JOURNAL OF SOLID STATE CHEMISTRY 69, 182–185 (1987)

Determination of Cu^{3+}/Cu^{2+} Ratio in the Superconductor $YBa_2Cu_3O_{8-x}$

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Communicated by J. M. Honig, April 27, 1987

The total copper content and Cu^{3+}/Cu^{2+} ratio were determined for three samples of the high-temperature (T_c = 90 to 100 K) superconductor, $YBa_2Cu_3O_{8-x}$, prepared in different laboratories under various final heating conditions. The X-ray diffraction patterns for the samples gave similar orthorhombic unit cell parameters. Iodometric titration and thermogravimetric analysis under hydrogen were used to determine the x-value in the formula $YBa_2Cu^{3+}{}_{3-2x}Cu^{2+}{}_{2x}O_{8-x}$. The final heating temperatures, cooling methods, and x-values from the titration measurements are: 900°C, O_2-annealed/slow-cooled, x = 1.06(5); 950°C, air-quenched, x = 1.35(5); 930°C, air/slow-cooled, x = 1.13(4). The approximate T_c values, taken as onset temperatures from magnetic susceptibility curves, are 93, 98, and 100 K, respectively.

Introduction

In the last year, superconductivity has been reported at temperatures above 30 K in La–Ba,Sr,Ca–Cu–O systems based on the K_2NiF_4 structure (*1–4*), and, most remarkably, above 90 K in multiphase products obtained upon substitution of yttrium for lanthanum (*5–7*). From a careful study (*8*) of the Y_2O_3–BaO–CuO phase diagram, the 90 K superconducting compound was recently identified as $YBa_2Cu_3O_{8-x}$. The unit cell is orthorhombic, and the structure is related to that of $La_3Ba_3Cu_6O_{14.1}$, which adopts a tetragonal defect-perovskite structure (*9*). We report here the determination of total copper and the Cu^{3+}/Cu^{2+} ratio in three different samples, prepared in different laboratories under slightly different conditions, of the high-temperature superconductor $YBa_2Cu_3O_{8-x}$.

Experimental Methods

Sample 1 was prepared by the H. Steinfink/J. S. Swinnea group at the University of Texas, sample 2 by B. L. Chamberland at the University of Connecticut, and sample 3 by T. A. Hewston at the Naval Weapons Center. All the samples were prepared by high-temperature solid-state reactions of Y_2O_3, $BaCO_3$, and CuO in stoichiometric quantities corresponding to the desired metal mole ratio of 1/2/3, respectively. Reactants were ground together using agate mortars and pestles. For sample 1, the reactants were ground with hexane or acetone for 5 to 10 min, dried in air, and heated at 950°C in a Pt crucible for 12 hr in air. After air-quenching, the product was ground for 5 min and heated again for 12 hr; the sample was then annealed under flowing oxygen at 400°C for 8 hr. The furnace was turned off,

0022-4596/87 $3.00

and the sample was removed at room temperature. For sample 2, the reactants were ground together for 30 min and then heated in an alumina combustion boat at 950°C in air for 19 hr. After air-quenching and grinding for 15 min, the product was heated for 6 hr and again air-quenched. For sample 3, the reactants were ground for 30 min and heated in a zircon combustion boat. Three heatings for 13, 6, and 16.5 hr of this latter specimen at 880°C in air, with air-quenching and regrinding between heatings, failed to effect complete reaction, yielding instead mixtures of the desired black product and undesired green Cu^{2+}-based ternary and quaternary oxides (*8*). The temperature was raised to 950°C with a dramatic difference in results: complete reaction appeared to occur in just 6.5 hr; the product sintered extensively, causing a marked shrinkage of the reaction cake into a hard, compacted mass. The product was black, brilliantly polycrystalline, and difficult to grind. After grinding for 15 min, a final heating in air was carried out at 930°C for 10 hr, and the sample was cooled by turning the furnace off.

The samples were identified as $YBa_2Cu_3O_{8-x}$ (*8*) by X-ray powder diffraction using Cu$K\alpha$ radiation (Table I). The data for samples 1 and 2 were obtained at the University of Texas using a Phillips diffractometer fitted with a diffracted-beam graphite monochromator. The data for sample 3 were obtained at the Naval Weapons Center using a Scintag PAD V diffractometer. Samples 1 and 3 are X-ray pure while sample 2 exhibited two weak lines not attributable to the orthorhombic phase.

The superconducting transition temperatures reported in Table I are onset temperatures obtained from magnetic susceptibility measurements using the Faraday method. The T_c for sample 1 was obtained on cooling while those for samples 2 and 3 were obtained during heating through the transition temperature region.

Iodometric titrations were carried out under Ar to prevent air-oxidation of iodide ion. Sodium thiosulfate titrant was standardized against 99.99% pure Cu wire. Starch indicator was added immediately before the endpoint.

$YBa_2Cu_3O_{8-x}$ was subjected to thermogravimetric analysis under flowing H_2/Ar, approximately 0.04/0.50 standard cubic feet per hour, using a DuPont 951 Thermogravimetric Analyzer with a 1090 Thermal

TABLE I

ANALYTICAL RESULTS FOR $YBa_2Cu^{3+}{}_{3-2x}Cu^{2+}{}_{2x}O_{8-x}$

Sample	T_c, K[a]	Å[b]			Volume, Å^3	x_{TGA}[c]	x_{WET}[c]	Formula	%Cu_{obs}	%Cu_{theor}[d]
		a	*b*	*c*						
1 (900°C, O_2-annealed/ slow-cooled)	93[e]	3.824(1)	3.891(1)	11.685(2)	173.86	0.97	1.06(5)	$YBa_2Cu^{3+}_{0.88}Cu^{2+}_{2.12}O_{6.94}$	28.5(2)	28.6
2 (950°C, air/ quenched)	98[f]	3.827(1)	3.885(1)	11.707(2)	174.06	1.33	1.35(5)	$YBa_2Cu^{3+}_{0.30}Cu^{2+}_{2.70}O_{6.65}$	28.0(4)	28.8
3 (930°C, air/ slow-cooled)	100[f]	3.817(1)	3.884(1)	11.681(2)	173.19	1.10	1.13(4)	$YBa_2Cu^{3+}_{0.74}Cu^{2+}_{2.26}O_{6.87}$	28.9(6)	28.7

[a] Superconducting transition temperature at which magnetic susceptibility begins to decrease.

[b] Orthorhombic unit cell parameters obtained by least-squares refinement of X-ray powder diffraction data.

[c] x is the stoichiometry coefficient in the title formula. x_{TGA} is from thermogravimetric analysis and x_{WET} is from iodometric titration. Numbers in parentheses are standard deviations in the last digit from three to five determinations.

[d] Calculated from formula weight derived from iodometric results.

[e] Obtained from cooling-curve data.

[f] Obtained from heating-curve data.

Analyzer control module. Conversion of the sample to Cu, Y_2O_3, and BaO was confirmed by X-ray diffraction. Samples were heated at 10°/min to 1000°C, held there for 30 min, and passively cooled.

Results

The formula for the superconducting compound may be written as $YBa_2Cu^{3+}_{3-2x}Cu^{2+}_{2x}O_{8-x}$, with copper in two oxidation states. When the solid was dissolved in 1 *M* HCl, bubbles of gas were observed. These might arise from the oxidation by Cu^{3+} of water to O_2 or of Cl^- to Cl_2. When the more readily oxidizable Br^- was present, the color of Br_2 was not observed. When I^- was present, no gas was evolved, but I_2 was formed as the solid dissolved. To test the hypothesis that O_2 is liberated when the solid dissolves in HCl, dissolution was conducted under a He atmosphere and the gas phase was sampled by gas chromatography using thermal conductivity detection. Oxygen gas was observed (using a Spherocarb column at 0°C, which separates O_2 and N_2), but no Cl_2 was found (using a glass column containing 5% Carbowax 400 on Anaport Tee Six Teflon support at 10°C).

The Cu^{2+} and Cu^{3+} content of $YBa_2Cu_3O_{8-x}$ was measured by two iodometric titrations. In Experiment A, approximately 25 mg of powder was dissolved under Ar in 7 ml of 1.0 *M* KI/0.7 *M* HCl solution. Cu^{3+} behaves as a two-electron oxidant and Cu^{2+} as a one-electron oxidant:

Experiment A:

$$Cu^{3+}_{(aq)} + 3I^-_{(aq)} \rightarrow CuI_{(s)} + I_{2(aq)} \quad (1)$$

$$Cu^{2+}_{(aq)} + 2I^-_{(aq)} \rightarrow CuI_{(s)} + 1/2I_{2(aq)} \quad (2)$$

The solution was diluted with 8 ml water and the liberated I_2 was titrated with sodium thiosulfate. One mole of thiosulfate corresponds to one equivalent of oxidant in the original sample:

$$2S_2O^{2-}_{3(aq)} + I_{2(aq)} \rightarrow S_4O^{2-}_{6(aq)} + 2I^-_{(aq)} \quad (3)$$

In Experiment B, approximately 30 mg of powder was dissolved in 5 ml of 1.0 *M* HCl in the air and boiled gently for 10 min. As stated earlier, Cu^{3+} reacts with solvent to liberate oxygen and is reduced to Cu^{2+}. Then 10 ml of 0.7 *M* KI was added under Ar and the liberated I_2 was titrated with thiosulfate. In this case, all copper is in the form of Cu^{2+}. It follows that the fraction of Cu in the trivalent state is $(A\text{-}B)/B$ where A and B represent the moles of titrant required per gram of sample in Experiments A and B, respectively. The results for the three samples are presented in Table I.

The reaction in the thermogravimetric experiment is represented by

$$YBa_2Cu_3O_{8-x} + (4.5-x)H_2 \rightarrow 1/2Y_2O_3 + 2BaO + 3Cu + (4.5-x)H_2O$$

The calculated mass loss may vary from 7.292% (x = 1.5, all Cu^{2+}) to 10.55% (x = 0.0, all Cu^{3+}). The x-values so obtained are presented in Table I. A typical thermogravimetric curve is shown in Fig. 1. Note the stepwise loss of mass as the sample is heated and the gradual increase in mass during cooling. The mass increase arises from the reaction of BaO with moisture; therefore, the final weights were taken out near 550°C.

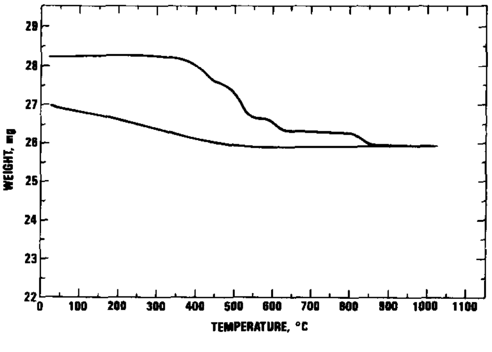

FIG. 1. Thermogravimetric analysis of $YBa_2Cu_3O_{8-x}$ under H_2/Ar. The upper (lower) curve represents the heating (cooling) cycle.

Conclusions

The analytical results obtained from the titration experiments and from thermogravimetric analyses are in good agreement, as can be seen in Table I. Sample 2 has significantly less trivalent copper than samples 1 and 3, but this has little effect on the onset temperature of the superconducting transition observed by magnetic susceptibility measurements. Slow-cooling under either oxygen or air appears to maximize the Cu^{3+} content and favor an x-value close to 1.0.

Acknowledgments

The authors thank Dr. Swinnea and Professors Steinfink and Chamberland for providing samples of $YBa_2Cu_3O_{8-x}$, Joseph H. Johnson for conducting the chromatography experiments, Michael A. Hasting for assistance in the thermogravimetric analyses, and Dr. Charlotte K. Lowe-Ma for obtaining the X-ray diffraction data for sample 3. This work was supported by the Office of Naval Research and the Naval Air Systems Command.

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