The Dissociation Pressure of Some Lithium Copper Oxides and Lithium Peroxide

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The oxygen dissociation pressures of $Li_3Cu_2O_4$, Li_3CuO_3, and Li_2O_2 have been measured in the temperature range 679 to 918 K where they range from 1.4 to 77 atm. The results have been fitted to an equation of the type $\log(P) = A - (B/T)$. The equilibrium dissociation is approached from the low-pressure side in order to obtain data in a finite length of time. Formation pressures are two to five times the dissociation pressure because of a substantial volume increase during oxygen uptake. A preliminary experiment on the flux growth of $Li_3Cu_2O_4$ crystals is described. © 1993 Academic Press, Inc.

Introduction

A number of different lithium copper oxides have been reported in the literature. These are formed from the known (*1–3*) lithium oxides Li_2O, Li_3O_2, and Li_2O_2 and the known (*4–5*) copper oxides Cu_2O, Cu_4O_3, and CuO under various oxygen pressures. The ternary compounds reported (*6–19*) to date are Li_6CuO_4 (*10*), Li_3CuO_3 (*8*), Li_2CuO_2 (*6, 7, 11, 12, 17*), $Li_3Cu_2O_4$ (*6, 13, 15, 16*), $LiCuO$ (*9, 17*), $Li_2Cu_2O_3$ (*10*), $LiCuO_2$ (*19*), $LiCu_2O_2$ (*14, 15, 17, 18*), and $LiCu_3O_3$ (*14, 15, 18*). The existence of Li_6CuO_4 and $Li_2Cu_2O_3$ found by Abdullaev *et al.* (*10*) has been questioned (*14*). The valence of Li in these compounds is $+1$ while the copper valence is $+1$, $+2$, or $+3$. Some of the compounds have different copper valences simultaneously. For Cu_4O_3, $LiCu_2O_2$, and $LiCu_3O_3$ that contain both Cu^{1+} and Cu^{2+}, the two different copper ions are on distinctly different crystallographic sites. In

$Li_3Cu_2O_4$ the sites for Cu^{2+} and Cu^{3+} are indistinguishable (*16*). The monovalent copper ions have an oxygen coordination of two while the divalent and trivalent ones have an oxygen coordination of four (square planar).

Almost all of the binary and ternary oxides have been made at atmospheric pressure (0.2 atm $P(O_2)$). The only one (*8*) requiring high oxygen pressure is Li_3CuO_3, for which 100 to 150 atm $P(O_2)$ was employed at 773 K. The $Li_3Cu_2O_4$ compound has also been made (*16*) at 300 atm $P(O_2)$ at 1023 K.

The lithium peroxide Li_2O_2 has a dissociation pressure (*20, 21*) of $P(O_2) = 1$ atm at 467 K. In previous works it could not be prepared (*21*) by the oxidation of Li_2O; it was made from $LiOH + H_2O_2$. Its melting point has been estimated (*21*) as 698 K, but this value was not measured.

Experimental Details

The aim of the present study was to determine the oxygen pressure at dissociation and at formation of the compounds Li_3
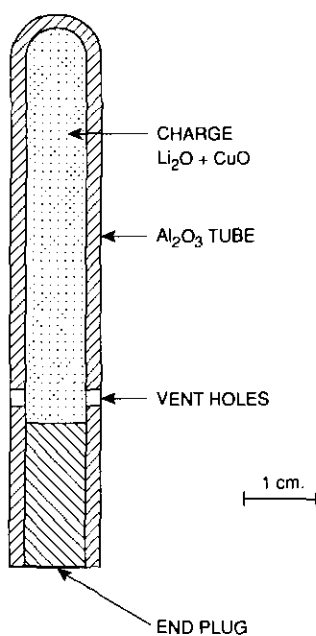
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FIG. 1. The Al_2O_3 ceramic tube used for measuring the oxygen dissociation pressure of lithium copper oxides.

Cu_2O_4 and Li_3CuO_3 at high temperature. This information is necessary for finding out how, eventually, to grow single crystals of the compounds.

The starting materials were commercial (22) 0.99999 pure CuO powder and Li_2O. The Li_2O was made in this laboratory from the vacuum decomposition of 0.9997 purity Li_2CO_3 powder at temperature just below the Li_2CO_3–Li_2O eutectic (23) at 978 K. These powders were mixed together in the ratio of 3 Li_2O + 2 CuO with a slight excess of Li_2O in a nitrogen-filled glove box. They were then placed in a round-bottom, high-purity Al_2O_3 ceramic tube (24) which was 1.25 cm O.D., 0.63 cm I.D., and 7 cm long. The inside diameter of this tube was machined with a diamond-bearing drill so that it would accept a centerless ground, close-fitting Al_2O_3 ceramic plug 2 cm long. Then two small holes, 3 mm in diameter, were drilled through the wall of the tube to permit oxygen gas free access to the powder inside. See Fig. 1, where the tube is shown inverted.

The inverted tube was placed in the bottom of a René 41 nickel–chromium-alloy pressure autoclave cell (25) as shown in Fig. 2. The space in the cell above the tube was filled with a solid Al_2O_3 ceramic rod in order to reduce the total oxygen gas volume and to reduce convection currents inside the cell. The lower 85% of the cell was placed in an electrically heated furnace while the upper 15% was at room temperature. This arrangement produced a vertical temperature gradient in the Al_2O_3 sample tube region of about 8 K/cm. The Al_2O_3 sample tube was inverted in order to prevent vapor migration of the Li_2O to the colder regions of the pressure cell. A chromel–alumel thermocouple was placed on the outer wall of the cell to measure the sample temperature at its warmer end. Thus the absolute sample temperature may be uncertain by ±10 K, but the relative values in any one run are probably good to ±5 K.

The pressure cell was connected to a silicon-crystal electronic strain-gage pressure
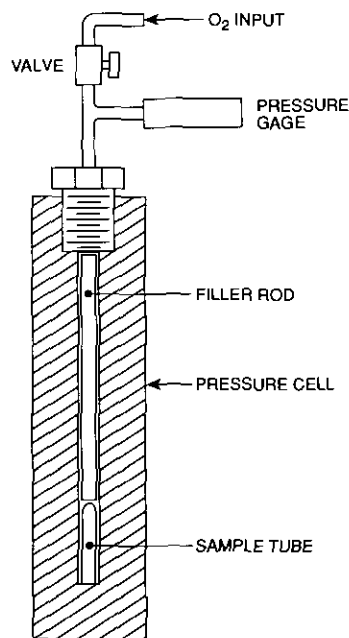

FIG. 2. The high-pressure cell used to hold the oxide samples in the furnace at high temperature.

transducer (26) capable of operating at pressures up to 340 atm. The gage had a sensitivity of ±0.07 atm and an accuracy of ±0.2 atm. This system was connected through a valve to a commercially available cylinder of oxygen gas at 180 atm. The method of operation was to raise the pressure cell temperature to 773 K under a few atmospheres pressure of oxygen gas. Then the oxygen pressure in the cell was increased to about 10 times the equilibrium dissociation pressure and the control valve was closed. The cell pressure was monitored versus time as the oxygen was absorbed to make the particular oxide desired. About 5 g of mixed powder was used in the cell, and the first oxygenation to produce $Li_3Cu_2O_4$ consumed about 0.02 moles of O_2 gas. A blank run showed no oxygen uptake in the empty cell at these temperatures. This oxygen uptake produces a substantial pressure drop in the cell because of its small gas volume of only a few cm^3. Thus a second pressurization is often needed to complete the oxygenation. The process may take several days.

After $Li_3Cu_2O_4$ is formed further oxidation is needed to make Li_3CuO_3. The rate of oxygen uptake as a function of the overpressure is shown in Fig. 3 for the conversion: $1.5\ Li_2O + Li_3Cu_2O_4 + 0.25\ O_2 \rightarrow 2\ Li_3CuO_3$ at 773 K. It can be seen from Fig. 3 that overpressure ratios of ≥ 5 are needed to obtain useful oxidation rates. Because of this overpressure effect it was not possible to determine the equilibrium dissociation pressure by the approach to equilibrium from above. The equilibration time for the formation of Li_3CuO_3 from Li_2O and $Li_3Cu_2O_4$ at 773 K for an overpressure ratio of $P/P_E = 1.05$ is estimated from Fig. 3 to be about 3 months if the rate is a quadratic function of the overpressure ratio.

The method of determining the equilibrium dissociation pressure, P_E, is to first fully oxidize the sample to form the desired compound. Then the $P(O_2)$ is reduced in a series of steps of about 1 atm each. After each reduction the pressure gage reading is monitored as a function of time. If no
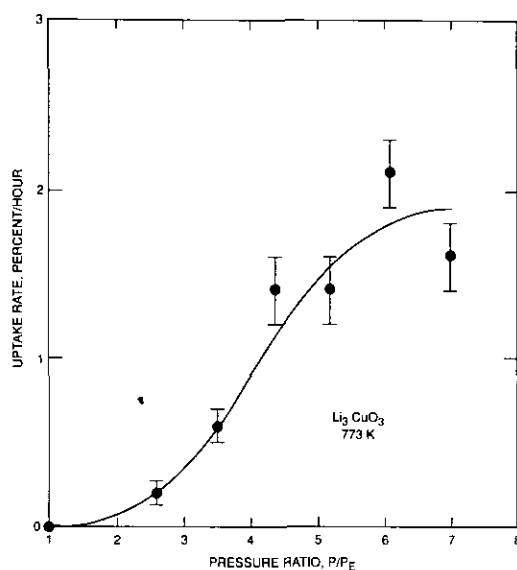

FIG. 3. The rate of formation of Li_3CuO_3 from the lower oxides as a function of the overpressure ratio P/P_E.

subsequent pressure increase is seen, then the applied oxygen pressure is greater than P_E. Another pressure reduction step is then taken. Once the applied pressure drops below P_E the sample starts to decompose and the pressure slowly returns to P_E and remains there. The equilibrium pressure is only measurable in a finite time when approached from below. This effect of approaching P_E from below was also observed by Blumenthal (20, 21) for many different peroxides. The reason for this asymmetry is explained later.

One important precaution in obtaining reliable P_E values needs to be observed. The newly formed oxide, say Li_3CuO_3, needs to be annealed for at least 24 hr before dissociation is attempted. If this is not done, one obtains dissociation pressures up to two or three times the true value. The crystal structure needs to recrystallize well after it is formed in order to obtain reproducible pressure values. No X-ray study of the poorly crystallized material was made, but the inordinately high decomposition pressures were encountered in at least three different runs
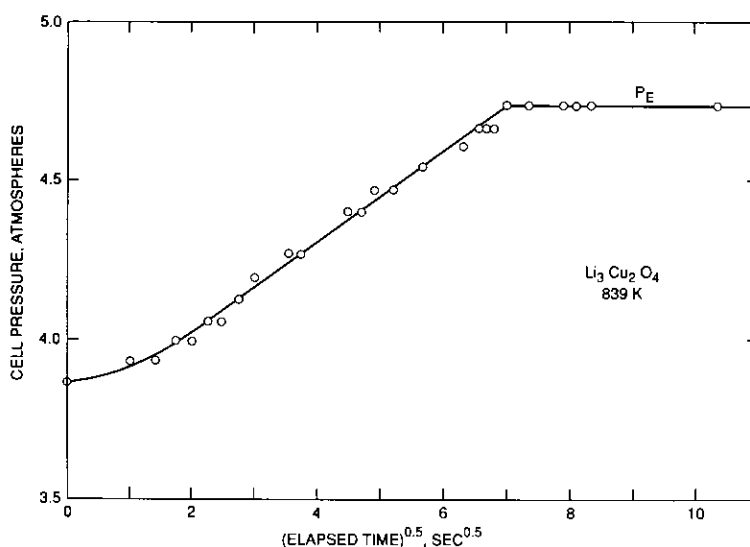
FIG. 4. The cell pressure versus time for $Li_3Cu_2O_4$ at 839 K when the pressure is suddenly reduced below the equilibrium dissociation pressure, P_E.

that were made within 1 or 2 hr after formation.

Approach to Equilibrium

When the oxygen pressure in the cell is reduced below P_E the return to equilibrium is governed by the outward permeation of the oxygen through the decomposed surface layer to the gas space above it. Thus the total thickness, l, of the decomposed layer varies as

$$l = \sqrt{Dt},$$

where t = the elapsed time, and D = the apparent diffusion coefficient of oxygen through the decomposed surface layer. The pressure rise versus time for $Li_3Cu_2O_4$ at 839 K is shown in Fig. 4. The equilibrium pressure, P_E, of 4.74 atm is clearly seen.

Volume Changes During The Reaction

The molecular volumes of the various lithium oxides, copper oxides, and their ternary compounds can be calculated from the known crystal structures (1–19). We have assumed that $Z = 35$ for the unit cell (2) of Li_3O_2 because no value is given in the origi-

nal paper. The percentage volume increases during a number of reactions are shown in Table I. The only binary copper oxide involved in the present reactions is CuO, which is the stable phase (27) up to pressures of at least 3000 atm of $P(O_2)$.

The first four reactions in Table I show that the reaction of CuO with the known binary lithium oxides can produce all of the known ternary compounds which contain Cu^{2+} or Cu^{3+}. In each of these there is a volume increase without any oxygen uptake. In Li_3O_2 and Li_2O_2 there are paired oxygen atoms in peroxide ions (O_2^{2-}), in the ternary compounds there are no peroxide ions. This change accounts for some of the volume increase.

The oxygen uptake in the fifth and sixth reactions of Table I produces a considerable volume increase in the binary lithium oxides. The seventh and eighth reactions are the ones that we are interested in for the present series of experiments. In both reactions the oxygen gas absorption leads to a volume increase. This means, for example, that a single crystal grain of Li_2CuO_2 whose surface is being oxidized has a surface layer of the new compounds which is under sub-

TABLE I

PERCENTAGE VOLUME INCREASES OF SOLID PHASES
DURING REACTIONS

Reaction number	Oxygen uptake	Reaction	$\Delta V/V$ (%)
1	No	$Li_2O + CuO \rightarrow Li_2CuO_2$	8.9
2	No	$Li_3O_2 + 2CuO \rightarrow Li_3Cu_2O_4$	8.0
3	No	$Li_3O_2 + CuO \rightarrow Li_3CuO_3$	10.5
4	No	$Li_2O_2 + 2CuO \rightarrow 2LiCuO_2$	2.1
5	Yes	$6Li_2O + O_2 \rightarrow 4Li_3O_2$	11.5
6	Yes	$2Li_3O_2 + O_2 \rightarrow 3Li_2O_2$	19.1
7	Yes	$8Li_2CuO_2 + O_2 \rightarrow 4Li_3Cu_2O_4 + 2Li_2O$	2.8
8	Yes	$4Li_3Cu_2O_4 + 6Li_2O + O_2 \rightarrow 8Li_3CuO_3$	8.5

stantial compression. The oxygen permeation through this layer toward the unoxidized grain center is a very slow process. This is to be contrasted to the surface cracks that appear in the surface of, say, $Li_3Cu_2O_4$ during deoxygenation. These cracks permit a rapid efflux of oxygen in such cases. These are the reasons that equilibrium is easy to approach in a short time during deoxygenation, but takes a very long time to approach during oxygenation. The large volume change of 8.5% for the formation or decomposition of Li_3CuO_3 in Reaction 8 makes this difference in equilibration times even larger.

X-Ray Study of Reaction Products

The ternary compounds Li_2CuO_2, $Li_3Cu_2O_4$, and Li_3CuO_3 appear from the published X-ray work (6–8, 11–13, 15) to have no appreciable range of stoichiometry. Our X-ray studies gave powder patterns identical to the ones previously published. We found that the conversion of Li_2CuO_2 powder to $Li_3Cu_2O_4$ powder almost always went to completion at the oxidation temperature in times of 24 to 48 hr if $P \geq 5 P_E$. The conversion of $Li_3Cu_2O_4$ to Li_3CuO_3 was never complete under such conditions, even in the presence of a considerable excess of Li_2O powder. The centers of the grains almost always contained some unreacted $Li_3Cu_2O_4$ due to the large volume expansion.

However, this is not a serious problem because the decomposing surfaces during deoxygenation rapidly approach equilibrium, and the measured $P(O_2)$ is characteristic of the four-phase equilibrium (28) where $P + F = C + 2 = 5$:

$$Li_3CuO_3 \rightarrow Li_3Cu_2O_4 + Li_2O + O_2(gas).$$
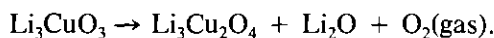
The decomposition of $Li_3Cu_2O_4$, in the presence of excess Li_2O, is just the reverse of Reaction 7 in Table I. In the absence of Li_2O its decomposition is

$$2 Li_3Cu_2O_4 \rightarrow 3 Li_2CuO_2 + CuO + O_2.$$
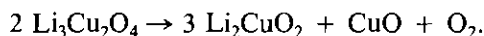
We believe that these two decomposition schemes will yield almost identical $P(O_2)$ values, but we always employed conditions with excess Li_2O.

Results

The equilibrium dissociation data points are given in Table II. The one point for Li_2O_2 was obtained when Li_3CuO_3 plus excess Li_2O at 775 K was subjected to an oxygen pressure of 273 atm. About 1% of the charge in the cell was converted to Li_2O_2 according to

$$Li_2O + \tfrac{1}{2} O_2 \rightarrow Li_2O_2,$$
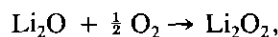
or by a combination of Reactions 5 and 6 in Table I. No X-ray study of these oxidation

TABLE II

EQUILIBRIUM OXYGEN DISSOCIATION PRESSURE, P_E, DATA VERSUS TEMPERATURE FOR THREE DIFFERENT COMPOUNDS

Compound	Temperature, K	Pressure, atm
$Li_3Cu_2O_4$	767 ± 5	1.37 ± 0.03
	787 ± 5	1.88 ± 0.07
	795 ± 5	2.09 ± 0.07
	819 ± 5	3.79 ± 0.08
	839 ± 5	4.74 ± 0.08
	867 ± 5	7.46 ± 0.10
	915 ± 5	15.29 ± 0.14
Li_3CuO_3	679 ± 5	4.8 ± 0.8
	705 ± 5	7.7 ± 0.2
	727 ± 15	9.0 ± 0.5
	768 ± 15	17.0 ± 1.0
	918 ± 5	77.2 ± 0.5
Li_2O_2 ?	775 ± 5	45.0 ± 0.5

products was made. It is assumed that some Li_2O_2 was made because the measured equilibrium pressure, P_E, falls very nearly on the line extrapolated from the data of Blumenthal (20) for Li_2O_2. The amount formed was estimated from the total oxygen pressure rise in the cell during decomposition.

Table III lists the three present attempts to form Li_2O_2 under high oxygen pressures. The applied oxygen pressure is P_A, which must be greater than P_E. The other two attempts used only Li_2O as the starting material. At low temperature there was no conversion for $P_A/P_E = 4.2$, where P_E is the equilibrium dissociation pressure. Only at 973 K was a small conversion effected. The oxidation of Li_2O to Li_2O_2 can probably be

TABLE III

ATTEMPTS AT THE FORMATION OF Li_2O_2

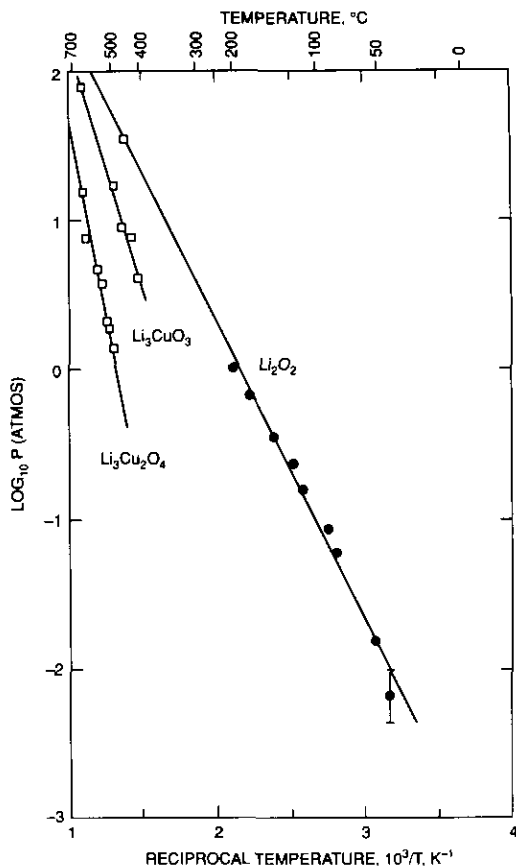| Starting material	Temperature (° K)	Time (hr)	P_E (atm)	P_A/P_E (atm)	Conversion amount
Li_2O	673	25	17.3	4.2	zero
Li_3CuO_3	775	23	40.5	6.8	~1%
Li_2O	973	82	126.7	1.2	4.8%

FIG. 5. The equilibrium dissociation pressures of three compounds as a function of the reciprocal temperature. The open squares are the present data. The data for the filled-in circles are from Blumenthal (20).

produced quite easily at high temperatures if $P_A/P_E \geq 5$ is employed.

For all three compounds a plot of P_E versus reciprocal temperature is given in Fig. 5. The data can be fitted quite well with an equation of the form

$$\log_{10} P_E \text{ (atm)} = A - (B/T),$$

where T = absolute temperature. The A and B coefficients are given in Table IV. No other equilibrium compounds were found between Li_2CuO_2 and Li_2O_2 as the oxygen pressure was reduced in successive steps. We looked for Li_3O_2 and $LiCuO_2$ both with X-rays and with pressure-rise experiments, but found neither.

TABLE IV

COEFFICIENTS FOR THE DISSOCIATION PRESSURE
EQUATION FOR THREE DIFFERENT COMPOUNDS

Compound	A	B (° K)	Validity range (° K)
$Li_3Cu_2O_4$	6.493	4893	754 → 915
Li_3CuO_3	5.155	2985	579 → 918
Li_2O_2	4.040	1885	316 → 471

We can now construct a table giving the temperature at which the oxygen dissociation pressure of the various compounds reaches 1 atm, see Table V. The data for CuO is from Smyth and Roberts (29), that for Li_2O is from Lamoreaux and Hildenbrand (30). The rest are from Table IV. According to Abdullaev et al. (10), Li_2CuO_2 melts (in air?) at 1293 K without decomposition.

Crystal Growth

The structure of $Li_3Cu_2O_4$ has been determined from X-ray powder diffraction (16). It would be useful to obtain single crystals in order to verify this structure. An attempt was made to grow crystals of $Li_3Cu_2O_4$ from molten LiOH as a solvent using Al_2O_3 crucibles. The LiOH melts (31) at 746 K and has a dissociation pressure (32) of H_2O of 0.0023 atm at this temperature. As long as the dissociation pressure is less than the vapor

TABLE V

TEMPERATURES AT WHICH THE OXYGEN
DISSOCIATION PRESSURE IS ONE ATMOSPHERE

Compound	Temperature (° K)
CuO	1393
Li_2CuO_2	>1293
$Li_3Cu_2O_4$	754
Li_3CuO_3	579
Li_2O_2	467
Li_2O	~2870

pressure of H_2O at room temperature, the temperature in the pressure gauge part of the apparatus, no water will condense inside. This sets an upper limit on the LiOH melt temperature of 933 K. We used a temperature of 800 K for the growth experiment.

The method of growth was to dissolve $Li_3Cu_2O_4$ powder in the LiOH and hold the melt at a fixed temperature in the pressure cell of Fig. 2. An Al_2O_3 crucible 1.25 cm O.D., 0.63 cm I.D., and 20 cm tall was employed; it was not attacked by the molten LiOH. No solid Al_2O_3 filler rod was used in this run, thus there was ample space to condense evaporating LiOH in the neck of the crucible above the melt. The vapor (33) over molten LiOH contains H_2O as well as LiOH and $Li_2(OH)_2$ molecules. The LiOH in the vapor condenses on the crucible walls at much higher temperatures than that at which the H_2O condenses. Hence the melt eventually entirely evaporates leaving the Li–Cu–O crystals behind.

In order to form $Li_3Cu_2O_4$ without forming Li_3CuO_3 we need an oxygen pressure, $P(O_2)$, of P_E (Li_3CuO_3) > $P(O_2)$ ≥ 5 P_E ($Li_3Cu_2O_4$). From Fig. 4 this can be realized for all temperatures less than 950 K. Thus the LiOH method might work for 723 K < T < 933 K with $P(O_2)$ between 2.7 and 90 atm. One experimental run at 800 K for 20 hr at 53 atm yielded a few small black crystals. A total of 0.62 g of LiOH was evaporated during this run. Unfortunately, the crystals of lithium copper oxide were too badly twinned to yield any useful X-ray structural data. It may be that the $P(O_2)$ was too high. It should have been less than 26 atm in order to avoid possible formation of Li_3CuO_3 along with the $Li_3Cu_2O_4$.

Conclusions

The oxygen dissociation pressures of $Li_3Cu_2O_4$ and Li_3CuO_3 have been measured for oxygen pressures above 1 atm at temperatures up to 915 K. The equilibrium pressures must be approached from below in order to

obtain accurate values in a finite length of time. These two compounds and $LiCuO_2$ appear to be the only ternary ones in the Li–Cu–O system between Li_2CuO_2 and Li_2O_2. The results of Blumenthal (20) for Li_2O_2 have been tentatively confirmed with one point at 775 K.

A technique for growing crystals of $Li_3Cu_2O_4$ under high oxygen pressure has been tried with only partial success.

Acknowledgments

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