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Thermochimica Acta 249 (1995) 295-300

thermochimica
acta

Low temperature intermediate phases in the formation of $YBa_2Cu_3O_{7-x}$ superconductor

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Received 13 December 1993; accepted 13 June 1994

Abstract

The synthesis of $YBa_2Cu_3O_{7-x}$ from Y_2O_3, BaO_2 and CuO has been studied in the temperature range 330–930°C in order to identify the intermediate phases which appear prior to the formation of the Y-123 compound. The first reaction between BaO_2 and CuO in the mixture begins at ≈ 330°C. Barium cuprates of composition $BaCuO_{2+x}$ ($0 \leqslant x \leqslant 0.5$) are formed, with $BaCuO_2$ as the most stable phase. BaO_2 is mainly consumed in these reactions up to ≈ 750°C. Barium cuprates and Y_2O_3 react finally above 750°C, giving $YBa_2Cu_3O_{7-x}$.

Keywords: Barium cuprate; HTS; Phase; Superconductor; Synthesis; TG

1. Introduction

Since the discovery of Y-123 superconductors, there has been a continuing interest in identifying the phases which appear in the course of preparation of the final compound. Isothermal thermogravimetry of the mixture Y_2O_3, $BaCO_3$, CuO in the temperature range 860–950°C reveals various nonstoichiometric phases of general composition $YBa_xCu_3O_y(BaCO_3)_z$ [1]. In a study of reaction mechanism by simultaneous TG, DTG and DTA using the same mixtures, Gadalla et al. [2] observed several steps in the formation of Y-123. In separate experiments, the mixtures were reacted at 800, 850, 900 and 950°C. It was found that $BaCuO_2$ and BaY_2CuO_5 were formed before the formation of Y-123. Parkin et al. [3] postulated that the two phases were formed in disproportionation reactions on cooling the

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SSDI 0040-6031(94)01940-I

samples. The final reaction on heating the mixture of Y_2O_3, $BaCO_3$ and CuO was ascribed to the decomposition of $BaCO_3$, with the formation of a perovskite structure [4]. Oxygen uptake to give $YBa_2Cu_3O_7$ takes place mostly during cooling [5].

In the binary BaO–CuO system, a number of different compounds were identified. $BaCuO_2$ was prepared at temperatures between 800 and 900°C [6–8]. Barium cuprate with an excess of oxygen, $BaCuO_{2+x}$, was prepared at various partial pressures of oxygen [9–12]. $BaCuO_{2.5}$ was obtained by heating a mixture of BaO_2 and $Cu(NO_3)_2$ in air at 580°C [6,13]. Recently, we prepared three crystallographically different phases of general composition $BaCuO_{2+x}$ $(0 < x < 0.5)$ by reacting CuO and BaO_2 under various experimental conditions [14]. Barium-rich and copper-rich phases have also been reported in the BaO–CuO system. Ba_2CuO_{3+x} and $Ba_3Cu_5O_{8+x}$ were prepared at 950°C in air [15]. The compound formulated as $Ba_2Cu_3O_{5+x}$ [16] obtained below 800°C has an X-ray diffractogram similar to that of $BaCuO_{2.5}$ [6]. The high-temperature form, prepared at 940°C, could be indexed with a tetragonal unit cell [16]. X-ray powder data on $Ba_2Cu_3O_{5+x}$ obtained by Thompson et al. [17] have shown that the two forms are structurally related depending on x. For both, incommensurate modulation has been observed.

There is still much uncertainty regarding the formation and composition of the phases that appear in the course of preparation of Y-123. Studies of the final stage in the temperature range 800–1000°C [16] and of oxygen uptake [17] have been carried out, but no data are available on low-temperature reactions.

This work is a continuation of our recent interest [14] in investigating barium cuprates. We have monitored here especially the early stages in the preparation of Y-123 superconductor in order to determine the succession of chemical reactions in the system and the relative stabilities of the corresponding phases.

2. Experimental

Reactive, amorphous CuO was prepared by low-temperature thermal decomposition (300°C, 10 h) of CuC_2O_4. Reagent-grade BaO_2 was purified to remove traces of $BaCO_3$ before use. The starting BaO_2 was heated in argon to 1400°C and cooled to 600°C. The atmosphere was switched to pure oxygen and maintained at 550°C for a few hours. $BaCuO_2$, $BaCuO_{2.36}$ and $BaCuO_{2.5}$ were prepared as described elsewhere [14].

The mixtures $Y_2O_3 + 4BaO_2 + 6CuO$ and $Y_2O_3 + 4BaCuO_2 + 2CuO$ were thoroughly homogenized in an agate mortar in an argon-filled dry-box. The reactions were followed by thermogravimetry (TG) with a Mettler TA 2000C thermoanalyzer in a dry air atmosphere free from CO_2. The samples, in alumina crucibles, were heated at rates of 2–4 K min^{-1} to temperatures between 330 and 930°C and then maintained isothermally for various time periods. Reductive TG measurements were performed in a mixture of 85 vol% of Ar and 15 vol% of H_2. X-ray diffraction patterns were recorded with a Guinier de Wolff camera using Cu $K\alpha$ radiation and NaCl as an internal standard.

3. Results and discussion

A TG curve for the mixture Y_2O_3 + $4BaO_2$ + 6CuO and the results of isothermal treatments are presented in Fig. 1 and in Table 1 respectively. The sample begins to lose mass at $\approx$330°C on dynamic heating. After isothermal treatment of the mixture at 330°C, only the initial substances could be found in the X-ray powder pattern. Pure BaO_2 begins to decompose at $\approx$ 530°C [14]. The low temperature for the start of the reaction in the mixture Y_2O_3 + $4BaO_2$ + 6CuO could probably be ascribed to the catalytic effect of active CuO. Similar effects were found for the mixtures BaO_2 + CuO [14] and Y_2O_3 + $BaCO_3$ + CuO [1], although not explicitly attributed to catalytic consequences.

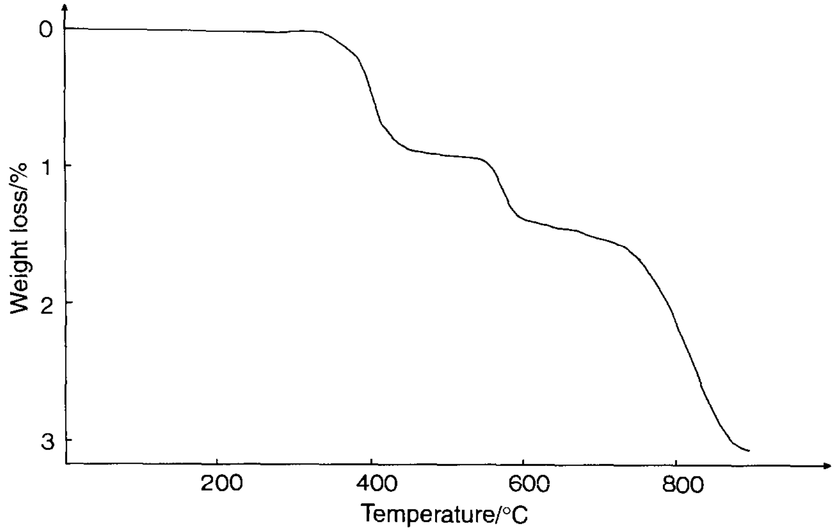

Fig. 1. TG curve for the mixture Y_2O_3 + $4BaO_2$ + 6CuO.

Table 1
Isothermal treatment data of mixture $Y_2O_3 + 4BaO_2 + 6CuO$

Temp. in °C	Time in h	Phases (X-ray)
330	0.5	Y_2O_3, BaO_2, CuO
500	0.5	Y_2O_3, BaO_2, CuO, $BaCuO_{2.5}$
580	0.5	Y_2O_3, BaO_2, CuO, $BaCuO_{2.5}$
750	–	Y_2O_3, BaO_2 (weak), $BaCuO_2$, $BaCuO_{2.5}$
750	0.5	Y_2O_3 (weak), $BaCuO_{2.5}$, $BaCuO_2$, $BaCuO_{2+x}$, Y-123
850	3	$BaCuO_2$, Y-123
850	8	$BaCuO_2$, Y-123
930	6	Y-123

After isothermal treatment of the reaction mixture at 500°C for a short period, the lines of $BaCuO_{2.5}$ appeared in the X-ray powder pattern in addition to those of the initial oxides. At 580°C the result was the same, although with stronger lines for $BaCuO_{2.5}$.

At 750°C $BaCuO_2$ is formed, which can be considered as a decomposition product of $BaCuO_{2.5}$ [14]. A small amount of unreacted BaO_2 could still be identified. Just a short period of isothermal heating sufficed for all barium cuprate phases to appear, together with the Y-123 superconductor, which shows weak lines. Y_2O_3 remained the only oxide not completely reacted.

Carrying out the reactions at 850°C for two different time periods resulted in the formation of $BaCuO_2$ and Y-123. Weaker lines for $BaCuO_2$ and stronger ones for Y-123 were found in the X-ray powder patterns after prolonged heating. The lines of $BaCuO_2$ disappeared finally at 930°C. As the reactions giving intermediate

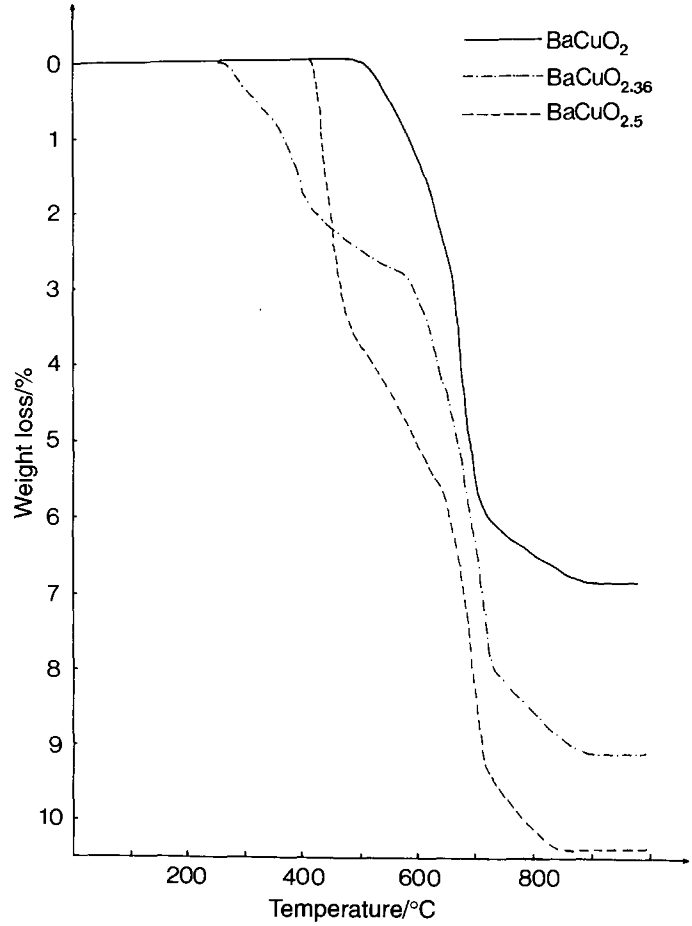

Fig. 2. TG curves of $BaCuO_{2+x}$ phases in a reducing atmosphere (85 vol% Ar, 15 vol% H_2).

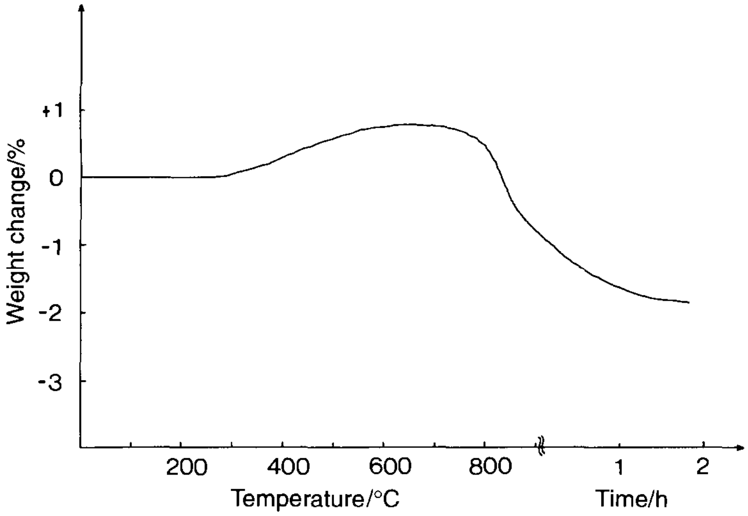

Fig. 3. TG curve of the mixture Y_2O_3 + $4BaCuO_2$ + 2CuO.

phases overlap, the steps on the TG curve (Fig. 1) at ≈ 1.0% and 1.5% mass loss do not correspond to well defined stoichiometries.

For the sample obtained isothermally at 850°C (3 h), a further TG curve was recorded. An uptake of oxygen at lower temperatures and a release at higher ones was observed, as already known for Y-123 superconductor [17].

The phases of general composition $BaCuO_{2+x}$ $(0 < x < 0.5)$ obviously appear prior to the formation of Y-123. The stoichiometry of the phases prepared as already stated in [14], together with their relative stabilities, were determined by recording the TG curves in a reducing atmosphere (85 vol% Ar, 15 vol% H_2) as shown in Fig. 2. The two compounds containing Cu(III) begin to react at lower temperatures, and the second part of their TG curves, which could be ascribed to the reduction of Cu(II), is similar to that of $BaCuO_2$.

Because $BaCuO_2$ is the most stable ternary intermediate cuprate in the system, it was reasonable to use it as a starting material.

The TG curve for the mixture Y_2O_3 + $4BaCuO_2$ + 2CuO recorded in air is shown in Fig. 3. There is a slight uptake of oxygen at lower temperatures, owing to partial formation of $BaCuO_{2.5}$ and $BaCuO_{2+x}$ $(x < 0.5)$; however, the reaction giving Y-123 begins above 700°C. After reaching 900°C the sample was kept isothermally for 3 h to complete the reaction. On cooling the sample slowly, an uptake of oxygen was observed down to 370°C, giving a typical Y-123 compound.

4. Conclusions

The synthesis of Y-123 superconductor from the binary oxides gives first the intermediate phases $BaCuO_{2.5}$, $BaCuO_{2+x}$ $(x < 0.5)$ and $BaCuO_2$, which are formed at lower temperatures. The formation and decomposition reactions of intermediate cuprate phases and those of BaO_2 overlap, so that several phases coexist below 750°C. $BaCuO_{2.5}$ and $BaCuO_{2+x}$ ($x < 0.5$) decompose to form $BaCuO_2$, which reacts afterwards with Y_2O_3 to give $YBa_2Cu_3O_{7-x}$.

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