Formation and Decomposition of BaCuO$_{2.5}$ Prepared from a Mixture of Nitrates

MASATO MACHIDA, KIYOSHI YASUOKA, KOICHI EGUCHI, AND HIROMICHI ARAI

Department of Materials Science and Technology, Graduate School of Engineering Sciences, Kyushu University 39, 6-1 Kasugakoen, Kasuga, Fukuoka 816, Japan

Phase relationships in a Ba–Cu–O system prepared from nitrates or from acetates were determined as functions of calcination temperature. It was first proved that the BaCuO$_{2.5}$ phase, which was known to be obtained only from peroxides, was produced in air at 650°C when a Ba(NO$_3$)$_2$/Cu(NO$_3$)$_2$ mixture was used as a precursor. From iodometric analysis, only the nitrate-derived sample was found to contain exclusively Cu^{3+} ions. This pseudobinary oxide of high oxidation state was decomposed easily into BaCuO$_{2+\alpha}$ ($\alpha = 0.07$) by heating above 700°C or by evacuating at 400°C. © 1991 Academic Press, Inc.

Introduction

The physical and chemical properties of mixed oxides which contain Cu^{+3} have received much attention in relation to the superconducting materials. The instability of Cu^{3+} ions is also expected to lead to interesting chemical activity. However, little is known about the Cu^{3+} species in oxides outside of perovskite-related materials. In the alkaline earth–copper oxide system, several Ba–Cu–O compounds, ACuO$_2$ (A = Ca, Sr, and Ba), are well known (*1*). Although SrCuO$_2$ and CaCuO$_2$ have Cu^{2+} ions with stoichiometric composition, BaCuO$_2$ exhibits oxygen nonstoichiometry due to the presence of Cu^{3+} (*2, 3*). Furthermore,

Arjomand and Machin (*4*) reported that another phase of barium copper oxide (III), BaCuO$_{2.5}$, in which all cooper ions were in the +3 state, could be prepared from a peroxide precursor.

In this communication we report the formation and decomposition of BaCuO$_{2.5}$ from nitrate mixtures. The formation mechanism of mixed oxides is discussed and compared to the phase relationships of the Ba–Cu–O system from some other precursors.

Experimental

The ternary oxide of Ba–Cu–O was prepared from an equimolar mixture of corre-

sponding nitrates and acetates (5). An aqueous solution of the starting materials was evaporated to dryness and then calcined in air at 600–900°C. The crystal phase of the product thus obtained was determined by powder X-ray diffraction with Cu$K\alpha$ radiation. The samples thus obtained were dissolved into a solution of hydrochloric acid and the average oxidation number of copper ion was determined by iodometry (6).

Results and Discussion

Figure 1 shows X-ray diffraction patterns of the Ba–Cu–O system prepared from an equimolar mixture of $Ba(NO_3)_2$ and $Cu(NO_3)_2$. After calcination at 600°C, the melting point of $Ba(NO_3)_2$, the black product solidified from the melt. X-ray diffraction indicated that the product contained not only $BaCuO_{2.5}$ but also unreacted $Ba(NO_3)_2$. The formation of $BaCuO_{2.5}$ was almost complete after calcination at 650°C for 5 hr. With calcination temperatures above 650°C, however, the $BaCuO_{2.5}$ phase disappeared with the simultaneous appearance of $BaCuO_2$. Thus, the $BaCuO_2$ phase was produced via decomposition of $BaCuO_{2.5}$ from the nitrate precursor. Weller and Lines (3) reported the oxygen nonstoichiometry of $BaCuO_2$; the actual chemical composition of an equimolar compound obtained from oxide mixtures in air is $BaCuO_{2.07}$. However, since they have basically the same crystal structure, we simply express the composition as $BaCuO_{2+\alpha}$ ($\alpha = 0.07$) in this communication.

Table I shows X-ray powder diffraction data of two $BaCuO_{2.5}$ samples, i.e., one prepared in this study and the other from a $BaO_2/Cu(NO_3)_2$ mixture as reported by Arjamond (4). Their d-values and peak intensities agree within experimental error. Recently, Thompson et al. (7) disagreed with the existence of $BaCuO_{2.5}$; they proposed that the actual phase of this composition is a mixture of $Ba_2Cu_3O_{5+\delta}$ and $BaCO_3$. They synthesized the $Ba_2Cu_3O_{5+\delta}$ ($0 < \delta < 1.0$) phase at 15–20 atm of O_2, in which the
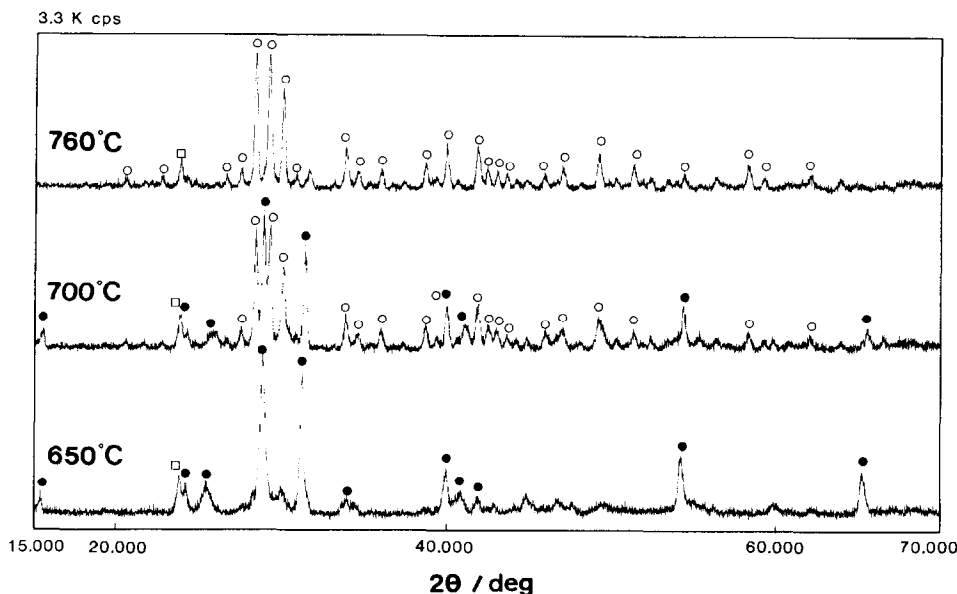

FIG. 1. X-ray diffraction of Ba–Cu–O prepared from nitrate mixtures. ●, $BaCuO_{2.5}$; ○, $BaCuO_2$; □, $BaCO_3$.

TABLE I

X-Ray Powder Diffraction Patterns of BaCuO$_{2.5}$ Prepared from Ba(NO$_3$)$_2$/Cu(NO$_3$)$_2$ and from BaO$_2$/CuO

Ba(NO$_3$)$_2$/Cu(NO$_3$)$_2$		BaO$_2$/CuO[a]	
d_{obs}/A	I_{obs}	d_{obs}/A	I_{obs}
5.72	11	5.71	5
3.73	44	3.72	35
3.67	20	3.66	25
3.50	16	3.50	10
3.42	14	3.47	10
—	—	3.23	5
—	—	3.20	5
3.09	100	3.09	100
2.86	97	2.85	60
2.66	13	2.66	10
2.64	5	2.63	15
2.59	10	2.60	10
2.26	30	2.25	35
2.223	11	2.191	10
2.152	18	2.148	15
2.121	12	2.115	10
2.097	5	2.103	10
2.031	4	2.046	5
2.020	18	2.017	10
—	—	2.003	5
—	—	1.941	5
—	—	1.934	5
—	—	1.854	5
1.838	8	1.829	5
1.691	39	1.687	30
1.428	23	1.426	5

[a] These diffraction data were reported by Ref. (4).

highest average oxidation number of Cu ions is 2.67. However, the sample obtained in this study showed a higher value, ca. 3.0.

When the Ba–Cu–O sample is prepared from acetate precursors, crystal phases in the heating course are quite different from those from nitrate mixtures. Although the decomposition of acetates took place below 600°C to give a mixture of BaCO$_3$ and CuO, formation of mixed oxides was hardly observed up to 850°C. After calcination at 850°C, solid state reaction between BaCO$_3$ and CuO produced BaCuO$_{2+\alpha}$. The BaCuO$_{2.5}$ phase could not be formed from acetate mixtures. We have also examined the phase relationship in the Ba–Cu–O system with other reactants such as carbonates and oxides; the BaCuO$_{2.5}$ phase could not be obtained.

To confirm the presence of BaCuO$_{2.5}$ in the Ba–Cu–O system the oxidation state of copper ions in the sample was analyzed by iodometry. Figure 2 shows the average oxidation state of copper as a function of calcination temperature. The oxidation number of copper in the sample prepared from nitrates was almost 3.0 after calcination at 650°C, in agreement with the X-ray diffraction measurement (Fig. 1), which shows only the single BaCuO$_{2.5}$ phase. The oxidation number decreased with increasing calcination temperatures accompanied by the disappearance of the BaCuO$_{2.5}$ phase. After the decomposition of BaCuO$_{2.5}$ into the single BaCuO$_{2+\alpha}$ phase was completed at 760°C, the oxidation number was almost constant at around 2. On the other hand, the oxidation number of copper ions was constant at ca. 2 and was independent of
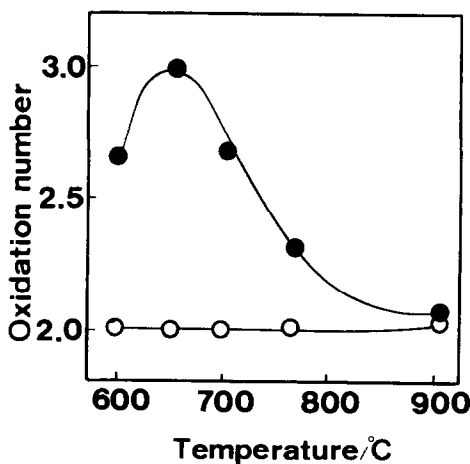

Fig. 2. Average oxidation number of copper ions in the Ba–Cu–O samples. ●, prepared from nitrate mixtures; ○, prepared from acetate mixtures.
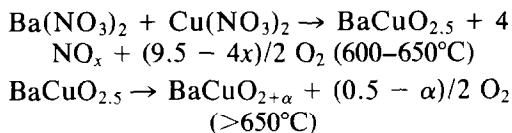
calcination temperatures when the sample was prepared from acetate, carbonates, or oxides.

As Arjamond and Machin reported previously (4), the $BaCuO_{2.5}$ phase is difficult to produce without a strong oxidizer, i.e., BaO_2 as a reactant. For instance, they suggested that ca. 4×10^7 Pa of oxygen pressure is necessary in order to transform $BaCuO_{2+\alpha}$ into $BaCuO_{2.5}$ at 600°C. Thus, our results showed a new and simple preparation route of $BaCuO_{2.5}$. Since the formation of $BaCuO_{2.5}$ was observed only for the nitrate precursors, their decomposition process may play an important role in promoting the oxidation of Cu ions. Field and Hardy (8) showed that the decomposition of $Ba(NO_3)_2$ accompanies the melting and proceeds via the two-step reaction as follows.

$$Ba(NO_3)_2 \rightarrow Ba(NO_2)_2 + O_2$$
$$Ba(NO_2)_2 \rightarrow BaO + NO + NO_2$$
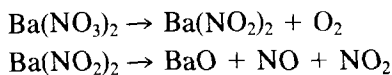
These reactions appear to be effective in attaining the high oxidation state of copper ions because of the strong oxidizing gas, NO_2. In addition, the chemical activity of barium oxide thus produced and homogeneous mixing in the molten state will promote formation of the binary oxides at low temperatures. Consequently, solid state reactions in the Ba–Cu–O system from nitrate mixtures may be expressed as the formation and the decomposition of $BaCuO_{2.5}$ as follows.

$$Ba(NO_3)_2 + Cu(NO_3)_2 \rightarrow BaCuO_{2.5} + 4 NO_x + (9.5 - 4x)/2\ O_2\ (600–650°C)$$
$$BaCuO_{2.5} \rightarrow BaCuO_{2+\alpha} + (0.5 - \alpha)/2\ O_2\ (>650°C)$$

The $BaCuO_{2.5}$ phase produced above 600°C is stable only below 650°C. Decomposition of the $BaCuO_{2.5}$ phase arises from the instability of Cu^{3+} ions at high temperatures. However, the resulting chemical activity, one of characteristics of this compound, is expected to be of use in some catalytic applications.

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