Synthesis and Structure of Lithium Cuprate $Li_3Cu_2O_4$

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The structure of $Li_3Cu_2O_4$, synthesised under high oxygen pressure, has been determined from powder X-ray data. The compound contains chains of edge-sharing CuO_4 square planes co-ordinated to lithium in both tetrahedral and square-planar sites.

All the alkali metals except lithium form compounds of stoichiometry $MCuO_2$ by direct reaction of the oxides under oxygen at around 400 °C.[1] These compounds contain CuO_4 square planes linked *via* their edges to form infinite chains; the chains are distributed in three dimensions to allow good co-ordination of the oxygen to the alkali metal. All attempts to prepare $LiCuO_2$ have been unsuccessful and in general the products are Li_2CuO_2 and CuO. The former has been much studied by neutron diffraction[2–4] and again consists of edge-sharing CuO_4 chains linked by LiO_4 tetrahedra. The magnetic structure of this compound has also beeen determined;[4] the chains are coupled ferromagnetically giving rise to ferromagnetic layers perpendicular to the cell *c* direction; the layers are coupled antiferromagnetically.

Klemm *et al.*[5] have synthesised a lithium cuprate containing copper 3+ by reaction over several weeks at 250–300 °C between lithium and copper oxides under oxygen. The product of this reaction, $Li_3Cu_2O_4$, formally contains 50% Cu^{2+} and 50% Cu^{3+}; this is supported by magnetic measurements. A powder X-ray diffraction pattern was also given in this publication but not indexed. More recently Berger[6] has described a synthesis of $Li_3Cu_2O_4$ from Li_2CuO_2 and $Li_xCu_{1-x}O$, although the material was contaminated with the reactants; powder X-ray diffraction data were indexed on a monoclinic unit cell but no further structural analysis was undertaken. As part of our program of work to study the synthesis of Cu^{III} under high oxygen pressure we have prepared crystalline $Li_3Cu_2O_4$ of high purity and report herein the synthesis and structure of this compound.

Results and Discussion

A stoichiometric mixture of Li_2O (99.9%) and CuO (99.99%) was ground thoroughly under nitrogen and transferred to a gold crucible. This was heated to 750 °C under 300 atm of oxygen for 4 h using a purpose built apparatus.[7] The dark grey product was of excellent crystallinity and a powder X-ray diffraction pattern collected using a Siemens D5000 diffractometer with primary monochromator (Cu-Kα_1 radiation) showed an identical phase to that described by Klemm *et al.*[5] with a few very weak reflections ($I/I_0 < 0.5\%$) which could be assigned to residual CuO.

Owing to the low temperatures and high pressures required in the synthesis it was likely that growth of single crystals would be very difficult. A structural determination from powder X-ray data was therefore undertaken.

A high quality data set was collected on the diffractometer in the 2θ range 10–70° over a period of 8 h. Careful analysis of peak positions produced over 30 well resolved peaks whose 2θ values were introduced to the VISSER indexing program.[8] A number of possible, closely related, unit cells of high figure of merit were obtained. Of these a monoclinic cell identical to that found by Berger[6] was selected [a = 9.963(4), b = 2.7793(8), c = 7.280(3) Å, β = 118.85(1)°]. With the *C* centring all possible reflections were generated by Lazy–Pulverix[9] and compared with the raw data. Nearly all the generated peaks were observed and no additional peak (except CuO) seen in the powder pattern (Table 1).

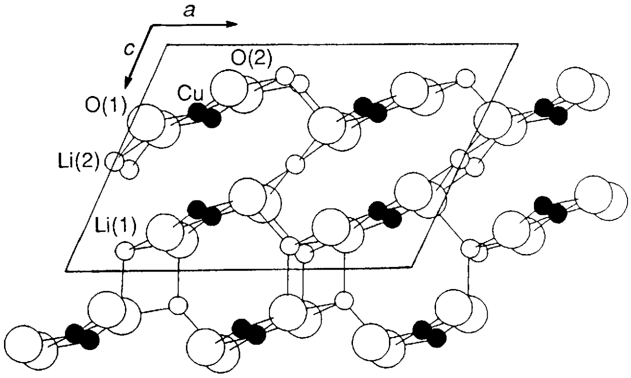

Fig. 1 Ball and stick representation of the structure of $Li_3Cu_2O_4$ viewed down a direction close to the *b* axis showing the edge-linked copper–oxygen chains. Copper small filled circles, lithium small open circles and oxygen large open circles. The unit cell in the *a*–*c* plane is shown

One dimension of this likely unit cell, 2.78 Å, is extremely small but is similar to that observed for Li_2CuO_2 and $NaCuO_2$[1] and corresponds to the repeat along edge-sharing CuO_4 chains. A structural model in which parallel chains of copper–oxygen lie along the *b* direction was proposed; with the *C* centring alternate chains along the *a* direction would be displaced by *b*/2. The space group *C*2/*m* was selected from the three possible (*Cm*, *C*2, *C*2/*m*; 001 reflection present) as this would allow symmetrical Cu–O chains along *b*. By consideration of the peak intensities a copper atom was placed on a 4*i* position at (0.16, 0, 0.27); this together with the cell symmetry would generate chains of copper atoms along the *b* direction separated by similar distances to those found in Li_2CuO_2.

An X-ray intensity analysis was initiated[10] using the integrated intensities from the 10–70° range. As a result of the high sample crystallinity and well separated peaks a full profile refinement was unnecessary; also some variation in the peak shape over the full angular range was observed which would have been difficult to fit. With refinement of the copper sites an R_I factor of *ca.* 0.26 was obtained ($R_I = \Sigma|I_{obs} - I_{calc}|/\Sigma I_{obs}$).

Table 1 Calculated and observed *d* spacings and peak intensities for $Li_3Cu_2O_4$; $R_I = 0.062$

h	*k*	*l*	d_{obs}/Å	d_{calc}/Å	I_{obs}	I_{calc}
0	0	1	6.344	6.340	493	488
−2	0	1	4.831	4.833	3567	3474
2	0	0	4.346	4.346	861	825
−2	0	2	3.489	3.491	29	18
0	0	2	3.179	3.179	2903	2814
2	0	1	2.983	2.983	3025	2809
1	1	0	2.643	2.642	226	222
−1	1	1	2.578	2.578	451	509
−4	0	1	2.453	2.454	245	160
−4	0	2	2.421	2.422	618	620
−2	0	3		2.422		
1	1	1	2.324	2.323	*a*	*a*
−1	1	2	2.1977	2.1977	520	524
4	0	0	2.1764	2.1776	80	86
−3	1	1	2.1266	2.1268	875	814
2	0	2		2.1272		
0	0	3	2.1215	2.1215	69	56
−4	0	3	2.1109	2.1122	50	30
−3	1	2	2.0289	2.0295	2118	2041
3	1	0	2.0069	2.0062	856	794
1	1	2	*b*	1.9017	*b*	2
4	0	1	1.8105	1.8108	134	118
−2	0	4	1.8008	1.8012	32	19
−1	1	3	1.7878	1.7879	847	762
−3	1	3	1.7854	1.7853		
3	1	1	1.7539	1.7536	8	1
−4	0	4	1.7473	1.7485	162	142
−6	0	2	1.6561	1.6575	96	81
2	0	3	1.6251	1.6245	154	219
−6	0	3	1.6152	1.6160	90	95
−5	1	2	*b*	1.6138		
0	0	4	1.5923	1.5921	99	92
−6	0	1		1.5920		
−5	1	1	1.5876	1.5879	1027	916
1	1	3	1.5485	1.5486	124	129
−5	1	3	1.5422	1.5430	346	324
−3	1	4	1.5170	1.5178	299	340
4	0	2	1.4940	1.4936	67	40
−6	0	4	1.4884	1.4889	269	250
3	1	2		1.4890		
5	1	0	1.4764	1.4764	50	39
−1	1	4	1.4620	1.4621	520	491
6	0	0	1.4531	1.4528	50	68
−4	0	5	*b*	*b*	*b*	2
−2	0	5	1.4207	1.4213	25	31
−5	1	4	1.4059	1.4065	31	16
0	2	0	1.3882	1.3882	288	266
0	2	1	*b*	*b*	0	5

[a] Overlap with CuO peak. [b] Not observed.

Table 2 Atomic positions for $Li_3Cu_2O_4$ with estimated standard deviations in parentheses

Atom	*x*	*y*	*z*
Cu(1)	0.1589(5)	0.000	0.2732(4)
O(1)	0.058(2)	0.500	0.340(2)
O(2)	0.242(2)	0.500	0.184(3)
Li(1)	0.143(5)	0.500	0.884(6)
Li(2)	0.000	0.000	0.500

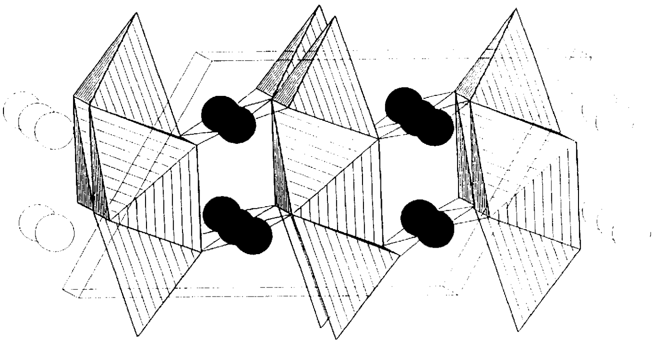

Fig. 2 STRUPLO[11] plot of $Li_3Cu_2O_4$ with a similar orientation to Fig. 1 showing clearly the LiO_4 tetrahedra and elongated LiO_6 octahedra. The copper atoms in the unit cell (outlined) are shown as filled circles

Two oxygens were introduced, again on 4*i* sites, at (*x*, 0.5, *z*), close to the two copper sites and their positions in the *xz* plane refined resulting in a drop of R_I to *ca.* 0.10. The refined positions indicate that the copper–oxygen chains are canted with the respect to the cell edges with almost planar copper atom co-ordinations (Fig. 1). This orientation generates tetrahedral sites near (0.15, 0.5, 0.9) similar to those found in Li_2CuO_2 between three neighbouring copper–oxygen chains and suitable for lithium. However, there is only one such site in the unit cell (giving $Li_2Cu_2O_4$) and three lithiums are required by compound stoichiometry. A third likely site has square planar co-ordination (plus two longer interactions) and is located between two adjacent CuO_4 groups on the special site (0, 0, 0.5). Lithium was introduced into the refinement on to these sites and with refinement R_I fell to 0.062 (Table 1). Later stages of the refinement included all atomic positions and isotropic thermal parameters constrained to be equal for identical atom types. The final atomic positions are summarised in Table 2.

Fig. 1 shows a ball and stick representation of the structure viewed down a direction close to the *b* axis; Fig. 2 shows a STRUPLO[11] plot viewed down the same direction which outlines the lithium oxygen tetrahedra and elongated octahedra. The copper co-ordination is close to square planar with refined Cu–O bond distances of 1.89(3) (× 2) and 1.19(3) Å (× 2); these values are intermediate between those expected for square-planar Cu^{2+} (typically 4 × 1.96 Å) and Cu^{3+} (typically 4 × 1.84 Å). The lithium–oxygen distances are also reasonable lying in the range 1.90–2.05 Å for the four-nearest interactions and comparable to those found in the other lithium cuprates.[2,4]

Acknowledgements

We thank the SERC for grants in association with this work.

References

1 M. T. Weller and D. R. Lines, *J. Solid State Chem.*, 1989, **82**, 21.
2 W. Losert and R. Hoppe, *Z. Anorg. Allg. Chem.*, 1984, **515**, 95.
3 R. Hoppe and H. Rieck, *Z. Anorg. Allg. Chem.*, 1970, **379**, 157.
4 F. Sapina, J. Rodríguez-Carrajal, M. J. Sanchis, R. Ibáñez, A Beltrán and D. Beltrán, *Solid State Commun.*, 1990, **74**, 779.
5 W. Klemm, G. Wehrmeyer and H. Bade, *Z. Elektrochem.*, 1959, **63**, 56.
6 R. Berger, *J. Less-Common Met.*, 1991, **169**, 33.
7 D. B. Currie and B. Cleaver, *High Temp. High Pressures*, in the press.
8 J. W. Visser, *J. Appl. Crystallogr.*, 1969, **2**, 89.
9 K. Yvon, W. Jeitschko and E. Parthe, *J. Appl. Crystallogr.*, 1977, **10**, 73.
10 P. Wiseman, D.Phil Thesis, Oxford University, 1974.
11 R. X. Fischer, *J. Appl. Crystallogr.*, 1985, **18**, 258.

Received 23*rd May* 1991; *Paper* 1/02440J