the sheets of octahedra in the (001) plane, but that the order between planes is of shorter range due to stacking faults. Even the (*hk*0) superstructure peaks are broader than the substructure peaks, which lowers the quality of the profile refinement, as is evident in Fig. 2. However, the results in Tables IV and V seem reasonable, as the refined displacement of O(1) toward Cu gives rise to plausible Cu–O(1) and Li–O(1) distances of 1.79 and 1.93 Å, respectively. There is evidence for similar cation ordering in $La_2Co_{0.5}Li_{0.5}O_4$ from both diffraction (*4*) and microscopy (*14*) studies.

Our preparations result in the greatest possible oxidation of copper, rather than in the creation of oxygen vacancies. We have listed in Table II the results for the $x = 0.10$, 0.15, and 0.25 materials with refined O(1) occupation factors, in order to show that a precision of greater than 1% was achieved for this variable. However, the deviation from full occupancy is not significant in the 3σ limit for any of the refinements, and so we conclude that these three

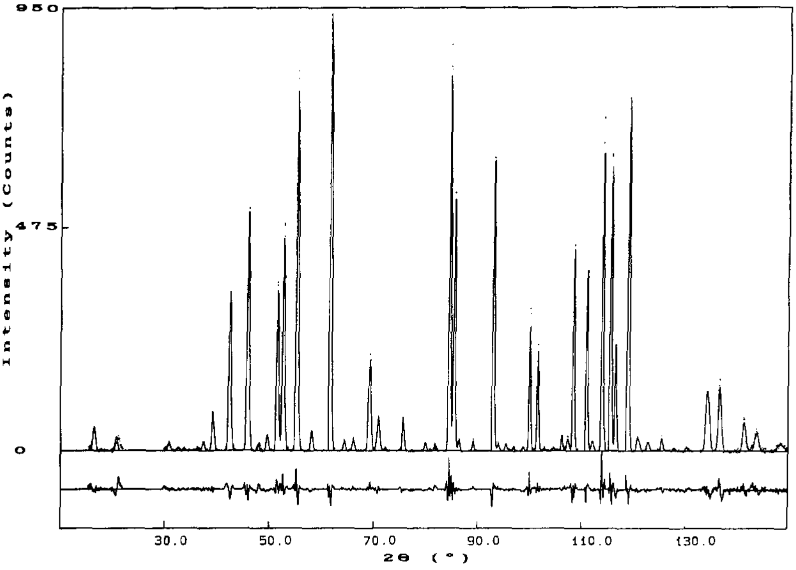

FIG. 2. Final observed (points), calculated (full line), and difference neutron diffraction profiles at 5 K for the $x = 0.50$ sample, which contains cation ordered $La_2Cu_{0.54}Li_{0.46}O_4$ and a small amount of La_2O_3.

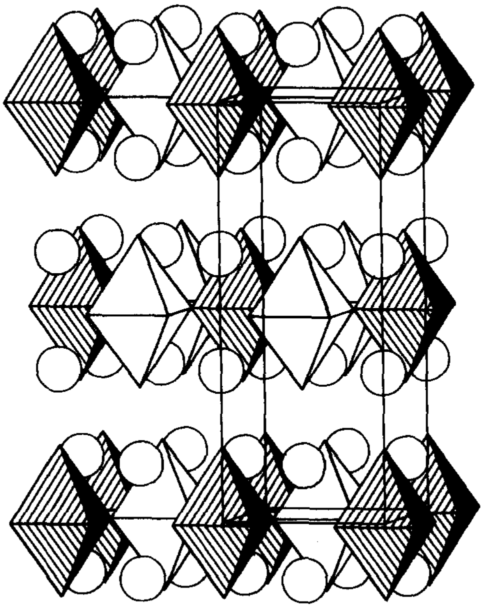

FIG. 3. A view of cation ordered $La_2Cu_{0.5}Li_{0.5}O_4$ close to (010). The CuO_6 octahedra are hatched, the LiO_6 octahedra are unshaded, and the La^{3+} cations are represented by circles. The unit cell is shown.

materials are fully oxidized. Although our refinements of the cation ordered phases in the $x = 0.50$ and 0.70 samples are less precise, the best fits for both structures do not contain oxygen vacancies, and the analyti-

TABLE VI

RESULTS OF THE REFINEMENT OF THE $La_4Li_2O_7$ COMPONENT IN THE $x = 0.70$ SAMPLE AT 5 K, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

$R_{NUC} = 6.3\%$	$a = 3.6534(1)$ Å	$c = 13.2342(3)$ Å

Coordinates in $I4/mmm$ (No. 139), isotropic B factors (Å^2), and occupancies

Atom	Site	x	y	z	B	Occ.
La	4(e)	0	0	0.3622(1)	0.72(4)	1.00
Li	2(a)	0	0	0	10.3(7)	1.00
O(1)	4(c)	0	1/2	0	3.21(9)	0.75
O(2)	4(e)	0	0	0.1771(2)	0.74(6)	1.00

Bond distances (Å)

La–O(2)	(×1)	2.459(3)	Li–O(1) (×3)	1.827(1)
La–O(1)	(×3)	2.575(1)	Li–O(2) (×2)	2.344(2)
La–O(2)′	(×4)	2.637(1)		
Mean La–O distance		2.592	Mean Li–O distance	2.034

TABLE VII

RESULTS OF THE REFINEMENT OF La_2O_3 COMPONENT IN THE $x = 0.70$ SAMPLE AT 5 K, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

$R_{NUC} = 5.0\%$ $a = 3.9280(3)$ Å $c = 6.1101(2)$ Å

Coordinates in $P\bar{3}m1$ (No. 164) and isotropic B factors (Å^2)

Atom	Position	x	y	z	B
La	2(d)	1/3	2/3	0.2465(7)	0.20(7)
O(1)	1(a)	0	0	0	0.6(1)
O(2)	2(d)	1/3	2/3	0.6464(6)	0.1(1)

Bond distances (Å)

La–O(2)	(×3)	2.360(2)	La–O(1)	(×3)	2.722(2)
La–O(2)	(×1)	2.443(6)	Mean La–O distance		2.527

cal results for the $x = 0.50$ material also give an oxygen content that does not differ significantly from 4.0 per formula unit. In addition, the Cu oxidation state for the mixture of nominal $x = 0.70$, in which $La_2Cu_{0.5}Li_{0.5}O_4$ is the only copper-containing phase, was found to be +2.98(5). Hence, these solid solutions are notable for a quantitative oxidation of Cu^{2+} to Cu^{3+} with lithium substitution according to the formula $La_2Cu^{2+}_{1-2x}Cu^{3+}_{x}Li_xO_4$ without annealing or high-pressure oxygen treatment. $La_2Cu_{0.5}Li_{0.5}O_4$ is the first example of a completely oxidized, thermodynamically stable, Cu(III) compound formed by reaction at high temperatures in air.

The ease of oxidation of Cu^{2+} in these materials reflects the tendency for Cu/Li ordering, as the substituted Li^+ cations tend to isolate the CuO_6 units from each other and so Cu^{3+} can be stabilized by the formation of four short, highly covalent Cu–O(1) bonds in the xy plane (*15*). In the $x = 0.50$ limit, each O(1) is connected to only one Cu^{3+} with a bond length of 1.79 Å. By contrast, fully oxidized $LaSrCuO_4$ requires 3 kbar oxygen pressure at 800°C, and contains 1.88 Å Cu–O(1) bonds with each O(1) connected to two Cu^{3+} cations (*15*). This illustrates well the importance of electropositive cations in stabilizing high oxidation states by inductive effects; in $La_2Cu_{0.5}Li_{0.5}O_4$ there are four La^{3+} and one Li^+ cation per $Cu^{3+}O_6$ unit, but in $LaSrCuO_4$ there is only one La^{3+} and one Sr^{2+}.

It is interesting to note the difference in color between black $La_2Cu_{0.54}Li_{0.46}O_4$ and red-brown $La_2Cu_{0.50}Li_{0.50}O_4$. The color of the latter is due to isolated Cu^{3+} cations, but the presence of a small amount of copper on the Li site in the former material produces regions of connected, mixed-valence CuO_6 units and the sample becomes much more absorbing in the visible region.

The oxide $La_4Li_2O_7$ is the first reported K_2NiF_4-type oxide to have purely monopositive cations in the Ni positions. One quarter of the O(1) sites are empty which reduces the mean La^{3+} and Li^+ coordination numbers to eight and five, respectively. The Li environment is irregular, with three short Li–O distances of 1.83 Å and two long 2.34 Å bonds. The randomly arranged oxygen vacancies give rise to many possible modes for displacing Li and O(1) in the xy plane which are reflected in the large B factors for these atoms. These vacancies may also account for the c/a value of 3.616 which is extremely high for a K_2NiF_4-type oxide (*14*). It is possible that there may be a superstructure or lowering of symmetry which was not detected in this study and so we are currently attempting to prepare a pure sample of this phase. Whereas there is a complete range of solid solutions between La_2CuO_4 and $La_2Cu_{0.5}Li_{0.5}O_4$, there appear to be none between the latter phase and $La_4Li_2O_7$ under our conditions of preparation. As compounds in the latter system would have to contain oxygen vacancies, according to the formula $La_2Cu_{0.5-z}Li_{0.5+z}O_{4-z}$, their nonexistence provides additional evidence that vacancy formation in the $La_2Cu_{1-x}Li_xO_4$ system is unfavorable.

Finally, it is interesting to compare the $La_2Cu_{1-x}Li_xO_4$ solid solutions with those prepared in the $La_{2-y}Sr_yCuO_{4-d}$ system in air (*16*). In both, the disorder due to the substitution lowers the temperature of the orthorhombic to tetragonal structural transition to below 300 K for x and $y > 0.10$. At 5 K the limit lies above $x = 0.25$ in the $La_2Cu_{1-x}Li_xO_4$ system. The orthorhombic phases have *Abma* symmetry, as was found in a recent single-crystal neutron diffraction study of $La_2Cu_{0.95}Li_{0.05}O_4$ (*17*). Strontium substitution results in the creation of oxygen vacancies and some oxidation of copper reaching a maximum at $y = 0.33$; however, at $y = 1.0$ all of the copper is divalent. This results in a maximum value of c at $y = 0.33$. By contrast, lithium substitution results only in the formation of Cu^{3+}, due to the tendency for Cu/Li ordering and the inductive effects described above, and the cell parameters change smoothly with x. The value $x = 0.50$ marks the limit of substitution at which all of the copper is in the +3 state and the cations are ordered in the (001) plane. The limit in the $La_{2-y}Sr_yCuO_{4-d}$ system is $y = 1.34$, and there is evidence for cation and vacancy-ordered phases in the $1.00 < y < 1.34$ region.

Acknowledgments

The authors thank Dr. J. Pannetier (ILL, Grenoble) for assistance with the collection of neutron data, Dr. M. Leblanc for recording the TGA, and Drs. B. Raveau and M. Hervieu (Caen) for useful discussions. J.P.A. thanks Christ Church, Oxford, for a Junior Research Fellowship and the Université du Maine for a "Maitre de Conferences" position.

References

1. G. Bednorz and K. A. Muller, *Z. Phys. B* **64,** 189 (1986).
2. R. J. Cava, R. B. van Dover, B. Batlogg, and A. Rietman, *Phys. Rev. Lett.* **58,** 408 (1987).
3. G. Blasse, *J. Inorg. Nucl. Chem.* **27,** 2683 (1965).
4. G. Demazeau, M. Pouchard, M. Thomas, J. F. Colombet, J. C. Grenier, L. Fournes, J. S. Soubeyroux, and P. Hagenmuller, *Mater. Res. Bull.* **15,** 451 (1980).
5. G. Demazeau, C. Parent, M. Pouchard, and P. Hagenmuller, *Mater. Res. Bull.* **7,** 913 (1972).
6. F. Abbattista, M. Vallino, and D. Mazza, *J. Less-Common Met.* **110,** 391 (1985).
7. D. C. Harris and T. A. Hewston, *J. Solid State Chem.* **69,** 182 (1987).
8. H. M. Rietveld, *J. Appl. Crystallogr.* **2,** 65 (1969).
9. D. B. Wiles and R. A. Young, *J. Appl. Crystallogr.* **15,** 430 (1982).
10. M. W. Thomas and P. J. Bendall, *Acta Crystallogr. Sect. A* **34,** 5351 (1978).
11. V. F. Sears, "Thermal Neutron Scattering Lengths and Cross-Sections for Condensed Matter Research," Chalk River Nuclear Lab., Internal Report AECL-8490 (1984).
12. B. Grande and H. R. Muller-Buschbaum, *Z. Anorg. Allg. Chem.* **433,** 152 (1977).
13. P. Aldebert and J. P. Traverse, *Mater. Res. Bull.* **14,** 303 (1979).
14. P. Ganguly and C. N. R. Rao, *J. Solid State Chem.* **53,** 193 (1984).
15. J. B. Goodenough, G. Demazeau, M. Pouchard, and P. Hagenmuller, *J. Solid State Chem.* **8,** 325 (1973).
16. N. Nguyen, J. Choisnet, M. Hervieu, and B. Raveau, *J. Solid State Chem.* **39,** 120 (1981).
17. J. M. Delgado, R. K. McMullan, G. Diaz de Delgado, B. J. Wuensch, P. J. Picone, H. P. Jenssen, and D. R. Gabbe, *Phys. Rev. B* **37,** 9343 (1988).