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PREPARATION AND CHARACTERIZATION OF Cu(II) OXIDE

by

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
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PREPARATION AND CHARACTERIZATION OF Cu(II) OXIDE

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ABSTRACT

Copper(II) oxide was prepared by oxidation of copper metal and decomposition of the nitrate. The presence of copper in the formal valence of Cu(III) has been confirmed in p-type CuO. The magnetic and electronic properties have been studied as a function of preparation and annealing conditions.

Introduction

Copper(II) oxide occurs in nature as the mineral tenorite. The structure[1] (Fig. 1) shows Cu(II) with essentially square planar coordination of oxygen around the copper. The space group is C2/c with unit cell dimensions a = 4.6837(5)Å, b = 3.4226(5)Å, c = 5.1288(6)Å and β = 99.54(1)°. The structure is a distorted PdO type, and each copper has 4 O' neighbors at 1.96Å and two apical oxygens, O", at 2.78Å. In Cu(II) oxide, the Jahn-Teller distortion due to the stabilization of a single d-hole per atom, Cu(II) $3d^9$, results in the observed difference of its structure with the monoxides of the first row transition metals.

The magnetic susceptibility of CuO shows an anomaly at 230 K which has been interpreted as an indication for antiferromagnetic ordering[2,3]. Neutron

diffraction studies have corroborated the magnetic ordering in CuO[4,5]. A reduced atomic moment (μ_{Cu} = 0.65±0.10 μ_B) at the copper atoms is observed. The antiferromagnetic behavior of CuO is not typical, since the reported susceptibility does not show a maximum of x at the ordering temperature.

The purpose of this work was to study the structural, electronic, and magnetic properties of copper(II) oxide and relate the electronic properties to small changes in the concentration of holes (Cu(III)).

Experimental

CuO was prepared by two different procedures. The first method involved heating copper metal powder (5-9's, Aesar chemical Co.) in a porcelain crucible in air at 600°C for 24 hrs. The product was reground and reheated for 24 hrs at 600°C. The second procedure consisted of dissolving the copper metal in 1:1 dilute nitric acid. The solution was evaporated on a hot plate to near dryness. Upon cooling, copper nitrate crystallized completely. Copper oxide was prepared by decomposing the nitrate in a silica boat at temperatures between 250 and 600°C in a predried oxygen atmosphere (flow rate of 60 sccm/min).

Characterization of Samples

X-ray powder diffraction patterns were obtained with a Philips-Norelco diffractometer using monochromatic high-intensity $CuK\alpha_1$ radiation (λ = 1.5405A). For qualitative phase identification, patterns were taken with a scan rate of 1° 2θ/min, while cell parameters were determined from scans taken at 0.25° 2θ/min. Diffraction patterns were obtained over the range 12° < 2θ < 72°, and the lattice parameters were determined by a least-squares refinement of the data using a computer program which corrected for the systematic errors in the measurement.

A Cahn 113 thermal balance was used to determine the decomposition behavior of copper nitrate. The sample was purged at room temperature in a stream of oxygen for two hours and then the temperature was increased to 600°C at a rate of 60°C/hr. In addition, the thermal stability of copper(II) oxide in flowing argon was determined. The temperature was increased to 1000°C at a rate of 60°C/hr. In all experiments, the flow rate of the gas was 60 sccm/min. The total active oxygen content of the samples was determined by the procedure of Ward and Struthers[6]. This method allows for the determination of total oxidation of copper, i.e., the amount of formal valent Cu(III) present in the samples.

Magnetic susceptibility measurements were carried out using a Faraday balance from 77 to 300 K with a field strength of 10.4 kOe. At both 77 and 300 K, the field dependence was determined from 6.22 to 10.4 kOe. The van der Pauw method[7] was used to measure the electrical resistivity. Pellets were cold-pressed at 6 kbar and sintered at 650°C in flowing oxygen or argon. Contacts were made by ultrasonically soldering indium directly onto the sintered pellets. Ohmic behavior was established by measuring the current-voltage characteristics. Qualitative Seebeck measurements were also made to characterize the carrier type of the samples.

Results and Discussion

Copper(II) oxide prepared from copper metal at 600°C is nearly stoichiometric. The total active oxygen content determination gives a stoichiometry of $Cu_{0.9995(2)}O$. Despite the small amount of Cu(III) present, the chemical analysis was reproducible from sample to sample. Attempts were made to change the Cu(III) content by annealing samples in flowing argon or oxygen at 650°C. Copper(II) oxide was also prepared by decomposing copper nitrate in

flowing oxygen from temperatures between 250 and 600°C. This preparation was used to try to stabilize increased amounts of Cu(III) in CuO. It can be seen from Table I that the range of stoichiometry for CuO is small. The largest value of copper defects in $Cu_{1-x}O$ is $x = 0.007$ which was obtained for a sample prepared from the decomposition of the nitrate which was heated slowly in flowing O_2 to 250°C (0.5°/min) and kept at 250°C for 1 hr.

TABLE I

STOICHIOMETRY OF $Cu_{1-x}O$

x	Sample Preparation
0.0005(2)	Cu metal heated to 600°C in air, 48 hrs, 1 grinding
0.002(1)	Cu nitrate heated to 250°C in O_2, 13.5 hrs, 1 grinding
0.007(1)	Cu nitrate heated to 250°C in O_2, 1 hr, no grinding

The x-ray powder diffraction patterns of some copper oxide samples prepared by nitrate decomposition at 250°C are compared with the pattern for CuO prepared by oxidation of the metal at 600°C (Fig. 2). It is observed that, for a reaction time of 1 hr with an oxygen flow rate of 60 sccm/min, extra peaks occur in the diffraction pattern. In addition, the relative intensity of the (110) reflection for CuO is quite high. Despite the differences in the x-ray diffraction patterns shown in Fig. 2, thermogravimetric analysis showed no appreciable weight loss from heating a sample from 250 to 600°C. With sufficient reaction time and intermediate grindings, CuO can be prepared with the same relative intensities as those for copper oxide prepared at 600°C by metal oxidation. These results suggest that in the low temperature preparation of CuO, long range order is not immediately achieved. Changes in the CuO cell constants were not observed for any of the samples.

The magnetic susceptibility data are shown in Fig. 3. The data for copper oxide prepared from copper metal (as made) agrees closely with that reported by O'Keefe and Stone[2]. An increased paramagnetic signal is observed for samples prepared by the low temperature (250°C) decomposition of copper nitrate. The largest paramagnetic signal is found for the sample with additional x-ray diffraction peaks and the highest amount of Cu(III) ($Cu_{1-x}O$, where $x = 0.007$). The magnetic properties of CuO prepared at low temperature are influenced by two opposing effects. The larger Cu(III) content results in the formation of more carriers and hence higher conductivity. However, the structure of CuO prepared at 250°C is less ordered, giving rise to increased amounts of localized Cu(II) caused by a noncooperative structural effect.

Room temperature resistivity measurements on CuO (as made) pellets annealed at 650°C in oxygen and argon gives values of 10^2 and 10^3 Ω-cm, respectively. This behavior was reversible. The same pellet was used for both the oxygen and argon anneals. All samples were p-type. Similar electrical behavior has been observed for polycrystalline thin films of CuO prepared by spray pyrolysis[8]. Koffeyberg[9] has reported that CuO can only be prepared as a p-type semiconductor. Recently[10], crystals of CuO have been grown by chemical vapor transport using both $TeCl_4$ and HCl as transporting agents. Crystals grown with $TeCl_4$ have $\rho_{(300\ K)}$ of 10^3 Ω-cm; whereas HCl grown crystals have a value of greater than 10^6 Ω-cm. The lower resistivity for the $TeCl_4$ grown crystals is consistent with the oxidizing environment of free Cl_2. This could result in the oxidation of some Cu(II) to Cu(III) in CuO. The copper(II) oxide crystals grown with HCl are stoichiometric or very nearly so.

The observed electrical properties of CuO indicate that as the amount of Cu(III) is increased, the number of holes is increased. This accounts for the increased conductivity of oxygen annealed pellets and crystals prepared with

$TeCl_4$ as transport agent. Magnetically, CuO shows antiferromagnetic ordering at 230 K. However, the susceptibility continues to increase above the ordering temperature. The p-type semiconducting and antiferromagnetic behavior observed in CuO is consistent with a model proposed by Goodenough[11,12] for La_2CuO_4 in which a correlation splitting was introduced which separates empty σ*-band states of the Cu(II/I) couple from the occupied σ*-band states of the Cu(III/II) couple. If the Cu(III/II) couple is placed below the top of the π* bands, increased oxidation, i.e., a larger concentration of Cu(III), results in increased hole concentration in the π* band. This model has been expanded upon by Wold and Dwight[13] for CuO.

Acknowledgements

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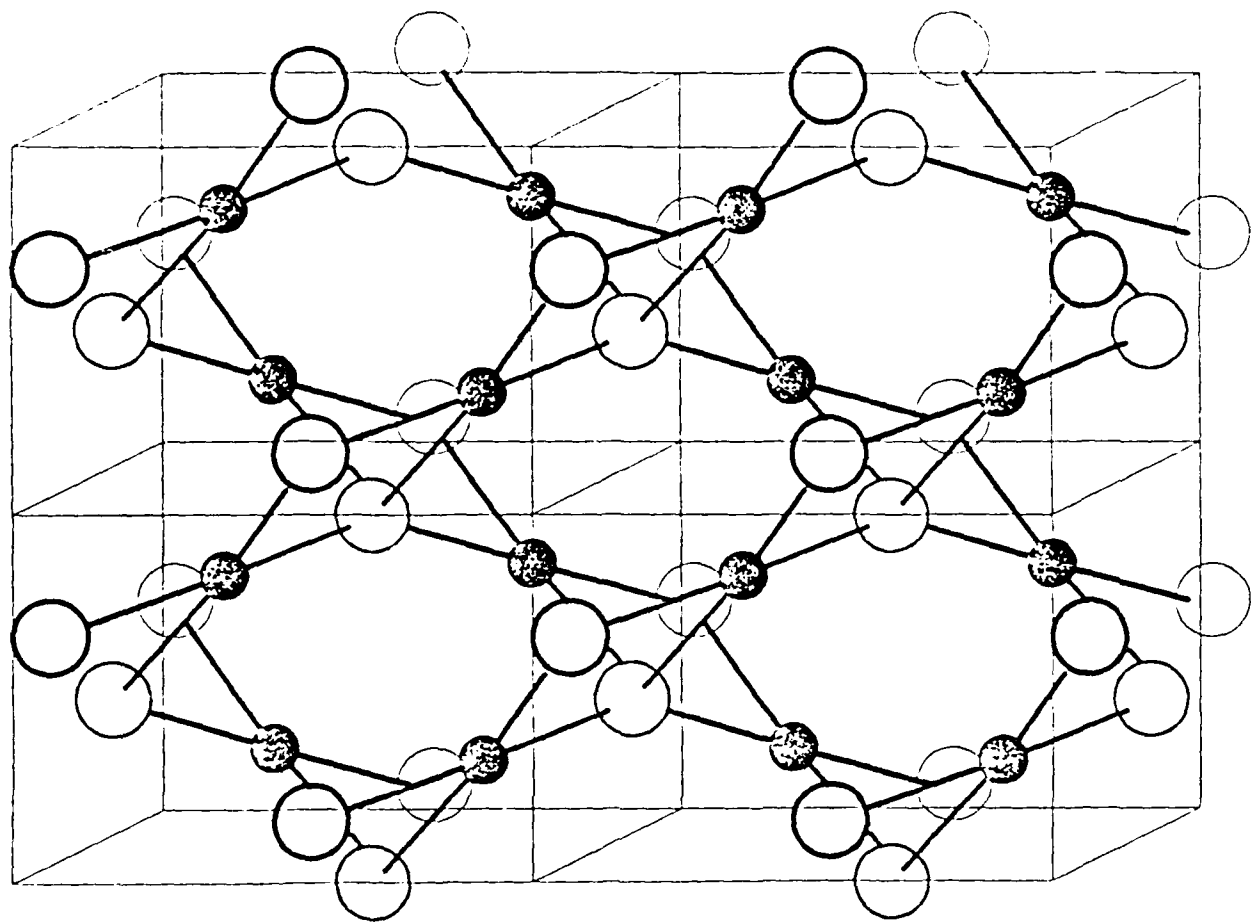11. J. B. Goodenough, J. Mat. Education, 9, 619 (1987).

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Figure Captions

Fig. 1. Structure of copper oxide.

Fig. 2. Comparison of the relative intensities of CuO prepared by
         decomposition of copper nitrate with copper oxide prepared
         from copper metal

Fig. 3. Variation of the magnetic susceptibility with temperature
         for CuO prepared from copper metal and copper nitrate.
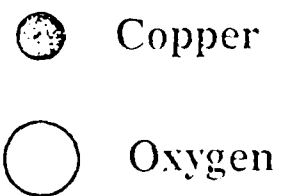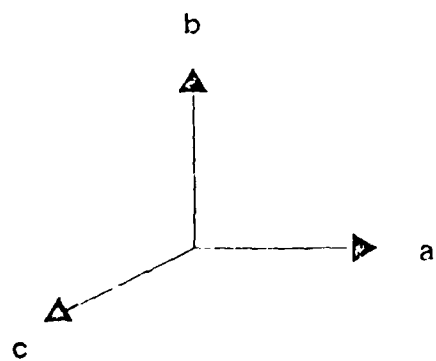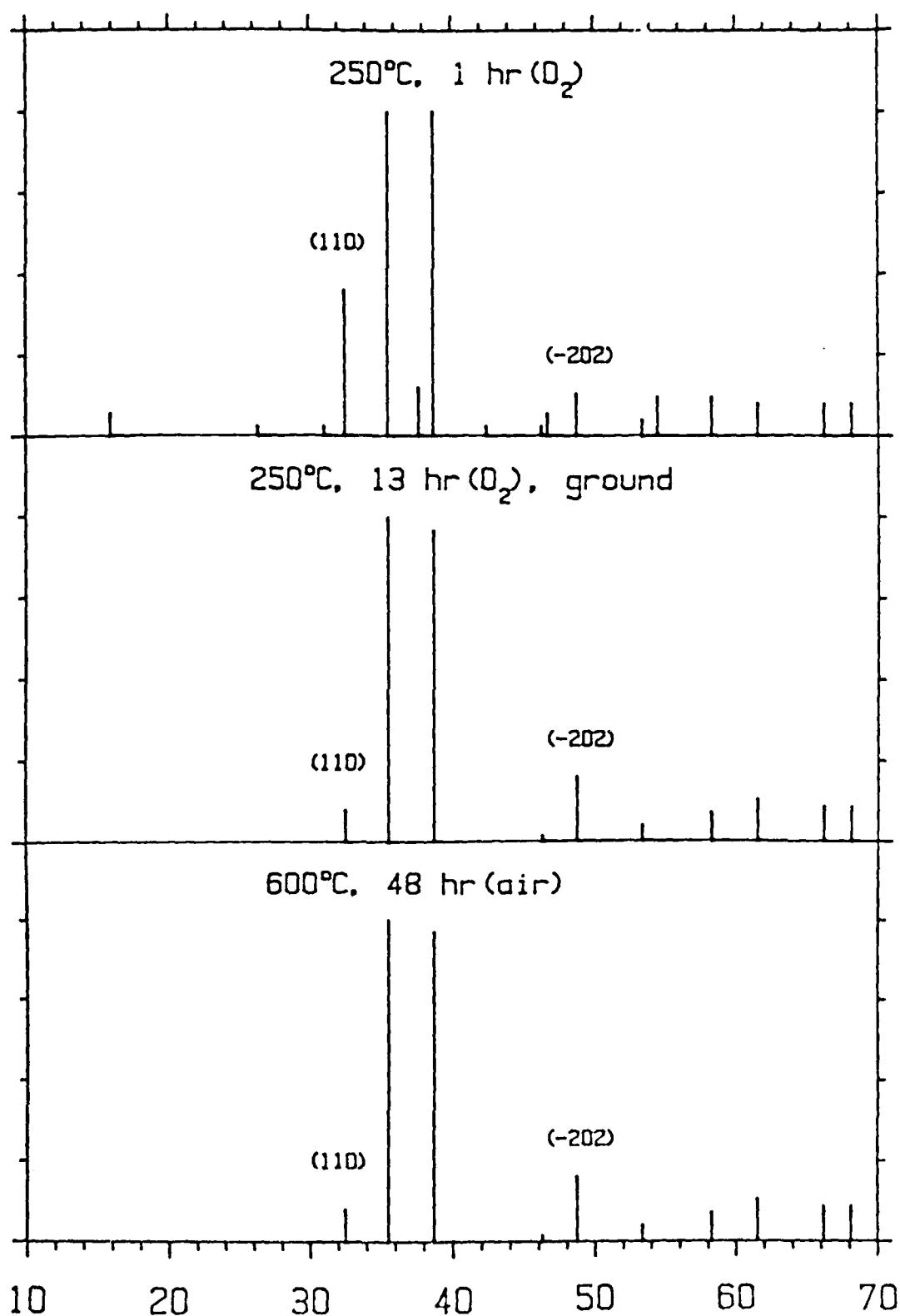
Copper(II) Oxide

Copper

Oxygen

b

a

c

CuO from Nitrate

250°C, 1 hr (O₂)

(110)

(-202)

250°C, 13 hr (O₂), ground

(110)

(-202)

600°C, 48 hr (air)

(110)

(-202)

Relative Intensity

Diffraction Angle 2θ (deg)

CuO

X_M (10^{-3}emu/mol)

Temperature (K)

△ 250°C, 1 hr
◇ 250°C, 4 hr, ground
▱ 250°C, 13 hr, ground
* as made