JOURNAL OF SOLID STATE CHEMISTRY **96**, 243–246 (1992)

# Preparation and Magnetic Properties of $Cu_6O_8 \cdot InCl$ and $Li_xCu_6O_8 \cdot InCl$

M. PARANTHAMAN AND H. STEINFINK

*Center for Materials Science and Engineering, The University of Texas at Austin, Austin, Texas 78712*

Received July 29, 1991

The compounds $Cu_6O_8 \cdot InCl$ and $Li_{1.23}Cu_6O_8 \cdot InCl$ were prepared. The powder X-ray diffraction pattern shows that both phases have the same cubic structure with $a = 9.144(5)$ Å. The introduction of $Li^+$ lowers the average valence of copper. Neither phase superconducts above 5 K. Measurements of magnetic susceptibility show ferrimagnetic behavior for both phases, with an onset temperature of 125 K for the copper phase and 75 K for the lithiated phase. The copper phase shows a constant magnetization over the range 125–50 K that may be due to a two-sublattice antiferromagnetic interaction. © 1992 Academic Press, Inc.

## Introduction

The preparation and single-crystal growth of compounds by electrolytic reduction of fused salts is a well-known technique (*1*). Oxidative methods are much less known and have received attention recently because of the promise that compounds with unusual valence states might be prepared in this way. Single crystals of $Ba_{1-x}K_xBiO_3$ and their Rb and Cs analogues were grown by electrodeposition on platinum anodes from $KOH–Ba(OH)_2 \cdot 8H_2O–Bi_2O_3$ melts (*2, 3*). Recently Grenier *et al.* (*4*) prepared the superconductor $La_2CuO_{4+\delta}$ by the anodic oxidation of $La_2CuO_4$ electrodes in KOH solution. It is noteworthy that single crystals of the mixed valence $Ag^+/Ag^{3+}$ compounds $Ag_7O_8 \cdot NO_3$, $Ag_7O_8 \cdot F$, and $Ag_7O_8 \cdot HF_2$ can be easily grown at the anode by the electrolysis of aqueous solutions containing the appropriate ions (*5, 6*). The nitrate was shown to superconduct with a transition temperature near 1 K. The compounds possess a complex cubic structure (*7, 8*). We grew single crystals of $Ag_7O_8 \cdot NO_3$ and redetermined the crystal structure by X-ray diffraction. Even though the refinement converged to $R = 0.046$, some of the parameters did not behave satisfactorily, and we feel that the correct structure is still an open problem. We then attempted to grow crystals electrolytically, in which copper was partially substituted for silver. These attempts were not successful. While this work was in progress, Hayakawa *et al.* (*9*) reported the preparation and crystal structure of the isostructural compound $Cu_6O_8 \cdot InCl$. The formal copper valence in this compound is +2.33 and it is metallic, properties that are present in the p-type high-$T_c$ copper-based superconductors in their normal state. The latter are layer structures containing square coplanar copper in $CuO_2$ sheets, while $Cu_6O_8 \cdot InCl$ has copper ions located in interstices of a three-dimensional framework. It

0022-4596/92 $3.00

is now well established that the high-$T_c$ property is a mixed-valent phenomenon and, for p-type $CuO_2$ sheets, is a function of the hole concentration in the sheets. On increasing this concentration, phase transitions occur from an antiferromagnetic semiconductor ($W < U$) to a metal ($W > U$) by passing through a narrow region $W \approx U$ where the material becomes superconducting (*10*). Hence, we decided to synthesize this compound, determine the valence state of copper, and change the hole concentration by Li insertion in an attempt to induce superconductivity.

TABLE I

X-RAY POWDER DIFFRACTION DATA FOR $Cu_6O_8 \cdot InCl$

| *hkl* | $d_{obs}$ | $d_{cal}$ | $I/I_0$ |
|---|---|---|---|
| 111 | 5.276 | 5.277 | 26.4 |
| — | 2.909[a] | — | 4.4 |
| 311 | 2.757 | 2.756 | 1.8 |
| 222 | 2.640 | 2.638 | 100.0 |
| 400 | 2.287 | 2.285 | 27.8 |
| 331 | 2.097 | 2.097 | 10.6 |
| 440 | 1.616 | 1.616 | 27.6 |
| 531 | 1.543 | 1.545 | 3.3 |

[a] Impurity line due to $In_2O_3$.

## Experimental

We have successfully prepared the polycrystalline samples of $Cu_6O_8 \cdot InCl$ from a starting composition of In metal, $Cu(NO_3)_2 \cdot 3H_2O$, and $CuCl_2 \cdot H_2O$ in the ratio 1 : 4 : 2.2. This mixture was dissolved in dilute $HNO_3$, the solution was evaporated to dryness, and the resultant mixture was introduced into a preheated furnace at 813 K in air, kept at that temperature for 10 min, and air quenched to room temperature. The grayish mixture was ground and heated in an alumina boat at 813 K for 1 hr and air quenched. Annealing this material for several hours at 673 K results in its decomposition to $In_2O_3$, $In_2Cu_2O_5$, and CuO. A nearly single-phase material was obtained and its X-ray diffraction powder pattern obtained with $CuK_\alpha$ radiation on a diffractometer equipped with a diffracted beam monochromator matched the published pattern (*9*). A listing of *d* spacings and relative intensities is shown in Table I. The cubic lattice parameter $a = 9.144(5)$ Å, obtained from a least-squares refinement of the measured $2\theta$ values, differs slightly from the published value $a = 9.1661(2)$ Å. Lithium insertion was carried out in a previously described apparatus (*11*). The lithium source was *n*-butyllithium in an *n*-hexane medium. The solution was stirred for one week under a $N_2$ atmosphere, and the lithiated sample was recovered by filtration. The Li content was analyzed by dissolving the sample in dilute HCl, diluting the solution to the optimum ppm level, and measuring the absorption with a Perkin–Elmer 100 atomic absorption spectrophotometer. A 2-ppm Li solution served as a standard. Chemical analysis was carried out by iodometric titration (*12*). About 100 mg of the sample was dissolved in 2*N*-HBr, 15 ml of 10% KI was added, and the liberated $I_2$ was titrated against standard 0.03-*N* thiosulfate solution with starch as indicator. The total redox power was calculated from the titer value. The magnetic susceptibility was measured with a SQUID magnetometer, cooling the sample in a field of 100 Gauss as well as without a field over the temperature range 5–300 K. No field dependence was observed. The $\chi$ values were corrected for the diamagnetic moment of the gelatin capsule sample holder.

## Results and Discussion

The crystal structure of $Cu_6O_8 \cdot InCl$ is similar to that of $Ag_7O_8 \cdot NO_3$ ($Ag_6O_8 \cdot AgNO_3$). It consists of a three-dimensional framework of oxygen ions forming a cubo-octadodecahedral lattice. The Cu ions are in

TABLE II

ANALYTICAL DATA FOR $Cu_6O_8 \cdot InCl$

| | | | Chemical analysis | | $1/\chi$ vs. $T$ data | |
|---|---|---|---|---|---|---|
| Compound | Cubic lattice parameters $a$ (Å) | Li content | Redox power | $Cu^{n+}$ | Curie–Weiss $\theta$ (K) | $p_{eff}/Cu$ |
| $Cu_6O_8 \cdot InCl$ | 9.144(5) | — | 7.99 | 2.33 | −553 | 1.70 |
| Lithiated $Cu_6O_8 \cdot InCl$ | 9.138(6) | 1.23 | 6.65 | 2.11 | −374 | 1.40 |

square coordination and In ions have eight oxygen near neighbors at the apices of a cube (*7, 9*). In Table II are shown the analytical data for $Cu_6O_8 \cdot InCl$ and the lithiated phase. Within experimental error the lattice parameters are the same. The chemically determined valence of +2.33 for Cu is precisely what is expected on the basis of the formula, and the introduction of 1.23 Li reduces the average valence. The measured value of +2.11 is in good agreement with the calculated value +2.13 based on the Li determination.

Both the lithiated and parent compounds were not superconducting above 5 K. Both phases showed Curie–Weiss behavior as shown in Fig. 1. The lithiated sample shows incipient ferrimagnetic ordering at about 75 K, with a Curie–Weiss constant and effective moment shown in Table II. The $1/\chi$ vs. $T$ curve for $Cu_6O_8 \cdot InCl$ shows a deviation from the straight line portion at about 125 K, a nearly flat section to about 50 K, and then decreases as expected for ferrimagnetic ordering. Its Curie–Weiss constant and effective moment are greater than that

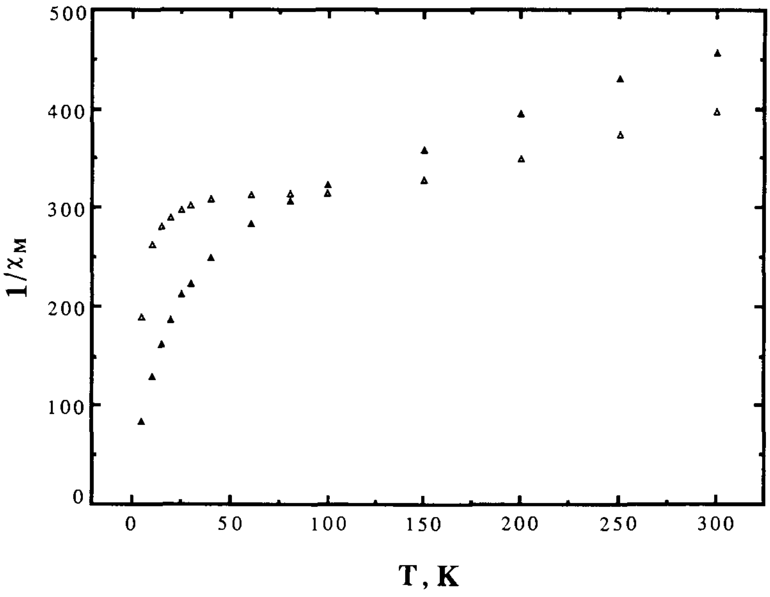

FIG. 1. $1/\chi_M$ (field cooled) vs. $T$ for $Cu_6O_8 \cdot InCl$ (△) and $Li_{1.23}Cu_6O_8 \cdot InCl$ (▲).

for the lithiated compound. Both phases display a paramagnetic and a ferrimagnetic region. In $Ag_7O_8 \cdot NO_3$, Ag is assigned to the 4*a* and 24*d* sites of *Fm*3*m* (*7*), while in $Cu_6O_8 \cdot InCl$, Cu is assigned to the 24*d* and In to the 4*b* sites (*9*). The structure is equally well-described by placing In into 4*a* and Cl into 4*b*. The appearance of a constant value of the magnetization for $Cu_6O_8 \cdot InCl$ can be explained by the molecular field theory of a two-sublattice system (*13*). This observation would imply that Cu is not exclusively in one crystallographic site, as stated by Hayakawa *et al.* (*9*). Neutron diffraction patterns at low temperature would be required to elucidate the magnetic phase diagram of $Cu_6O_8 \cdot InCl$. Evidently the introduction of Li into the structure not only lowers the average valence but disrupts the sublattice interaction that appears to be present in $Cu_6O_8 \cdot InCl$.

## Acknowledgments

The support of the R. A. Welch Foundation of Houston, Texas is gratefully acknowledged. We thank Dr. Bogdan Wnetrzewski for helping with the lithium insertion and analysis procedures, and Drs. J. B. Goodenough, J. T. Markert, and A. Manthiram, University of Texas, for helpful discussions.

## References

*1.* A. Wold and D. Bellavance, *in* "Preparative Methods in Solid State Chemistry" (P. Hagenmuller, Ed.), Academic Press, New York (1972).
*2.* M. L. Norton, *Mater. Res. Bull.* **24,** 1391 (1989).
*3.* M. L. Norton, H.-Y. Tang, and J. Eglin, *in* "Chemistry of Electronic Ceramic Materials" (P. K. Davies and R. S. Roth, Eds.), NIST Special Publication 804, U.S. Govt. Printing Office, Washington, D.C. (1991).
*4.* J. C. Grenier, A. Wattiaux, N. Lagueyte, J. C. Park, E. Marquestaut, J. Etourneau, and M. Pouchard, *Physica C* **173,** 193 (1991).
*5.* I. Naray-Szabo and K. Popp, *Z. Anorg. Chem.* **322,** 286 (1963).
*6.* M. B. Robin, K. Andres, T. H. Geballe, N. A. Kuebler, and D. B. McWhan, *Phys. Rev. Lett.* **17,** 917 (1966).
*7.* I. Naray-Szabo, G. Argay, and P. Szabo, *Acta Crystallogr.* **19,** 180 (1965).
*8.* C. H. Wong, T.-H. Lu, C. N. Chen, and T. J. Lee, *J. Inorg. Nucl. Chem.* **34,** 3253 (1972).
*9.* H. Hayakawa, E. Akiba, I. Yazawa, H. Ihara, and S. Ono, *Jpn. J. Appl. Phys.* **29,** L1796 (1990).
*10.* J. B. Goodenough, A. Manthiram, and J. Zhou, *Mater. Res. Soc. Symp. Proc.* **156,** 339 (1989).
*11.* A. Manthiram and J. B. Goodenough, *J. Solid State Chem.* **71,** 349 (1987).
*12.* A. Manthiram, J. S. Swinnea, Z. T. Sui, H. Steinfink, and J. B. Goodenough, *J. Am. Chem. Soc.* **109,** 6667 (1987).
*13.* A. H. Morrish, "The Physical Principles of Magnetism," John Wiley & Sons, New York (1966).