

Powder diffraction study of LiCu_2O_2 crystals

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LiCu_2O_2 crystals grown by spontaneous crystallization from the fluxed melt were studied by powder X-ray diffraction. The phase analysis shows that the applied growth conditions are suitable for preparation of a single-phase compound. The as-grown crystals contain only traces of foreign phases (Li_2CuO_2 , CuO , Cu_2O) typical for preparation of the LiCu_2O_2 compound. Attempts to anneal or quench the as-grown crystals led to two-phase samples containing LiCu_2O_2 and LiCu_3O_3 . X-ray powder diffraction pattern of a LiCu_2O_2 crystal is reported and compared with literature data. The crystal structure is orthorhombic, space group $Pnma$, in agreement with literature data. Lattice parameters of the studied sample are $a = 5.7286(2) \text{ \AA}$, $b = 2.8588(1) \text{ \AA}$, and $c = 12.4143(3) \text{ \AA}$. Time evolution of a diffraction pattern illustrates a slow increase of the secondary-phases contribution assumed to be due to interaction of the powdered crystal with humid air. A brief summary of compounds known in the Li-Cu-O system is included. © 2001 International Centre for Diffraction Data. [S0885-7156(00)00804-6]

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I. INTRODUCTION

Lithium copper oxides are known as materials applicable for batteries (Iijima *et al.* 1980, Ewing 1983, Rhemes 1986, Kuksenko *et al.* 1997, Jacob *et al.* 2000) and as battery discharge products (Ritchie and Mullins, 1994). The atomic environment of Cu atoms in compounds belonging to the Li-Cu-O ternary system is similar to that of high- T_c superconductors. Therefore, the properties of some of them have been discussed in relation to HTC materials (Wizansky *et al.* 1989, Kuznetsov 1995, Fritschij *et al.* 1998, Mizuno *et al.* 1998). The enthalpies of formation of several Li-Cu-O compounds have been used to construct a theoretical Li-Cu-O phase diagram at 298 K (Patat *et al.* 1991). The crystallographic data for compounds identified in the Li-Cu-O system are collected in Table I based on literature data and PDF records within the ICDD database together with some references to physical properties. In general, the existence of compounds quoted in Table I is well established. Li_6CuO_4 is an exception. Its structure has not been reported by either Abdullaev *et al.* (1982) or by Fleischer *et al.* (1993); it is probably unknown. Attempts to prepare this compound by other authors (Hibble *et al.* 1990) were unsuccessful so there is even some doubt concerning its existence. Suba *et al.* (1994) have shown that for the $\text{Cu}_{1-x}\text{Li}_x\text{O}_{1-\delta}$ solid solution there is a broad solubility range up to $x = 0.25$. Besides that, a possibility of formation of an unknown phase has been mentioned by Lin *et al.* (1996).

LiCu_2O_2 has been known since the work by Hibble *et al.*

(1990). An unindexed powder pattern for “ $\text{Li}_2\text{Cu}_2\text{O}_3$ ” phase containing probably many lines (shifted toward higher d -s) from this phase has been published earlier (Abdullaev *et al.* 1982). Its unit cell is orthorhombic, with $a = 5.730(1) \text{ \AA}$, $b = 2.8606(4) \text{ \AA}$, $c = 12.417(2) \text{ \AA}$, space group $Pnma$ (62) (Berger 1991, Berger *et al.* 1991) being confirmed by results of neutron diffraction by Berger *et al.* (1992). The characteristic feature of the cell is that $a \approx 2b$; the value of the relative difference, $|a - 2b|/a$, being as small as about 0.2%.

Physical properties of the LiCu_2O_2 phase have been determined only recently. Its electron and magnetic structure has been studied by Zatsepin *et al.* (1998) and Vorotinov *et al.* (1998). Its magnetic properties (studied by nuclear magnetic resonance, magnetic susceptibility measurements, and microwave magnetic resonance) have been discussed in connection with its specific atomic arrangement (the so-called ladder structure) by Fritschij *et al.* (1998) and Vorotynov *et al.* (1998).

Usually, the LiCu_2O_2 crystals have been reported to contain a large amount of foreign phases. It has been argued by Berger *et al.* (1991) that one of the possible reasons for difficulties in obtaining pure LiCu_2O_2 is its decomposition at room temperature. Metastability of this phase has been concluded by Lin *et al.* (1996).

Hibble *et al.* (1990) have grown the LiCu_2O_2 single crystals using two methods: (i) by melting the mixture of Li_2CO_3 with CuO at 800–1150 °C and cooling rapidly to room temperature (however, for the sample for which the powder pattern is published the preparation temperature is given as 750 °C), (ii) by cooling the melt with a speed of

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TABLE I. Compounds in the Li-Cu-O ternary system and their available crystallographic data. *m* refers to the nominal M:(O+M) ratio. PDF numbers refer to PDF2 database distributed by International Centre for Diffraction Data® (USA). Calculated X-ray densities are given (those in parentheses concern the experimental ones).

Formula	<i>m</i>	Space group, (structure type)	<i>a</i> ₀ (Å)	<i>b</i> ₀ (Å)	<i>c</i> ₀ (Å)	β (°)	Density (g/cm ³)	References to unit cell and density	Other references to structural and physical properties
LiCuO ₂	0.500	<i>Cmmm</i>	5.707 8(6)	9.639(2)	2.717 2(3)		4.554	Imai <i>et al.</i> (1992), PDF48-0798	Berger (1995), Aydinol <i>et al.</i> (1997)
		<i>C2/m</i> (NaCuO ₂)	5.733(1)	2.717 6(3)	5.622(1)	120.68(2)		Berger and Tergenius (1994)	Arai <i>et al.</i> (1998), Fritschij <i>et al.</i> (1998), Okada and Kotani (1998), Owens (1999)
Li ₃ Cu ₂ O ₄	0.556	<i>C2/m</i>	9.958(2)	2.777 0(4)	7.281(1)	118.77	4.0	Berger (1991) (PDF 42-477)	Klemm <i>et al.</i> (1959), Wizansky <i>et al.</i> (1989), Mehta <i>et al.</i> (1992), Berger <i>et al.</i> (1993), Currie and Weller (1993), Slack and Mroczkowski (1993)
			9.946(5)	2.778(2)	7.260(5)	119.10(2)		Berger <i>et al.</i> (1993)	
Li ₃ CuO ₃	0.571	<i>P4₂/mmm</i> (Li ₃ AuO ₃)	8.71		3.58		3.237 (3.170)	Migeon <i>et al.</i> (1975), PDF70-1740	
LiCu ₃ O ₃	0.571	<i>P4/mmm</i>	2.810(1)		8.889(4)		5.809 ^a	Hibble <i>et al.</i> (1990)	Lin <i>et al.</i> (1996)
			2.813 9(2)		8.877 7(6)			Berger (1991) (PDF 42-476)	
			2.814 2(1)		8.895 6(5)			Berger <i>et al.</i> (1992)	
Li ₂ CuO ₂	0.600	<i>Immm</i>	3.654	2.859	9.374		3.73 (3.67)	Losert and Hoppe (1984) (PDF 38-917)	Berger <i>et al.</i> (1992) Okuda <i>et al.</i> (1992), Arai <i>et al.</i> (1998), Boehm <i>et al.</i> (1998), Mizuno <i>et al.</i> (1998)
							3.711 ^b		Wehr and Pickett (1998), Mizuno <i>et al.</i> (1999), Kucharski and Gontarz (2000), Staub <i>et al.</i> (2000)
							(3.630) ^b		
			3.669	2.863	9.396		3.688 (3.620)	Hoppe and Rieck (1970), PDF73-2423	
			3.659	2.862	9.386		3.697	PDF 20-623	
			3.661 53(5)	2.862 77(2)	9.392 58(9)			Sapina <i>et al.</i> (1990)	
			3.661 4(8)	2.861 4(6)	9.394(2)			Hoffman <i>et al.</i> (1989) (PDF 43-266)	
			3.663	2.862	9.399			Kuznetsov (1995), Kuznetsov <i>et al.</i> (1995)	
LiCu ₂ O ₂ ^c	0.600	<i>Pnma</i>	5.730(1)	2.860 6(4)	12.417(2)		(3.68)	Abdullayev <i>et al.</i> (1982)	Hibble <i>et al.</i> (1990)(PDF 46-1214), Ritchie and Mullins 1994), Lin <i>et al.</i> (1996), Fritschij <i>et al.</i> (1998), Zatsopin <i>et al.</i> (1998)
			5.726 0(4)	2.858 7(2)	12.413 7(7)			Berger (1991), Berger <i>et al.</i> (1991) (PDF 42-475)	
			5.728 6(2)	2.858 8(1)	12.414 3(3)		5.424	Berger <i>et al.</i> (1992) this work	
Li ₆ CuO ₄	0.636						2.53	Abdullayev <i>et al.</i> (1982)	Hibble <i>et al.</i> (1990), Fleischer <i>et al.</i> (1993) (PDF 36-660)
LiCuO	0.666	<i>I-4m2</i> (KAgO)	8.515		3.81		4.159	Migeon <i>et al.</i> (1976), PDF70-0142	Goshall (1986), Shirvinskaya and Petrova (1987), Hibble <i>et al.</i> (1990), Suba <i>et al.</i> (1994), Kucharski and Gontarz (2000)
			8.5200		3.8160		4.148 (4.090)	PDF 33-795	
							4.150	Klassen and Hoppe (1982) (PDF 36-1074)	
			8.519		3.815			Kuznetsov (1998)	
			8.511		3.824			Losert and Hoppe (1985)	
			8.514		3.809				
Li-Cu-O	?								Lin <i>et al.</i> (1996)

^a Value corrected in the present work.

^b Values given in PDF2.

^c A different but related unit cell has been reported in by Hibble *et al.* (1990).

TABLE II. Diffraction-data-collection conditions for LiCu_2O_2 (sample 1).

Radiation source	Cu
Wavelength (\AA)	1.540 60
Generator voltage (kV)	40
Generator current (mA)	25
Wavelength discrimination	Ni filter discrimination
Detector	Proportional
Instrument description	29.1 cm radius horizontal diffractometer
Divergence slit ($^\circ$)	1
Receiving slit (mm)	0.7
Soller slits	At incident and diffracted beam
Sample rotation	Spinner
Sample holder	Amorphous quartz
Instrumental profile breadth ($^\circ(2\theta)$) in the range 30° – 60°	0.11
Temperature (K)	$296(\pm 3)$
Specimen form	Powder dusted onto a thin vaseline layer
Particle size μm	Less than 10
Color	Single crystal—black; powdered crystal—dark greyish brown
Measured range $2\theta(^\circ(2\theta))$	4 to 160
Standard	None
2θ error correction	Correction by extrapolation according to the extrapolation function $\cos(\theta)\cot(\theta)$
Intensity measurement technique	Amplitude (peak height) and integrated intensity from fitting of Pearson-VII profiles
Peak position meas. technique	Position from fitting of Pearson-VII profiles
Peak detection level (peak height %)	At intensity 1
Resolution for this material ($^\circ(2\theta)$ at $45^\circ(2\theta)$)	0.13
Scan increment ($^\circ(2\theta)$)	0.03
Counting time (s)	35

10°C/h from 1150 to 900°C and then cooling rapidly.

Berger *et al.* (1991) have prepared platelike single crystals by heating above 827°C a mixture of Li_2CO_3 with CuO in air. Both powder and single-crystal X-ray diffraction and electron diffraction have shown that the crystals contain other phases. This finding has been attributed to decomposition of LiCu_2O_2 at room temperature. A decomposition product present at the surface has not been identified.

In the work by Berger *et al.* (1992), a mixture of Li_2CO_3 with CuO was heated at 900°C for 1 h and then several times homogenized and reheated at 970 – 980°C . This procedure yielded a sample containing LiCu_2O_2 , Li_2CuO_2 , and CuO . Li_2CuO_2 was removed by treating the product with ammonia. The final (polycrystalline) product showed only the presence of LiCu_2O_2 and CuO phases. In a more recent work, the reported secondary phases include CuO , Li_2CuO_2 , and Li_2CO_3 (Berger and Tergenius 1994).

The above-mentioned results show that obtaining a pure single or polycrystalline LiCu_2O_2 phase is not easy. A particular problem is that one of the usual reaction components, Li_2CO_3 , is a weak scatterer. Therefore, only a relatively large amount of this phase may be detected by X-rays. The aim of the present work was to grow the LiCu_2O_2 phase with minimal second phases and to collect a complete powder X-ray data set. Preliminary results of an early stage of this work have been briefly presented by Paszkowicz *et al.* (1995).

II. EXPERIMENTAL

LiCu_2O_2 crystal was grown by spontaneous crystallization from the fluxed melt in L.V. Kirenskii Institute of Physics from the melted mixture of Li_2CO_3 and CuO loaded into alumina crucibles. A similar method has been used for growing some Li–Cu–O oxide crystals (e.g., by Slack and Mroczkowski, 1993, and for other lithium-based crystals, e.g., LiCoO_2 , see Akimoto *et al.*, 1998). Samples 1 and 2 were grown using $T_{\text{max}}=1150^\circ\text{C}$ with a cooling rate of 5°C/min down to 800°C . Samples 3 and 4 were prepared in the same way and afterwards submitted to additional treatment. Sample 3 was annealed at 820°C for 6 h and cooled with a cooling rate 20°C/h , while sample 4 was quenched from 920°C .

Powder diffraction patterns were measured with a Bragg–Brentano diffractometer using step-scanning mode and $\text{Cu } K\alpha$ radiation. To reduce the preferred-orientation effect, the finely ground powder was dusted on a specimen holder covered with a thin layer of vaseline. The conditions for diffraction data collection are given in Table II. Information about the orientation of the largest faces of the crystals was obtained from Lauegrams and from diffraction patterns of crystals mounted in the sample holder of the Bragg–Brentano diffractometer. Least-squares calculations were performed using SCANIX 2.60PC program, an updated version of an indexing/refinement software (Paszkowicz 1989).

Chemical analysis was performed using an emission spectrometer with plasma excitation, ICP2070, supplied by

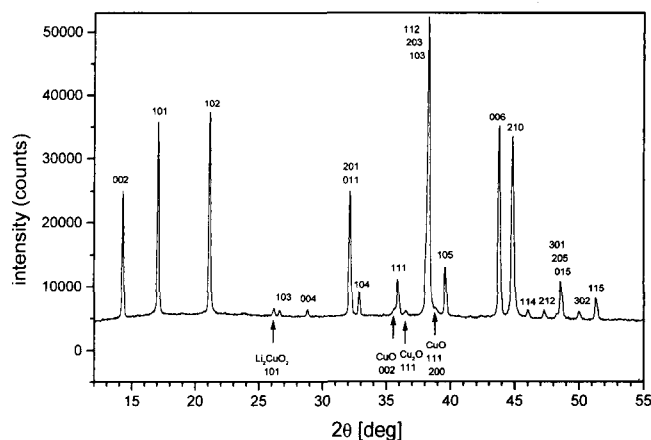


Figure 1. Raw x-ray powder-diffraction pattern of LiCu_2O_2 (sample 1). Miller indices of all reflections are indicated. The contribution of foreign phases Li_2CuO_2 , CuO , and Cu_2O is indicated by arrows.

BAIRD. The crystal of mass 2.01(1) mg was dissolved in HCl. Then, using the de-ionized water, it was stored in a 25 ml container. Five measurement cycles were performed. Every cycle included the following operations:

- (1) a measurement of the Li and Cu standards (0.5 and 1.0 $\mu\text{g}/\text{ml}$, respectively),
- (2) a measurement of the sample,
- (3) a remeasurement of both standards.

New standards were prepared for each cycle. The standards were prepared from the certified base standards, 1000 $\mu\text{g}/\text{ml}$, supplied by TEKNOLAB. Certified pipettes supplied by EPPENDORF were used for dissolving.

III. RESULTS AND DISCUSSION

The crystals grew in the form of approximately rectangular black plates with the following maximum dimensions of several square mm on the large face and thickness of the order 0.5–1 mm. The color of the powdered crystals (all samples) was dark greyish-brown. Chemical ICP analysis of a LiCu_2O_2 crystal obtained in the same growth process as sample 2 gives $\text{Cu}/(\text{Cu}+\text{Li})$ atomic ratio equal $75(\pm 5)\%$. This result shows that the Li:Cu ratio is close to the stoichiometric one, with possibly some Cu excess at Li sites.

The powder patterns of samples 1 and 2 (cf. Figures 1 and 2) represent the orthorhombic LiCu_2O_2 phase. They differ only slightly in their peak intensities and by the amount of foreign phases. The patterns contain more than 70 peaks of LiCu_2O_2 and several weak peaks (peak intensity $< 2\%$) that came from trace foreign phases CuO (monoclinic), Cu_2O (cubic), and Li_2CuO_2 (orthorhombic), which are typical impurities for the preparation of the investigated crystals. There is no trace (within the limits of detectability) of Li_2CO_3 in these samples. Samples 3 and 4 are phase mixtures. The dominant phase in sample 3 is LiCu_3O_3 , and a second main phase is LiCu_2O_2 . Weak lines of CuO impurity phase also were detected. In sample 4, the LiCu_2O_2 phases dominates, but all intense peaks (002, 003, 100, 102, 004, 110, 006, 114) characteristic for LiCu_3O_3 are present. An identified impurity phase in this sample is CuO . A weak spurious peak at 2θ

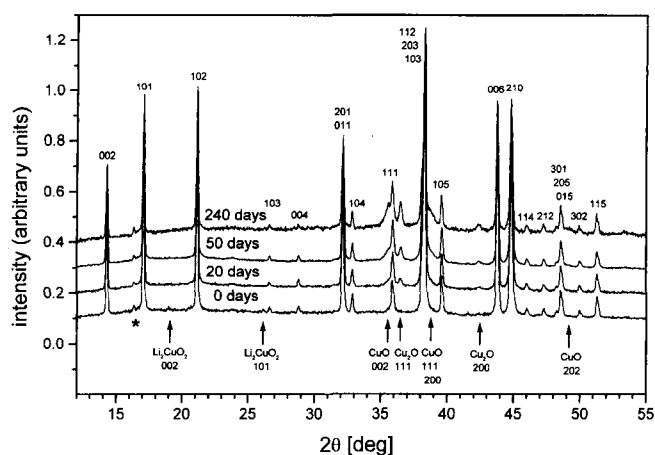


Figure 2. Evolution of the diffraction pattern of a powdered LiCu_2O_2 specimen (sample 2) stored in air for 0, 20, 50 and 240 days. Miller indices of all reflections are indicated. The contribution of foreign phases CuO and Cu_2O (peaks indicated by arrows) rises with time. Starred is a weak reflection due to sample holder.

$= 31.28^\circ$ found for sample 4 matches the strongest peak of LiCu_2O_2 but there is some uncertainty in this identification due to the absence of other peaks. The results for samples 3 and 4 show that the preparation conditions applied for them are not suitable for growth of LiCu_2O_2 crystals. Further optimization of these conditions may be expected to be helpful in the growth of single phase LiCu_3O_3 crystals.

LiCu_2O_2 phase in samples 1 and 2 as well as both Li–Cu–O phases in samples 3 and 4 have the 001 crystallographic plane parallel to the large face of the crystal plates. CuO tends to be 111 oriented, but there is a difference in behavior observed between both Li–Cu–O phases and CuO : For Li–Cu–O phases only 00l peaks are found in the patterns of single crystalline plates while for CuO , apart from the enhanced 111 peak, other weak peaks are present as well.

Diffraction experiments taken on the powdered specimen exposed to air for 20, 50, and 240 days have shown a slow evolution of the powder pattern: The intensity of peaks ascribed to foreign phases varies with time (see Figure 2). The single crystals were stored in air for approximately 3 months before performing this study. It would be interesting to determine whether the foreign phases detected are native or formed (probably at the surface) during storage. Analysis of Figure 2 is helpful in this matter: Li_2CuO_2 impurity phase disappears after a short time (20 days) of storage of the powdered crystal. Thus, it is believed to be a native (and more susceptible for decomposition) impurity phase. Peak intensities of both CuO and Cu_2O oxides increase with time, so these foreign phases are concluded to be products of hydrolysis occurring in contact of the powder with humid air. This reaction is slow for the bulk crystals but increases in powder due to the large contact area of small crystallites with air. The observed reaction rate is probably somewhat reduced due to the use of vaseline during sample mounting.

In Table III, the powder data of sample 1 are given and compared with previously reported data (Berger *et al.* 1991). The existing discrepancies between the observed peak intensities and those of the cited paper are assumed to be due to differences in sample preparation and a hypothetical possibility of deviations from stoichiometry. The lattice constants

TABLE III. Diffraction data for LiCu_2O_2 (sample 1). Intensities for poorly resolved peaks are given in parentheses. I_{max} refers to peak height, I_{int} to integrated intensity, I_0 to peak height reported by Berger *et al.* (1991).

No.	<i>hkl</i>	$2\theta_{\text{exp}}$	$2\theta_{\text{th}}$	d_{exp}	d_{th}	I_{max}	I_{int}	I_0	No.	<i>hkl</i>	$2\theta_{\text{exp}}$	$2\theta_{\text{th}}$	d_{exp}	d_{th}	I_{max}	I_{int}	I_0
		[°]	[°]	[Å]	[Å]						[°]	[°]	[Å]	[Å]			
1	002	14.232	14.257	6.218	6.207	51	49	15	40	413	78.110	78.059	1.222 6	1.223 2	12	20	43
2	101	17.016	17.033	5.207	5.202	78	76	37		223				78.158			
3	102	21.075	21.087	4.212	4.210	86	80	38	41	125	79.010	79.018	1.210 9	1.210 8	2	2	4
4	103	26.548	26.551	3.354 8	3.354 5	3	3	...	42	308	79.505	79.529	1.204 6	1.204 3	<1	1	...
5	004	28.736	28.742	3.104 2	3.103 6	3	4	4	43	406	81.770	81.706	1.176 8	1.177 6	10	19	13
6	201	32.073	32.043	2.788 4	2.791 0	57	64	34		026				1.176 0			13
	011		32.103		2.785 9				44	415	85.210	85.199	1.137 9	1.138 0	2	4	9
7	104	32.784	32.793	2.729 5	2.728 8	12	12	4	45	322	86.364	86.393	1.125 6	1.125 3	<1	2	3
8	111	35.813	35.813	2.505 3	2.505 3	18	19	15	46	318	87.904	87.907	1.109 8	1.109 8	2	2	4
9	112	38.020	38.017	2.364 8	2.365 0	24	24	37	47	1011	88.160	88.160	1.107 3	1.107 3	1	1	
10	203	38.175	38.182	2.355 6	2.355 2	(88)	(77)	100	48	028	94.206	94.223	1.051 5	1.051 3	2	3	
11	013	38.243	38.234	2.351 5	2.352 1	(90)	(79)		49	0111	94.390	94.412	1.049 9	1.049 7	2	2	
12	105	39.525	39.526	2.278 2	2.278 1	26	24	13	50	505	95.534	95.540	1.040 4	1.040 3	1	2	
13	006	43.710	43.714	2.069 3	2.069 1	100	99	43	51	0012	96.248	96.248	1.034 5	1.034 5	6	8	
14	210	44.756	44.753	2.023 3	2.023 4	92	100	89	52	1111	96.495	96.494	1.032 5	1.032 5	1	<1	
15	114	45.940	45.939	1.973 9	1.973 9	5	5	5	53	420	99.179	99.173	1.011 7	1.011 7	3	5	
16	212	47.214	47.207	1.923 5	1.923 8	5	5	10	54	419	10.384	110.335	0.938 17	0.938 45	5	10	
17	301	48.183	48.176	1.887 1	1.887 3	2	2	...		4010		110.402		0.938 06			
18	205	48.508	48.482	1.875 2	1.876 1	20	23	20		229		110.438		0.937 86			
	015		48.525		1.874 6				55	603	111.776	111.785	0.930 38	0.930 33	2	3	
19	302	49.922	49.928	1.825 3	1.825 1	4	4	9	56	033	112.082	112.097	0.928 70	0.928 62	2	4	
20	115	51.238	51.235	1.781 5	1.781 6	13	15	19	57	2112	113.492	113.496	0.921 14	0.921 12	4	7	
21	304	56.558	56.541	1.625 9	1.626 4	1	2	4		328		113.522		0.920 98			
22	311	58.570	58.558	1.574 8	1.575 1	4	5	4	58	3111	113.699	113.727	0.920 05	0.919 90	1	2	
23	008	59.518	59.523	1.551 9	1.551 8	8	8	5	59	426	115.890	115.889	0.908 87	0.908 87	3	8	
24	312	60.100	60.097	1.538 3	1.538 3	5	5	6	60	0113	116.541	116.522	0.905 66	0.905 75	2	4	
25	305	61.195	61.181	1.513 3	1.513 7	2	3	...		610		116.553		0.905 60			
26	207	61.454	61.442	1.507 6	1.507 8	4	5	6	61	230	116.837	116.841	0.904 22	0.904 20	2	5	
	017		61.479		1.507 0				62	0014	120.601	120.613	0.886 79	0.886 74	2	4	
27	108	61.892	61.899	1.498 0	1.497 8	5	4	...		4011		120.684		0.886 43			
28	216	64.349	64.346	1.446 6	1.446 6	44	49	51	63	1014	123.068	123.052	0.876 24	0.876 30	1	2	
29	400	65.084	65.076	1.432 0	1.432 2	11	12	35	64	1211	123.305	123.279	0.875 26	0.875 37	<1	4	
30	020	65.223	65.218	1.429 3	1.429 4	11	12	15	65	4111	130.939	130.959	0.846 73	0.846 66	1	9	
31	314	66.084	66.038	1.412 7	1.413 6	1	2	2	66	4012	133.408	133.426	0.838 67	0.838 62	2	3	
32	402	67.079	67.007	1.394 2	1.395 5	1	2	4	67	0212	133.622	133.603	0.838 00	0.838 06	3	7	
	022		67.147		1.392 9				68	616	136.410	136.405	0.829 60	0.829 62	2	6	
33	121	67.964	67.957	1.378 2	1.378 3	1	2	5	69	236	136.797	136.779	0.828 49	0.828 54	3	7	
34	122	69.376	69.378	1.353 5	1.353 5	2	2	5	70	2114	143.030	143.043	0.812 20	0.812 17	2	7	
	403		69.383		1.353 4			...	71	5011	146.694	146.695	0.804 02	0.804 02	2	7	
35	315	70.310	70.316	1.337 8	1.337 7	4	4	5		138		146.703		0.804 00			
36	118	70.988	70.985	1.326 7	1.326 7	5	6	5	72	2015	151.313	151.305	0.795 08	0.795 10	3	9	
37	411	74.475	74.425	1.273 0	1.273 7	2	4	7		0115		151.372		0.794 98			
	221		74.525		1.272 2				73	711	157.709	157.642	0.785 11	0.785 20	1	5	
38	209	76.620	76.606	1.242 6	1.242 8	17	16	20		609		157.749		0.785 05			
	019		76.640		1.242 3				74	039	158.546	158.526	0.784 00	0.784 03	1	3	
39	218	77.450	77.447	1.231 3	1.231 4	5	6	10									

of the orthorhombic cell (cf. Table IV) as determined for sample 1 are $a = 5.7286(2) \text{ \AA}$, $b = 2.8588(1) \text{ \AA}$, and $c = 12.4143(3) \text{ \AA}$, in agreement with the data of Berger *et al.* (1991) (cf. Table I). The studied crystals do not have the tetragonal unit cell reported by Hibble *et al.* (1990); we note that the third strongest line reported by Hibble *et al.* (1990) should be at $d = 5.20 \text{ \AA}$ but not at 5.90 \AA (this printing error has been unfortunately repeated in PDF46-1214).

The calculated density of LiCu_2O_2 , 5.424 g/cm^3 , is consistent with densities of other compounds of the Li–Cu–O system (cf. Table I). Namely, LiCu_2O_2 is less dense than LiCu_3O_3 (of higher copper content) and more dense than all six remaining Li–Cu–O compounds (the density from 2.53

to 4.554 g/cm^3) being dominated by lighter elements, lithium and oxygen.

IV. CONCLUSIONS

Small LiCu_2O_2 single crystals were grown from the fluxed melt. The phase analysis for samples 1–4 shows that the growth conditions for samples 1 and 2 are suitable for growing small single crystals of LiCu_2O_2 with a negligible creation of foreign phases. Powder data for LiCu_2O_2 were obtained over a broad angular range. The lattice parameters of the orthorhombic cell (space group $Pnma$) are $a = 5.7286(2) \text{ \AA}$, $b = 2.8588(1) \text{ \AA}$, and $c = 12.4143(3) \text{ \AA}$. Its density is 5.424 g/cm^3 . Storage in air causes a slow decom-

TABLE IV. Unit cell data for LiCu₂O₂ (sample 1).

Crystal system	Orthorhombic
Space group	<i>Pnma</i>
<i>Z</i>	4
<i>a</i> (Å)	5.728 6(2)
<i>b</i> (Å)	2.858 8(1)
<i>c</i> (Å)	12.414 3(3)
<i>V</i> (Å ³)	203.31(2)
<i>b/a</i>	0.499 04(3)
<i>c/a</i>	2.167 1(1)
Calculated density (g/cm ³)	5.424

position of the powdered crystal manifesting itself by increasing contribution of CuO and Cu₂O phases.

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- Abdullayev, G.K., Rza-Zade, P.F., and Mamedov, K.S. (1982). "Physicochemical study of ternary system Li₂O-CuO-B₂O₃," *Russ. J. Inorg. Chem.* **27**, 1037–1040 (transl. from *Zh. Neorg. Khim.* **27**, 1837–1841).
- Akimoto, J., Gotoh, Y., and Oosawa, Y. (1998). "Synthesis and structure refinement of LiCoO₂ single crystals," *J. Solid State Chem.* **141**, 298–302.
- Arai, H., Okada, S., Sakurai, Y., and Yamaki, J. (1998). "Electrochemical and structural study of Li₂CuO₂, LiCuO₂ and NaCuO₂," *Solid State Ionics* **106**, 45–53.
- Aydinol, M.K., Kohan, A.F., Ceder, G., Cho, K., and Joannopoulos, J. (1997). "Ab initio study of lithium intercalation in metal oxides and metal dichalcogenides," *Phys. Rev. B* **56**, 1354–1365.
- Berger, R. (1991). "A note on the Li–Cu–O system," *J. Less-Common Met.* **169**, 33–43.
- Berger, R., Meetsma, A., van Smalen, S., and Sundberg, M. (1991). "The structure of LiCu₂O₂ with mixed-valence copper from twin-crystal data," *J. Less-Common Met.* **175**, 119–129.
- Berger, R., Onnerud, P., and Tellgren, R. (1992). "Structure refinements of LiCu₂O₂ and LiCu₃O₃: from neutron powder diffraction data," *J. Alloys Compd.* **184**, 315–322.
- Berger, R., Onnerud, P., Laligant, Y., and Le Bail, A. (1993). "The structure of Li₃Cu₂O₄, a compound with formal mixed valence," *J. Alloys Compd.* **190**, 295–299.
- Berger, R., and Tergenius, L.-E. (1994). "Room temperature synthesis and structural characterization of monoclinic LiCuO₂ by X-ray and neutron diffraction," *J. Alloys Compd.* **203**, 203–207.
- Berger, R.A. (1995). "On the symmetry of LiCuO₂," *J. Solid State Chem.* **114**, 590–591.
- Boehm, M., Coad, S., Roessli, B., Zheludev, A., Zolliker, M., Boni, P., Paul, D.M., Eisaki, H., Motoyama, N., and Uchida, S. (1998). "Competing exchange interactions in Li₂CuO₂," *Europhys. Lett.* **43**, 77–82.
- Currie, D.B., and Weller, M.T. (1993). "Structure of the mixed-valence lithium cuprate Li₃Cu₂O₄ by powder neutron diffraction," *J. Mater. Chem.* **3**, 229–232.
- Ewing, M. (1983). "Lithium copper oxide for memories and other low-drain devices," *New Electronics* **16**, 51–53.
- Fleischer, N.A., Lyubomirsky, I., Scolnik, Y., and Manassen, J. (1993). "Electrochemical reduction of the high *T_c* superconductor YBa₂Cu₃O_y by lithium via new compound formation," *Solid State Ionics* **59**, 59–70.
- Fritschij, F.C., Brom, H.B., and Berger, R. (1998). "NMR and susceptibility characterization of two oxocuprates with antiferromagnetic Cu-chains: LiCuO₂ and LiCu₂O₃," *Solid State Commun.* **107**, 719–723.
- Goshall, N.A. (1986). "Lithium transport in ternary lithium-copper-oxygen cathode materials," *Solid State Ionics* **18–19**, 788–793.
- Hibble, S.J., Koehler, J., Simon, A., and Paider, S. (1990). "LiCu₂O₂ and LiCu₃O₃: New mixed valent copper oxides," *J. Solid State Chem.* **88**, 534–542.
- Hoffman, R., Hoppe, R., and Schäfer, W. (1989). "Neutron diffraction on Li₂CuO₂," *Z. Anorg. Allg. Chem.* **578**, 18–26.
- Hoppe, R., and Rieck, H. (1970). "Die Kristallstruktur von Li₂CuO₂," *Z. Anorg. Allg. Chem.* **379**, 157–164.
- Iijima, T., Toyoguchi, Y., Nishimura, J., and Ogawa, H. (1980). "Button-type lithium battery using copper oxide as a cathode," *J. Power Sources* **5**, 99–109.
- Imai, K., Koike, M., Takei, H., Sawa, H., Shiomi, D., Nozawa, K., and Kinoshita, M. (1992). "Preparation, crystal structure and magnetic property of a new compound LiCuO₂," *J. Phys. Soc. Jpn.* **61**, 1819–1820.
- Jacob, M.M.E., Hassan, M.S., Daud, J., and Arof, A.K. (2000). "A new cathode material LiCu₂O₂ for secondary lithium batteries," *J. New Mater. Electrochem. Syst.* **3**, 3–7.
- Klassen, H., and Hoppe, R. (1982). "Die K₄{Ag₄O₄}—Strukturfamilie," *Z. Anorg. Allg. Chem.* **485**, 101–114.
- Klemm, W., Wehrmeyer, G., and Bade, H. (1959). "Weitere Beiträge zur Kenntnis der Alkalimetallcuprate(III)," *Z. Elektrochem.* **63**, 56.
- Kucharski, R., and Gontarz, Z. (2000). "Reduction and oxidation of simple oxocuprates," *J. Thermal Anal. Calorim.* **60**, 219–227.
- Kuksenko, S.P., Lugovoi, V.P., and Prokopenko, V.T. (1997). "On the possibility of direct replacement of mercury-zinc cells by lithium cells with copper-oxide cathode," *Russ. J. Appl. Chem.* **70**, 915–918.
- Kuznetsov, M.V. (1995). "External action on immobile and mobile elements of 1-23 high-temperature superconductors," *Int. J. Self-Propag. High-Temp. Synthesis* **4**, 59–67.
- Kuznetsov, M.V., Morozov, Yu.G., and Neresyan, M.D. (1995). "The self-propagating high-temperature synthesis of alkali cuprates," *Inorg. Mater.* **31**, 221–223 (transl. from *Neorg. Mater.* **31**, 237–239).
- Kuznetsov, M.V. (1998). "Self-propagating high-temperature synthesis of alkali cuprites," *Inorg. Mater.* **34**, 44–45 (transl. from *Neorg. Mater.* **34**, 55–56).
- Lin, J.H., Li, K., Ruan, S.K., Su, M.Z., and Schweda, E. (1996). "Thermodynamic stability of LiCu₂O₂ and LiCu₃O₃," *Chin. Chem. Lett.* **7**, 195–198.
- Losert, W., and Hoppe, R. (1984). "On Li₂CuO₂," *Z. Anorg. Allg. Chem.* **515**, 95–100.
- Losert, W., and Hoppe, R. (1985). "Zur Kenntnis der K₄{Ag₄O₄} Verwandtschaft," *Z. Anorg. Allg. Chem.* **524**, 7.
- Mehta, A., DiCarlo, J., and Navrotsky, A. (1992). "Nature of hole states in cuprate superconductors," *J. Solid State Chem.* **101**, 173–185.
- Migeon, H.-N., Courtois, A., Zanne, M., Gleitzer, C., and Aubry, J. (1975). "Preparation and properties of a lithium-copper (III) oxide: Li₃CuO₃," *Rev. Chim. Miner.* **12**, 203–209.
- Migeon, H.-N., Zanne, M., and Gleitzer, C. (1976). "Preparation and study of LiCuO," *J. Solid State Chem.* **16**, 325–330.
- Mizuno, Y., Tohyama, T., Maekawa, S., Osafune, T., Motoyama, N., Eisaki, H., and Uchida, S. (1998). "Electronic states and magnetic properties of edge-sharing Cu–O chains," *Phys. Rev. B* **57**, 5326–5335.
- Mizuno, Y., Tohyama, T., and Maekawa, S. (1999). "Interchain interactions and magnetic properties of Li₂CuO₂," *Phys. Rev. B* **60**, 6230–6233.
- Okada, K., and Kotani, A.J. (1998). "Large-cluster effects on core-level photoemission spectra of quasi-one-dimensional copper compounds," *J. Electron Spectrosc. Relat. Phenom.* **88**, 255–260.
- Okuda, K., Noguchi, S., Konishi, K., Deguchi, H., and Takeda, K. (1992). "Magnetism of one-dimensional copper oxides related to HTSC," *J. Magn. Magn. Mater.* **104**, 817–818.
- Owens, F.J. (1999). "Evidence of a phase transition in Cu–O chains of LiCuO₂," *Physica C* **313**, 65–69.
- Paszkowicz, W. (1989). "INDEXING—Program for indexing powder patterns of cubic, tetragonal, hexagonal and orthorhombic substances on personal computers," *J. Appl. Crystallogr.* **22**, 186–187.
- Paszkowicz, W., Vorotynov, A., Sablina, K., and Petrakovskii, G. (1995). "Powder diffraction data for LiCu₂O₂," *Bull. Czech Slovak Crystallogr. Assoc.* **2**, 68.
- Patat, S., Blunt, D.P., Chippindale, A.M., and Dickens, P.G. (1991). "The thermochemistry of LiCuO, Li₂CuO₂ and LiCu₂O₃," *Solid State Ionics* **46**, 325–329.
- PDF2 database (1999). International Centre for Diffraction Data® (PA).
- Rhemes G. (1986). "Batteries: A solution for each need," *Electron. Industr.* **110**, 87–90.
- Ritchie, A.G., and Mullins, A.P. (1994). "Copper oxide as a high tempera-

- ture battery cathode material," J. Power Sources **51**, 403–407.
- Sapina, F., Rodríguez-Carvajal, J., Sanchis, M.J., Ibáñez, R., Beltrán, A., and Beltrán, D. (1990). "Crystal and magnetic structure of Li_2CuO_2 ," Solid State Commun. **74**, 779–784.
- Shirvinskaya, A.K., and Petrova, M.A. (1987). *Diagrammy Sostoyaniya Sistem Tugoplavkikh Oksidov. Spravochnik. Dvoynye Sistemy*, Constitution Diagrams of Refractory Oxides Handbook. Binary Systems, Vol. 5 part 3 (Nauka, Leningrad), p. 6 (in Russian).
- Slack, G.A., and Mroczkowski, S. (1993). "The dissociation pressure of some lithium copper oxides and lithium peroxide," J. Solid State Chem. **107**, 489–496.
- Staub, U., Roessli, B., and Amato, A. (2000). "Magnetic ordering in Li_2CuO_2 studied by μ SR technique," Physica B **289**, 299–302.
- Suba, K., Singh, O.G., Padalia, B.D., Prakash, O., Chandrasekharan, D., and Udupa, M.R. (1994). "On the substitution of lithium in copper oxide," Mater. Res. Bull. **29**, 443–450.
- Vorotinov, A.M., Pankrats, A.I., Petrakovskii, G.A., Vorotnova, O.V., and Szymczak, H. (1998). "ESR study of LiCu_2O_2 single crystals," J. Magn. Magn. Mater. **188**, 233–236.
- Vorotynov, A.M., Pankrats, A.I., Petrakovskii, G.A., Sablina, K.A., Paszkowicz, W., and Szymczak, H. (1998). "Magnetic and resonance properties of LiCu_2O_2 single crystals," J. Exp. Theor. Phys. **86**, 1020–1025 (transl. from Zhurn. Eksp. Teor. Fiziki, **113**, 1866–1876).
- Weht, R., and Pickett, W.E. (1998). "Extended moment formation and second neighbor coupling in Li_2CuO_2 ," Phys. Rev. Lett. **81**, 2502–2505.
- Wizansky, A.R., Rauch, P.E., and DiSalvo, F.J. (1989). "Powerful oxidizing agents for the oxidative deintercalation of lithium from transition-metal oxides," J. Solid State Chem. **81**, 203–207.
- Zatsepin, D.A., Galakhov, V.R., Korotin, M.A., Fedorenko, V.V., Kurmaev, E.Z., Bartkowski, S., Neumann, M., and Berger, R. (1998). "Valence states of copper ions and electronic structure of LiCu_2O_2 ," Phys. Rev. B **57**, 4377–4381.