

On the Synthesis and Characterization of BaCuO_{2+x} ($0 \leq x \leq 0.5$)

SAŠA PETRIČEK, NATAŠA BUKOVEC, AND PETER BUKOVEC*

*Department of Chemistry, University Ljubljana, P.O. Box 537,
61001 Ljubljana, Slovenia*

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Barium cuprates with the general formula BaCuO_{2+x} ($0 \leq x \leq 0.5$) have been prepared from CuO and BaO_2 with various experimental conditions. At 500°C , in an inert atmosphere, a unique X-ray powder pattern has been obtained for $0.29 < x < 0.36$. Increasing temperature and oxygen partial pressure resulted in the formation of $\text{BaCuO}_{2.5}$, which exhibits an antiferromagnetic ordering and undergoes a transition to diamagnetism at about 3 K, probably due to superconductivity. The two phases are unstable at higher temperatures, with formation of cubic BaCuO_2 at 850°C . © 1992 Academic Press, Inc.

Introduction

Ternary oxides containing barium and copper have been studied by several authors. Arjomand and Machin (1) prepared BaCuO_2 by heating CuO and BaO —or BaCO_3 —at 850°C . They suggested the compound to be ferromagnetic at low temperatures. Migeon *et al.* (2) prepared BaCuO_2 from CuO and BaO_2 at 800°C . The mixture was heated in air, first at normal pressure and then at 1.33 Pa. They found a cubic unit cell with $a = 1.826$ nm. Single crystals of BaCuO_2 have been prepared from CuO and $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ (3) at 900°C . The cubic structure consists of complicated polyhedral framework with Cu^{2+} mainly in square planar coordination.

Barium cuprate may contain a nonstoichiometric excess of oxygen (4). BaCuO_{2+x} solid solutions with $0 < x < 0.12$ were obtained at 800°C using various partial pressures of oxygen. The unit cell constant in-

creases with increasing x . BaCuO_{2+x} phases are paramagnetic with a positive Weiss constant and a magnetic moment decreasing as the concentration of $\text{Cu}(\text{III})$ increases. The oxygen distribution in the lattice of cubic $\text{BaCuO}_{2.07}$ (5) was studied by neutron diffraction. A nonstoichiometric cubic phase of the composition between $\text{Ba}_{0.92}\text{CuO}_{2+y}$ and $\text{Ba}_{1.10}\text{CuO}_{2+y}$, with unit cell parameters in the range 18.25–18.33 Å, was found in the BaO – CuO phase diagram study (6).

BaCuO_{2+x} (x not specified) has also been prepared by heating BaCO_3 and CuO in air or in oxygen (7). X-ray powder data could be indexed with either a tetragonal or an orthorhombic unit cell. The compound was paramagnetic but became diamagnetic on cooling down to 82.5 K.

Arjomand and Machin (1) described also $\text{BaCuO}_{2.5}$, which was prepared by heating BaO_2 and $\text{Cu}(\text{NO}_3)_2$ at 580°C in air, or by heating BaCuO_2 at 600°C in oxygen at 4.05×10^7 Pa. The room temperature effective magneton number of 3.06 agreed with an octahedrally coordinated d^8 H.S. copper ion. The authors mentioned even the forma-

* To whom correspondence should be addressed.

tion of $\text{BaCuO}_{2.63}$ —i.e., containing some Cu(IV)—at 500°C under the same oxygen pressure, where some copper(IV) should be formed. It was shown later that X-ray powder pattern of $\text{BaCuO}_{2.5}$ described in Ref. (1) contained also the lines of BaCO_3 (8). $\text{BaCuO}_{2.5}$ could also be formed when a $\text{Ba}(\text{NO}_3)_2/\text{Cu}(\text{NO}_3)_2$ mixture was heated in air at 650°C (9).

Recently, crystal structure of the cubic phase with the stoichiometry $\text{Ba}_{0.92}\text{Cu}_{1.06}\text{O}_{2.28}$ has been redetermined (10). The structure consists of an ordered and a disordered part. The ordered part resembles the structure of BaCuO_2 (3), and is composed of Cu_6O_{12} and $\text{Cu}_{18}\text{O}_{24}$ clusters. The disordered part consists of another two copper–oxygen units with the atomic occupancy factors of 0.20–0.89.

The stoichiometry of barium cuprate depends strongly on the experimental conditions of preparations. The carbonation of barium oxide and the high decomposition temperature of barium carbonate represent additional difficulties in obtaining pure samples. Barium-rich phases, such as $\text{Ba}_2\text{CuO}_{3+x}$ and $\text{Ba}_3\text{Cu}_5\text{O}_{8+x}$, have also been reported in the BaO – CuO system (11). In that case, the difficulties with BaCO_3 were mentioned as well.

In the present work, a number of solid-state reactions were carried out, together with usual characterization studies, to get new data on barium cuprate phases of general formula BaCuO_{2+x} .

Experimental

CuO , prepared by thermal decomposition of $\text{CuC}_2\text{O}_4 \cdot x\text{H}_2\text{O}$ (300°C , 10 hr), was amorphous and more reactive than the commercial, crystalline one. Reagent grade BaO_2 always contained some BaCO_3 . In order to prepare pure BaO_2 the starting material was heated in argon to 1400°C —to decompose all the carbonate—and cooled to 600°C . Then the atmosphere was switched to oxy-

gen, carefully purified from carbon dioxide. The sample was cooled slowly to 550°C and kept at that temperature for 4 hr.

Equimolar mixtures of CuO and BaO_2 were used for the syntheses. The samples were placed in alumina boats and heated in air, free from carbon dioxide or put into alumina tubes, which were sealed in quartz ampules under various pressures of oxygen or argon and heated in tube furnaces at various temperatures.

Thermogravimetric analysis (TGA) was performed with a Mettler TA 2000C thermo-analyzer with alumina crucibles, in argon and air atmospheres. For reduction experiments a mixture of 85 vol% Ar and 15 vol% H_2 was used. The flow rate was of 35 ml/min and the heating rates were 0.7 to 6 K/min. X-ray powder patterns have been recorded with a Guinier de Wolff camera using $\text{CuK}\alpha$ radiation and NaCl as an internal standard. Magnetic susceptibilities have been measured with a Faraday method in a temperature range 3.3–250 K, and at 10 magnetic fields in the range 2.5–17 kOe.

Results and Discussion

All the samples heated between 850 and 950°C in argon or air for various time periods (2 to 40 hr) exhibit the same X-ray powder pattern, which is identical to that reported in literature for BaCuO_2 (1–3). A typical synthesis, carried out in thermoanalyzer under argon atmosphere, is shown in Fig. 1. Thermal decomposition of BaO_2 in the reaction mixture begins already at 320°C and the synthesis is completed at about 850°C . The TG curve for pure BaO_2 , recorded under the same conditions (Fig. 1), shows the beginning of the reaction at about a 200°C higher temperature. The calculated mass loss for the reaction between CuO and BaO_2 to BaCuO_2 (6.43%) agrees well with the experimental one (6.52%). The stoichiometry of each BaCuO_2 sample has also been verified by TGA under reducing atmosphere. The

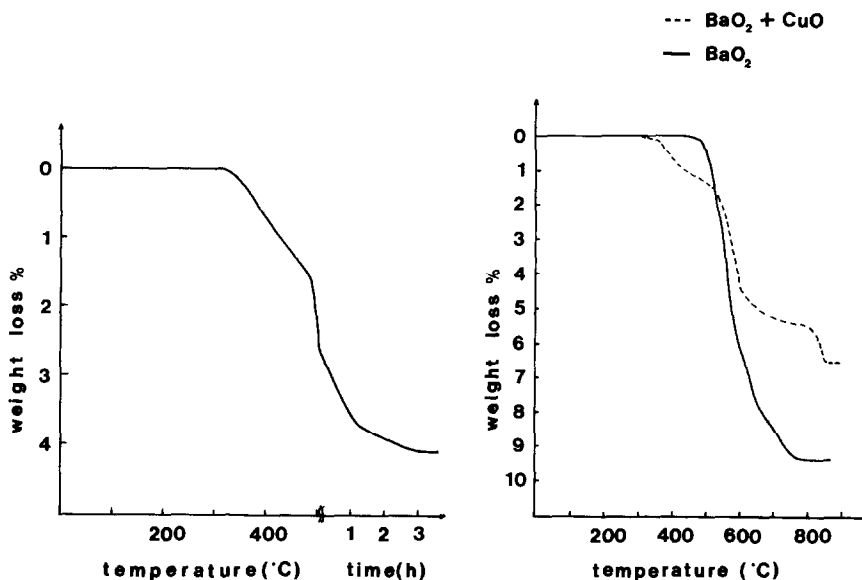


FIG. 1. TG curves for: (left) Synthesis of $\text{BaCuO}_{2.36}$ from BaO_2 and CuO in argon. Heating up to 500°C and isothermally for 3.5 hr; (right) Synthesis of $\text{BaCuO}_{2.5}$ from BaO_2 and CuO in argon (dashed line). Thermal decomposition of BaO_2 in argon (solid line).

best results were obtained for the samples prepared in argon.

The TG curve for the synthesis of BaCuO_2 (Fig. 1) exhibits at least two steps, so a number of trials were carried out in thermoanalyzer to isolate the intermediate phases. Equimolar mixtures of BaO_2 and CuO were heated under an argon flow up to 500°C and kept at that temperature between 1 and 60 hr. Under such conditions, X-ray powder patterns reveal a new phase (Table I). Again, the stoichiometry BaCuO_{2+x} , $x = 0.29\text{--}0.36$, has been determined from TG curves for the synthesis and for the reduction, as illustrated for the composition $\text{BaCuO}_{2.36}$, in Fig. 1. At temperatures above 540°C the lines of BaCuO_2 begin to appear in X-ray powder patterns. The X-ray powder pattern of $\text{BaCuO}_{2.36}$ could be indexed as either tetragonal or orthorhombic as reported in Ref. (6).

In order to increase the oxygen partial pressure mixtures of CuO and BaO_2 were

heated in sealed ampules that were evacuated or filled with argon or oxygen. At 500°C the starting materials did not react completely as shown by X-ray diffraction. The strongest lines of a new phase agreed with the pattern of $\text{BaCuO}_{2.5}$ described by Arjomand and Machin (1). In argon-filled ampules the reactions could be carried to completion in 4 days between 540 and 560°C . The partial pressure of oxygen and the total pressure in ampules were 90 and 385 kPa, respectively. At higher temperatures the mixtures of $\text{BaCuO}_{2.5}$ and the previous mentioned phases were obtained. The mixtures have also been obtained in evacuated (680°C , 4 days) or oxygen-filled ($540\text{--}620^\circ\text{C}$, 4 days) ampules.

Thompson *et al.* (12) mentioned $\text{Ba}_2\text{Cu}_3\text{O}_{5+x}$, which has similar X-ray powder pattern as $\text{BaCuO}_{2.5}$. They calculated a hexagonal unit cell from the powder pattern, however, it was impossible to index all the lines. We repeated the synthesis with a

TABLE I
X-RAY POWDER DIFFRACTION PATTERNS
OF BaCuO_{2.36} AND OF BaCuO_{2.5}

| BaCuO _{2.36} | | BaCuO _{2.5} | |
|-----------------------------|-------------------------|-----------------------------|-------------------------|
| <i>d</i> _{obs} (Å) | <i>I</i> _{obs} | <i>d</i> _{obs} (Å) | <i>I</i> _{obs} |
| 5.145 | 15 | 6.419 | 5 |
| 4.867 | 15 | 5.702 | 15 |
| 4.446 | 80 | 4.701 | 15 |
| 4.227 | 30 | 3.684 | 20 |
| 3.976 | 10 | 3.493 | 45 |
| 3.882 | 10 | 3.096 | 100 |
| 3.232 | 10 | 2.994 | 10 |
| 3.182 | 15 | 2.859 | 50 |
| 3.106 | 90 | 2.587 | 15 |
| 3.024 | 100 | 2.565 | 15 |
| 2.692 | 10 | 2.400 | 15 |
| 2.572 | 15 | 2.323 | 15 |
| 2.544 | 15 | 2.256 | 25 |
| 2.410 | 10 | 2.211 | 10 |
| 2.340 | 20 | 2.151 | 15 |
| 2.222 | 15 | 2.118 | 15 |
| 2.125 | 15 | 2.015 | 15 |
| 2.113 | 15 | 1.958 | 10 |
| 1.980 | 15 | 1.906 | 10 |
| 1.936 | 10 | 1.843 | 10 |
| 1.870 | 10 | 1.695 | 25 |
| 1.790 | 10 | | |

BaO₂:CuO mole ratio of 2:3 and obtained BaCuO_{2.5} and CuO, which remained in excess.

The structural evolution of BaCuO_{2+x}, (0 ≤ x ≤ 0.5) phases resembles that in 123 superconductors. In the cubic unit cell of BaCuO₂ (3) there are 72 Cu atoms in square planar, 12 Cu atoms in square pyramidal, and 6 Cu atoms in trigonal coordination. The structural difference between BaCuO₂ and BaCuO_{2.07} (5) is in the occupancy factor of oxygen O(VI) (0.25 and 0.379, respectively). On incorporation of additional oxygen a part of trigonally coordinated Cu becomes square planar. With an occupancy of 0.5 for O(VI) the stoichiometry of BaCuO_{2.13} could theoretically be reached, without significant structural changes. In fact, the compositions Ba

CuO_{2+x}, with x = 0.0–0.12 (4), were found to be cubic.

Recent study on cubic Ba_{0.92}Cu_{1.06}O_{2.28} (10) reveals strong disordering of Cu and O atoms. Some crystallographic positions occupied by these atoms have low occupancy factors (0.20–0.89), so a wide range of nonstoichiometry could be adopted by the proposed structural model. Further oxidation of copper gives new phases, the structure of which is not known.

Temperature dependence of magnetic susceptibilities for BaCuO_{2.36} and BaCuO_{2.5} are given in Fig. 2. The effective magneton number of BaCuO_{2.5} (1.07 at 250 K and 0.95 at 80 K) lies significantly below the spin-only value expected for an octahedrally coordinated H.S. *d*⁸ ion, in contradiction with the value of 3.06 found by Arjomand and Machin (1). Our magnetic data would suggest that Cu-ions in BaCuO_{2.5} could have different coordination numbers (such as square planar, square pyramidal, octahedral), giving both diamagnetic (L.S.) and paramagnetic (H.S.) Cu(III).

Magnetic susceptibility of BaCuO_{2.5} obeys the Curie law down to about 20 K, where antiferromagnetic coupling sets in. The last measurement at 3.3 K shows an abrupt fall into diamagnetism. Unfortunately, we could not measure electrical conductivity at 3 K to find out whether the negative susceptibility can be ascribed to superconductivity. For BaCuO_{2+x}, with x not specified (6), the change from para- to diamagnetism was found at 82.5 K, however, the temperature dependence was much more smooth.

BaCuO_{2.36} exhibits a temperature dependence of magnetic susceptibility similar to that of NaSrCuO₃ containing about 10% Cu²⁺ (13), where a combination of Curie-type and temperature-independent contributions has been suggested. In BaCuO_{2.36}, the behavior of the susceptibility at about 10 K could be due to the onset of the antiferromagnetic ordering.

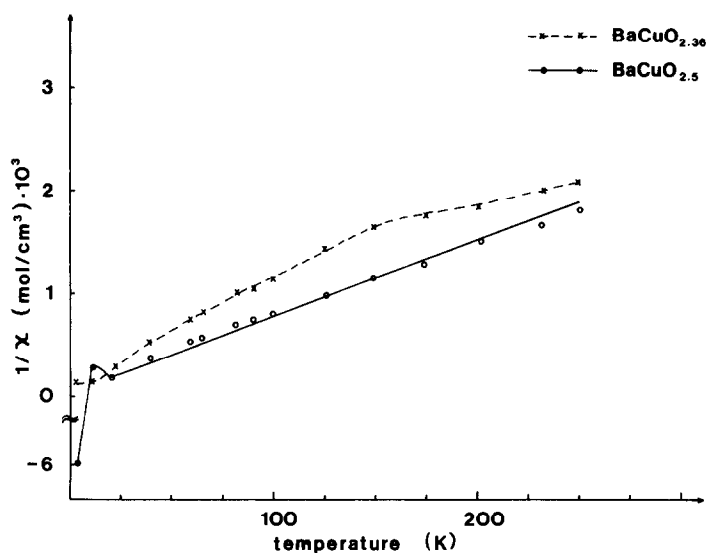


FIG. 2. Reciprocal magnetic susceptibility of $\text{BaCuO}_{2.36}$ and of $\text{BaCuO}_{2.5}$ as a function of temperature.

Conclusion

In summary, reactions between BaO_2 and CuO in equimolar ratio, carried out under various experimental conditions, give three crystallographically different phases. At lower temperatures (500°C), copper oxidizes to give first BaCuO_{2+x} ($x = 0.29\text{--}0.36$). Then the oxidation to $\text{BaCuO}_{2.5}$ occurs at 550° in an oxidative atmosphere. Finally, these phases decompose above 800°C to give BaCuO_2 . Magnetic-susceptibility behavior of $\text{BaCuO}_{2.5}$ suggests a transition to a superconducting state at about 3 K.

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