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The Superconductive Compound of the Ba-Y-Cu Oxide

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Synopsis. Chemical composition of a novel compound in the Ba-Y-Cu-O system is determined. Formulae of the phase is $Ba_4Y_2Cu_7O_{14}$. X-Ray powder pattern can be indexed successfully on the basis of an orthorhombic unit cell. Stability of the phase is preliminary studied by a thermogravimetric method.

Recently, superconductivity of oxide compounds has been reported in the Ba-La-Cu-O and Ba-Y-Cu-O systems.[1-3] In the latter system, the resistivity drop sets in at 95 K, above the stability range of liquid N_2.[3] The phase responsible for the superconductivity is, however, not identified. We have synthesized a novel compound as a nearly pure single phase of which resistivity is zero at 77 K. This paper describes the synthesis, stability, chemical composition, X-ray, and resistivity properties of this novel compound in Ba-Y-Cu-O system.

The compound was prepared by mixing the prescribed amount of powders of Y_2O_3, $BaCO_3$, and CuO followed by reacting the mixture at 900 °C for 10—15 h in air. Re-mixing and re-heating for each run were carried out at least two times during the heat-treatment. The compound prepared was pelletized and sintered at 900—950 °C in air.

The crystalline phases were analyzed on a polished section of the sintered specimen with an electron probe microanalyzer, JXA 5A using standard crystals of a synythetic xenotime (YPO_4), polycrystalline CuO and a synthetic $Ba_{0.75}Al_{11.0}O_{17.25}$.[4] Correction procedure used was the Bence-Albee method.[5] Based on the analytical data of the superconductive material, the mixing ratio of Ba, Y, and Cu of the starting material were determined as 4 : 2 : 7 in the atomic ratio.

The X-ray properties of the material prepared were recorded with a diffractometer JEOL TDX-7F using Cu$K\alpha$ radiation with quartz as internal standard. Thermogravimetric analysis was carried out with an thermogravimetor, ULVAC TA 1500, at a heating rate of 10 K min^{-1}. Surfaces of the powdered specimens were observed with a scanning electron microscope, Akashi, DS 130.

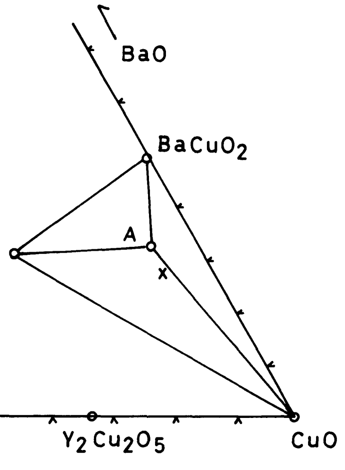

Fig. 1. Phase relations in the BaO-Y_2O_3-CuO system at 900 °C in air. A: $Ba_4Y_2Cu_7O_{14}$. B: $Ba_4Y_8Cu_5O_{21}$.

Figure 1 shows the phase relation in the BaO-Y_2O_3-CuO system at 900 °C in air. Three phases, CuO, $Ba_4Y_2Cu_7O_{14}$, and $BaCuO_2$ exist in the vicinity of the superconduction phase "A". A sintered specimen of the bulk composition X in Fig. 1 consist of CuO, $Ba_4Y_8Cu_5O_{21}$, and the superconductive phase. The chemical compositions of these phases are given in Table 1. These analyses are based on the assumption that the valency of Cu is +2 in these crystals. Y and Ba contents in the crystalline CuO are negligibly small. $Ba_4Y_8Cu_5O_{21}$ has a large and euhedral crystal form. Chemical formula of the superconductive phase may be represented as $Ba_4Y_2Cu_7O_{14}$.

X-Ray powder patterns of the superconductive

Table 1. Chemical Compositions of the Crystalline Phases

	(A)[a)]	(B)[b)]
Y_2O_3	17.56	47.23
CuO	39.01	20.45
BaO	43.30	32.02
Total	99.87	99.70

a) $Ba_4Y_2Cu_7O_{14}$. b) $Ba_4Y_8Cu_5O_{21}$.

Table 2. X-Ray Powder Diffraction Data for the Superconductive Phase

h k l	2θ	d_{obs} / Å	d_{calcd} / Å	I_{obs}
0 0 1	7.54	11.72	11.681	2
0 0 2	15.14	5.847	5.841	2
1 0 0	22.84	3.890	3.886	10
0 1 0	23.21	3.829	3.827	3
1 0 2	27.60	3.2291	3.235	5
0 1 2	27.84	3.2018	3.2008	5
1 0 3	32.55	2.7484	2.7504	63
0 1 3	32.81	2.7280	2.7292	100
1 1 2	36.34	2.4700	2.4705	4
1 0 4	38.53	2.3345	2.3345	10
0 1 4	38.74	2.3224	2.3215	7
1 1 3	40.34	2.2339	2.2334	15
2 0 0	46.71	1.9430	1.9429	15
0 2 0	47.50	1.9125	1.9133	8
1 1 5	51.48	1.7736	1.7740	3
2 1 3	58.22	1.5823	1.5827	21
1 2 3	58.72	1.5710	1.5707	10
2 1 4	62.20	1.4912	1.4899	3
2 2 0	68.80	1.3634	1.3633	8

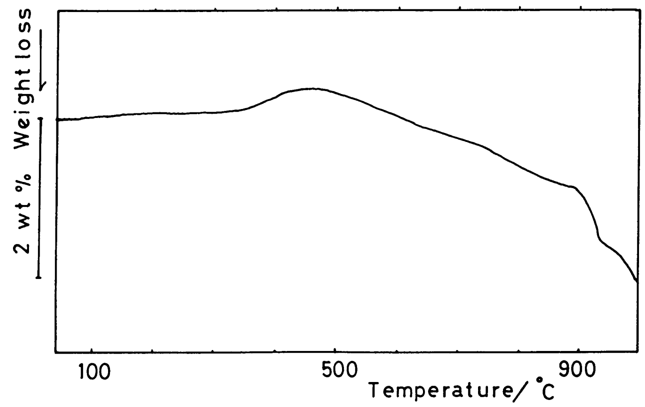

Fig. 2. Thermogravimetric data of the superconductive phase.

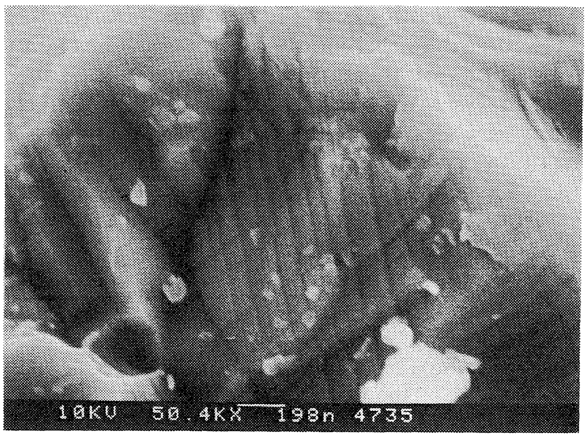

Fig. 3. Scanning electron microscopic image of the superconductive phase. Scale bar: 198 nm.

phase change considerably with heating time. Difference of the lattice parameters *a* and *b* become large with increasing heating time. At the same time X-ray peaks of impurity phases decrease its intensities with increasing heating time. An X-ray pattern of well-crystallized material is given in Table 2, which can be indexed on the basis of orthorhombic unit cell with $a=3.8857(9)$ Å, $b=3.8267(8)$ Å, $c=11.681(4)$ Å. Possible space groups are P222, P*mm*2, and P*mm*. The unit cell dimensions are similar to those of $LaSrVO_4$,[6] and the presence of 001 peak indicates that the crystal symmetry differs from that of La_2CuO_4. The value $c/3$ is similar to those of *a* and *b*, so that this crystal is a distorted cubic phase.

Figure 2 illustrates a thermogravimetric curve of powdered superconductive materials synthesized at 900 °C in air. Weight gain takes place near 400 °C with subsequent gradual weight loss. These weight changes may be due to the change of oxygen content in the specimen. However, further study is needed for the confirmation. Considerable weight losses take place in the two different temperature ranges, namely from 900 to 950 and from 950 to 1000 °C. The former loss is due to partial decomposition of the superconductive phase. The latter one may be due to its partial melting.

Our specimens were obtained at 900 °C in air. The heating temperature is slightly above the decomposition temperature of the superconductive phase. This is a reason why small amount of impurity phases (mainly CuO of about 5—10% by volume) were detected in the X-ray diffraction pattern and on the polished section of the sintered material. A study on the compositional change of the superconductive phase as a function of temperature is now in progress.

A scanning electron microscopic image of the fractured surface of the superconductive crystal is shown in Fig. 3. Fine banding structure was observed in most of the crystals. This structure may be transition twin induced during the transformation of high temperature phase with tetragonal or higher symmetry to low temperature orthorhombic phase.

Electrical resistivity of the superconductive phase has been measured from 65 K to room temperature. The methods of the measurements and the results will be described in detail in near future. The resistivity is several m Ω cm at room temperature. Onset temperature of the superconductivity is 103 K, and the final drop is ended at 85 K.

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