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Synthesis and Properties of a Compound Barium Copper Oxide Chloride, $Ba_2Cu_3Cl_2O_4$

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Large single crystals of a new oxy-chloride $Ba_2Cu_3Cl_2O_4$ were grown in a $Ba(OH)_2$–KCl flux. Single crystal and powder X-ray diffraction pattern methods show that the compound has the space group, *I*4/*mmm* and unit cell constants $a = 5.519(1)$, $c = 13.834(2)$ Å. Electrical measurements indicate that the compound has metallic behavior in the temperature range between 213 and 273 K. © 1996 Academic Press, Inc.

INTRODUCTION

The discovery of high transition temperature (T_C) superconductivity in cuprates by Bednorz and Muller (1) and its confirmation by Takagi *et al.* (2) as being due to the phase $La_{2-x}Ba_xCuO_4$ led to a world-wide search for other compounds with higher T_C. Cuprates with mixed-valent copper in a formal oxidation state between Cu(II) and Cu(III) has attracted attention recently because several classes of these oxides are high temperature superconductors (3–5). In order to gain a better understanding of the electronic properties of these cuprates it is important to have good model compounds for Cu(II), Cu(III) coordinated to oxygen (6).

A new copper oxide chloride has been crystallized from a $Ba(OH)_2$–KCl flux in ambient atmosphere. Large plate-like crystals up to 1 cm across grew on the surface of the melt and were isolated easily. The compound has been analyzed by the single crystal diffraction and powder X-ray diffraction methods and characterized by electrical resistivity by the four-probe technique.

EXPERIMENTAL PROCEDURES

$Ba_2Cu_3Cl_2O_4$ was prepared from a mixture of 1.0 g of CuO (99.9%), 5.0 g of $BaCl_2 \cdot H_2O$ (99.9%), 14.0 g of $Ba(OH)_2$ (99.9%), and 5.0 g of KCl (99.9%). The anhydrous $Ba(OH)_2$ (99.9%) was used as purchased from Wako Pure Chemical Industries, Ltd., and the $BaCl_2 \cdot H_2O$ (99.9%) (7) was dried at 110°C before use. The powders were mixed intimately, packed in a platinum crucible tightly, and placed in the furnace. The furnace was heated from room temperature to 800°C over 3.0 hr, held at 800°C for 6.0 hr, and cooled gradually to 650°C over 48 hr.

The crucible was then removed and placed in a dry atmosphere. The crystals formed a thick layer on the surface of the solidified melt, and were isolated mechanically. Any flux remaining on the crystals was removed by ultrasonic cleaning in absolute methanol. The crystals were a deep red color.

The ratio of Ba : Cu : Cl was analyzed by electron-probe microanalyses (EPMA, JEOL-JSM-T220). The chloride content was analyzed by a thermogravimetric technique. That is, the sample was heated at a rate of 5°C/min under O_2 gas flow in order to change the chloride sample to an oxide. The resultant oxide sample was analyzed by X-ray powder diffraction and then the chloride content was calculated from the difference in weight between the chloride sample and the resultant oxide.

Single crystal X-ray diffraction by a precession camera (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å in 35 KV 20 mA) and an AFC-5R diffractometer (Mo$K\alpha$ radiation, $\lambda = 0.71073$ Å in 40 KV 25 mA) was used to determine the lattice constants and the Laue group. X-ray powder diffraction was done by an X-ray diffractometer with Cu$K\alpha$ radiation ($\lambda = 1.5418$ Å).

The electrical resistivity was measured from room temperature down to 213 K employing a standard four-probe technique.

RESULTS AND DISCUSSION

Precession photos of single crystals of $Ba_2Cu_3Cl_2O_4$ showed 4/*mmm* Laue symmetry. Single crystal intensity data were collected on an AFC-5R diffractometer. Automatic peak search and indexing procedures yielded a body-centered tetragonal cell which was used for all further

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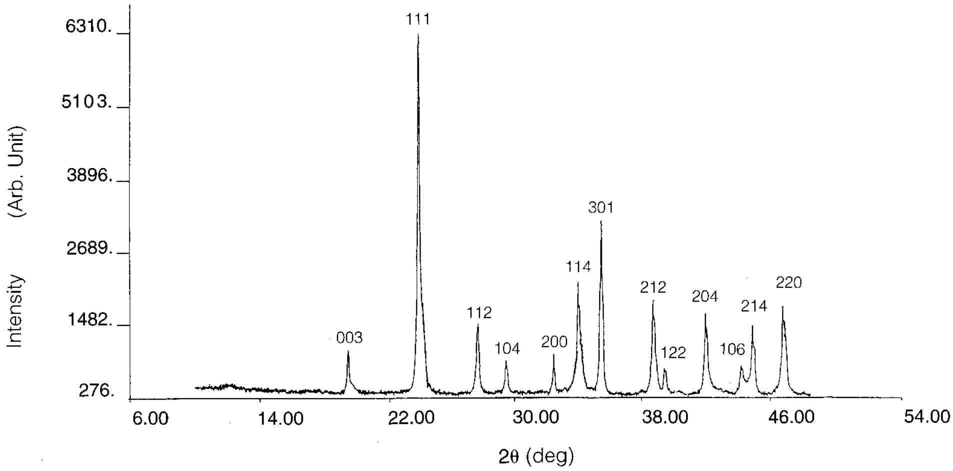

FIG. 1. X-ray powder diffraction patterns of the tetragonal phase $Ba_2Cu_3Cl_2O_4$; Intensity is in arbitrary units.

work. The cell parameters were refined using the setting angles of 24 reflections with $2\theta > 36°$: $a = 5.519(1)$, $c = 13.834(2)$ Å. Systematic absences for reflections with $h + k + l = 2n + 1$ were observed and no other special absences exist. As a result, the structure belongs to the tetragonal system, space group *I*4/*mmm*. The crystal structure will be published elsewhere.

Powder diffraction patterns were also analyzed using the bulk specimen. The indexed X-ray powder diffraction pattern of the $Ba_2Cu_3Cl_2O_4$ sample is shown in Fig. 1. It can be seen in Fig. 1 that the intensity of the (1 1 1) peak is strong compared to the other reflections. All of the diffraction peaks were successfully indexed based on the lattice constants and the space group determined previously.

The electron probe microanalysis (EPMA) showed that the Ba : Cu : Cl ratio in the single crystal sample was 2 : 3 : 2. Figure 2 shows the thermogravimetric (TG) curve of the sample heated under O_2 gas flow. The α-Al_2O_3 was used as a standard. The TG curve shows that the final weight of the sample is 90.83% of the initial weight. Therefore, since the weight ratio between the starting $Ba_2Cu_3Cl_xO_4$ and $Ba_2Cu_3O_5$ (8) was found to be 100 : 90.83, the chemical composition of initial chloride should be given by $Ba_2Cu_3Cl_2O_4$. This result is in good agreement with the EPMA. The results of the present experiments are summarized in Table 1.

Figure 3 shows the smoothness of the plate crystal and the grown crystals. The smoothness of the plate crystals is shown in Fig. 3a; the composition was $Ba_2Cu_3Cl_2O_4$. Figure 3b shows that the plate crystals were grown near the $Ba(OH)_2$–KCl flux surface. The distance from the melt surface to the bottom is about 25 mm, and the temperature at the bottom is slightly higher that at the surface.

Resistivity measurements on a single crystal were made

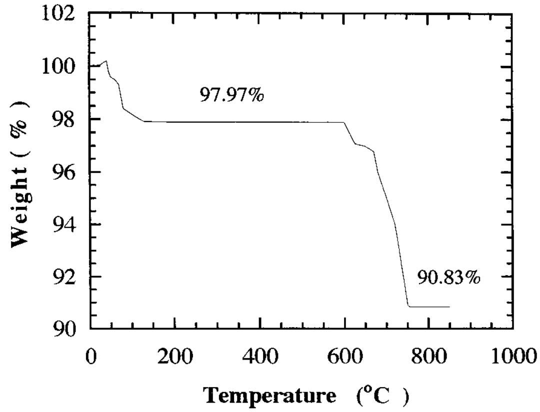

FIG. 2. Thermogravimetric (TG) curve of the $Ba_2Cu_3Cl_2O_4$ sample heated under O_2 gas flow.

TABLE 1
Synthetic Conditions and Results of the Present Experiments

	$Ba_2Cu_3Cl_2O_4$
Flux	$Ba(OH)_2$–KCl
Cooling range (°C)	800 ~ 650
Ion ration of the grown crystal	Ba : Cu : Cl 2 : 3 : 2
Crystal size (cm)	1.0 × 1.0 × 0.3
Crystal color	Deep red
Lattice parameters (Å)	a = 5.519 (1)
	c = 13.8334 (2)
	$\alpha = \beta = \gamma = 90°$
Z	2
V (Å^3)	421.39 (6)
Space group	D_{4h}^{17}

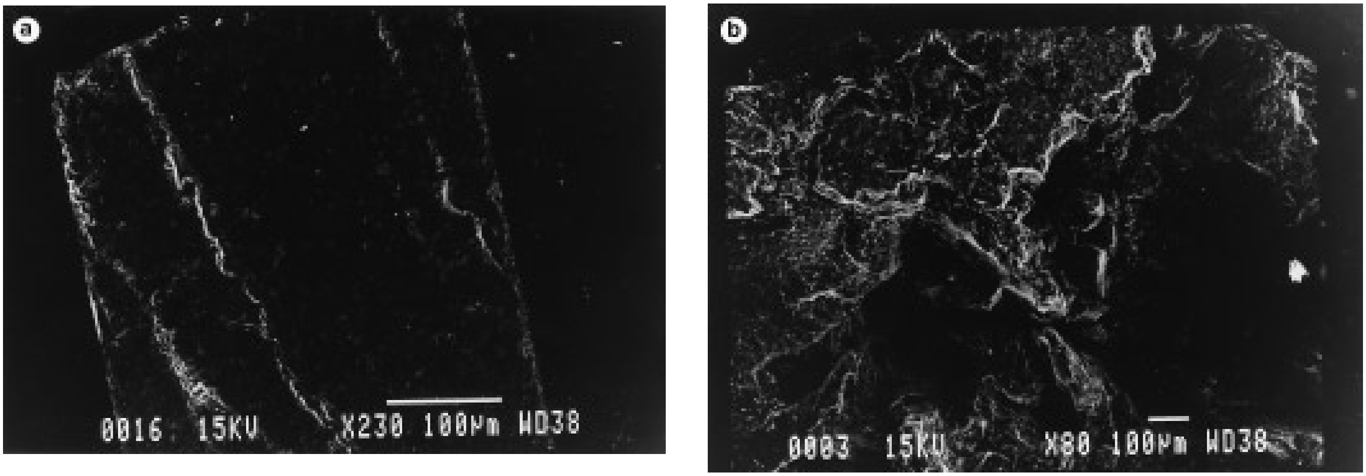

FIG. 3. SEM images of the crystals. (a) The surface of the $Ba_2Cu_3Cl_2O_4$ crystals; (b) The grown crystals as $Ba_2Cu_3Cl_2O_4$ and flux.

using direct current and the four-probe technique. Platinum wires and tungsten electrodes were used. Ohmic contact between the sample and the electrodes was confirmed for all the measurements. The temperature dependence of the electrical resistivity for $Ba_2Cu_3Cl_2O_4$ is shown in Fig. 4. The magnitude of resistivity is on the order of $10^4 \sim 10^{-3}$ Ω:cm and the temperature dependence is metallic

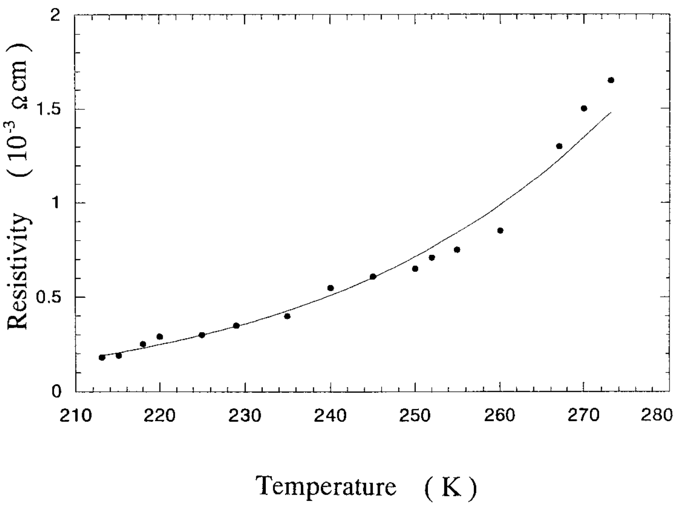

FIG. 4. Temperature dependence of electrical resistivity for $Ba_2Cu_3Cl_2O_4$.

in the temperature range between 213 and 273 K. The resistivity ratio, R_{273K}/R_{213K}, is about 8.2.

In conclusion, we prepared single crystal samples of a new barium copper oxide chloride, $Ba_2Cu_3Cl_2O_4$, by the flux method, and investigated its electrical properties. Because it can be grown easily as large single crystals and without the need for any special condition, we believe the crystals will be useful as standards for the measurement of oxidation states of copper.

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