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A Study on Reaction Mechanism in Preparation of Y–Ba–Cu–O Superconducting Material from the Thermoreaction Method of Nitrates

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X-ray diffraction-coupled thermogravimetric differential thermal analysis (TG-DTA) has been used to study the reaction mechanism in the preparation of Y–Ba–Cu–O superconducting material from the thermoreaction method of nitrates. It is shown that there are three compound phases (Y_2O_3, CuO, $Ba(NO_3)_2$) before decomposition of $Ba(NO_3)_2$ and a mutual chemical reaction immediately occurs as soon as $Ba(NO_3)_2$ decomposes. The superconducting phase begins to form at a temperature of about 650°C and the suitable treatment temperature is between 750 and 800°C, which is much lower than that of the preparation reaction from oxides and/or carbonates. © 1990 Academic Press, Inc.

Introduction

Structures and composition of Y–Ba–Cu–O superconducting material are reported [1–4]. The mechanism of reaction in preparation of $YBa_2Cu_3O_{6.5+\delta}$ from corresponding oxides is also reported [5], but the study on the reaction mechanism in preparation of such material from the thermoreaction method of nitrates is not yet found in literature. The present work studies the thermoreaction of corresponding nitrates in preparation of Y–Ba–Cu–O superconducting material by X-ray diffraction-coupled TG-DTA. The results are important for choosing the best technique in the preparation of $YBa_2Cu_3O_{6.5+\delta}$ from nitrates.

Experimental

Preparation of Samples

According to Y : Ba = 1 : 2, Y : Cu = 1 : 3, Ba : Cu = 2 : 3, and Y : Ba : Cu = 1 : 2 : 3 (mole ratio), the AR grade-corresponding nitrates ($Y(NO_3)_3 \cdot 6H_2O$, $Ba(NiO_3)_2$, and $Cu(NO_3)_2 \cdot 3H_2O$) are weighed, mixed, and ground together, resulting in four samples labeled "1Y + 2B," "1Y + 3C," "2B + 3C," and "1Y + 2B + 3C," respectively.

Method of Measurement

Rigaku D/Max-RA X-ray diffraction equipment was used to study the phase structure of samples, $CuK\alpha$, 40 kV, 50 mA. Thermoflex equipment was used to study the TG-DTA of samples. Experimental conditions: reference material, α-Al_2O_3; sensitivity, ± 100 μV; atmosphere, O_2 (50 ml/min); heating rate, 10°C/min. Standard four-point variable temperature resistance measurements were performed on compacted pellets.

Results and Discussion

TG-DTA curves of starting materials ($Y(No_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$ and $Cu(NO_3)_2 \cdot 3H_2O$) are shown in Fig. 1.

From Fig. 1a, we can see that $Y(NO_3)_3 \cdot 6H_2O$ begins to lose crystallized H_2O. At very low temperature, it has lost 6 moles H_2O up to 250°C. $YONO_3$ [6] is formed be-

FIG. 1. TG-DTA curves of starting materials. a, $Y(NO_3)_3 \cdot 6H_2O$; b, $Ba(NO_3)_2$; c, $Cu(NO_3)_2 \cdot 3H_2O$.

tween 397 to 469°C (weight loss, 56.4%; theoretical value, 56.4%). The endothermic peaks of DTA (482 and 534°C) correspond to the decomposition of $YONO_3$. Up to 560°C, samples weight is constant (see TG line, weight loss, 70.6%; theoretical value, 70.5%); however, it is shown that $Y(NO_3)_3$ finally decomposes to Y_2O_3.

It can be seen from Fig. 1b that the weight of $Ba(NO_3)_2$ is constant before 590°C. At 581°C the endothermic peak of DTA corresponds to the phase transition of $Ba(NO_3)_2$ [7]. It begins to melt and decompose at 591°C (endothermic peak), followed by further decomposition (endothermic peak at 640°C). Up to 749°C, the peak of thermoreaction disappears and the weight is constant. Total weight loss is 41.2% which agrees with the theoretical value (forming BaO, weight loss 41.3%). The endothermic peak at 810°C corresponds to the BaO phase transition.

$Cu(NO_3)_2 \cdot 3H_2O$ gradually loses H_2O above room temperature. The endothermic peak at 116°C corresponds to melting and decomposition, followed by several endothermic peaks corresponding to further decomposition [8]. Weight is constant after 300°C and the total weight loss is 67.2%, which agrees with the theoretical value (forming CuO, weight loss, 67.1%; see Fig. 1c).

TG-DTA curves of samples 1Y + 2B, 1Y + 3C, 2B + 3C, and 1Y + 2B + 3C are shown in Fig. 2. It can be seen from Fig. 2a that the weight of sample 1Y + 2B is constant after 744°C. sample 1Y + 2B is heated at the rate of 10°C/min in O_2 (30–40 ml/min) to 750°C for 6 hr, in order to observe the changes of phase structure in the sample during heating. As a result, we obtain a new sample YB-12 which includes two compound phases (BaO_2 and $Ba_3Y_4O_9$) identified by XRD. It is shown that the two substances ($Y(NO_3)_3 \cdot 6H_2O$, $Ba(NO_3)_2$) undergo a combining reaction during heating to form the new compound phases.
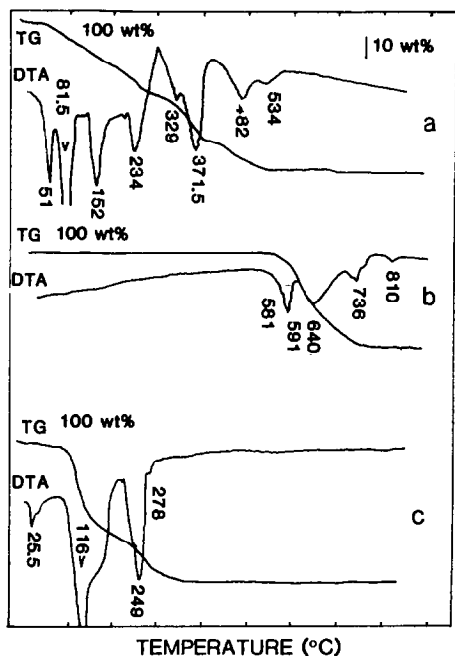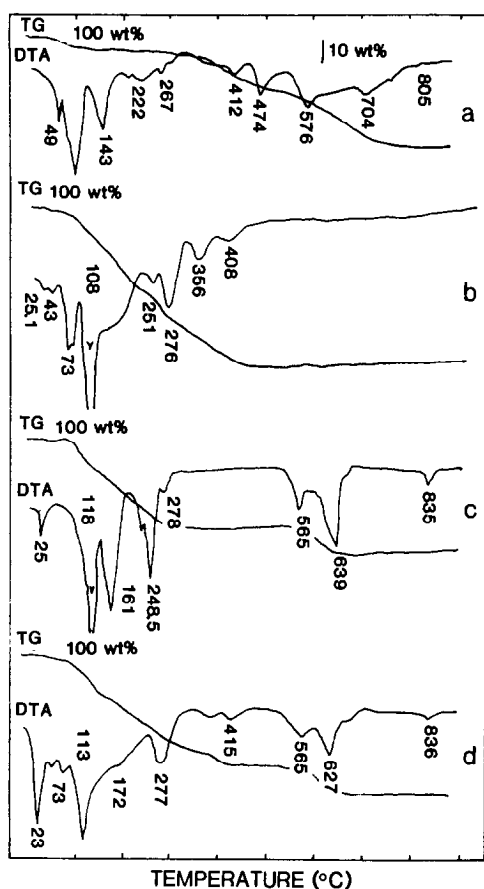
FIG. 2. TG-DTA curves of samples. a, 1Y + 2B; b, 1Y + 3C; c, 2B + 3C; d, 1Y + 2B + 3C.

From Fig. 2b, we can see that the weight of sample 1Y + 3C is constant after 450°C. The sample was treated in 450°C for 6 hr, using the heating procedure mentioned above to give a new sample YC-13. YC-13 includes two compound phases (Y_2O_3, CuO), which are the same as the individual nitrate decomposition products (to give Y_2O_3 or CuO). We conclude that the two salts do not undergo a mutual reaction during the above heating procedure.

The test results of sample 2B + 3C are shown in Fig. 2c. It is obvious that the sample decomposes in two steps: first, $Cu(NO_3)_2 \cdot 3H_2O$ loses H_2O and decom-

poses to form CuO. The horizontal TG curve corresponding to $2CuO + 3Ba(NO_3)_2$ which is detected between 290 and 540°C. Then, $Ba(NO_3)_2$ begins to decompose after 543°C, giving several endothermic peaks; the position and shape of the peaks are different from those depicting, individual $Ba(NO_3)_2$ decomposition. It is shown that the two compounds react together. After 660°C the weight is constant. XRD results of sample BC-23 (2B + 3C treated 6 hr at 700°C in O_2) show that the two salts have formed a new compound phase ($BaCuO_2$) and the XRD pattern includes a few diffraction lines—which are not identified—called the unidentified transition phase.

TG-DTA curves of sample 1Y + 2B + 3C are shown in Fig. 2d. The peaks of DTA before 565°C correspond to the loss of crystallized H_2O and the decomposition of $Y(NO_3)_3 \cdot 6H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$, because the decomposition temperature of $Ba(NO_3)_2$ is about 590°C. A CuO, Y_2O_3, and $Ba(NO_3)_2$ mixture is formed after 400°C, which is identified by XRD. The weight of sample 1Y + 2B + 3C is constant after 662°C, and it is estimated that the mutual chemical reaction immediately occurs as $Ba(NO_3)_2$ decomposes. In order to determine the reaction of the sample in a different range of temperatures, we treated the sample in O_2 (30–40 ml/min) for 6 hr at six different temperatures (400, 500, 600, 700, 800, 900°C); then the XRD method was used to identify the yield phases. The typical X-ray diffraction patterns of samples treated under 600, 700, 800, and 900°C, are shown in Fig. 3. XRD patterns of samples treated at 400 and 500°C are not given here.

It can be determined from our experimental results that the samples treated for 6 hr at 400 or 500°C include $Ba(NO_3)_2$, CuO, and Y_2O_3 compound phases; some unidentified phases can be detected also. Samples treated at 600°C still include CuO and Y_2O_3, but not the $Ba(NO_3)_2$ compound phase; the superconducting phase YBa_2
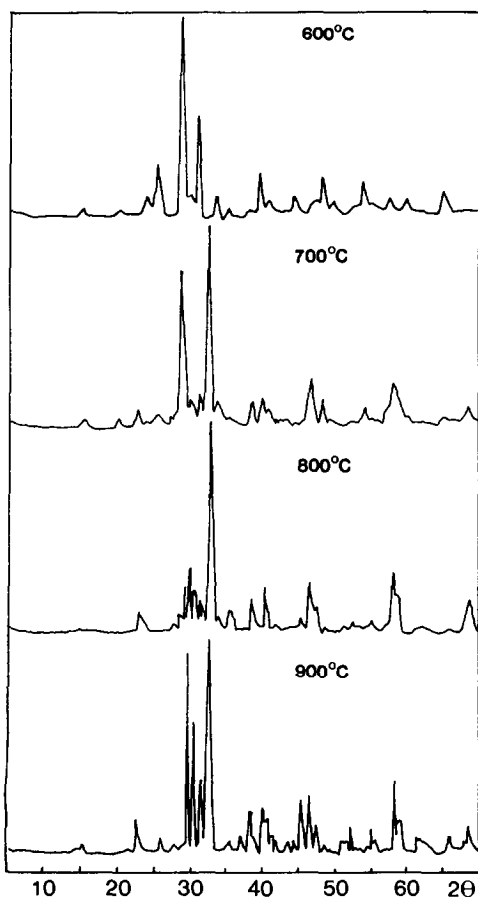
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FIG. 3. X-ray diffraction patterns of sample 1Y + 2B + 3C treated under different temperatures.

$Cu_3O_{6.5+\delta}$ is also not detected. It is shown that the superconducting phase cannot be formed at 600°C (Fig. 3).

The superconducting phase is formed obviously for the 700°C-treated sample (Fig. 3b). For the 800°C-treated sample, the main X-ray diffraction lines belong to the superconducting phase, but nonsuperconducting phases (mainly Y_2BaCuO_5) can also be detected (Fig. 3c). The content of the nonsuperconducting phase for the 900°C-treated

sample is higher than that for the 800°C-treated sample; all of the samples include some unidentified compound phases. It can be concluded from our present work that the 800°C-treated sample includes a higher content of superconducting phase than others.

Our experiments show that by using a suitable technique (treating temperature held at 800°C for 6 hr, and slowly cooling down followed with O_2), we can produce the superconducting pellet (closed to $YBa_2Cu_3O_{6.5+\delta}$ single phase) with zero resistance temperature ($T_{R=0}$) 90 K and onset temperature (T_o) 93 K. The heat treatment temperature cannot be higher than 900°C, otherwise the percentage of Y_2BaCuO_5 will increase. The superconducting phase begins to form at a temperature of about 650°C and is mainly obtained between 750 and 800°C, which is much lower than that of the preparation reaction from oxides and/or carbonates (~900°C), and the reaction rate is also much faster than that of the preparation reaction from oxides.

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