Thermochimica Acta, 124 (1988) 147–156
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THERMOANALYTICAL INVESTIGATION OF THE $(YBa_2)_2Cu_6O_y$ SUPERCONDUCTOR. I. REACTIONS FORMING THE SUPERCONDUCTOR AND ITS PHASE CHANGES

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(Received 28 April 1987)

ABSTRACT

Thermogravimetry (TG)–differential thermal analysis (DTA) and high-temperature microscopy studies of oxalates of yttrium, barium and copper have been made to investigate the formation processes of the $(YBa_2)_2Cu_6O_y$ superconductor. TG, DTA and high-temperature X-ray diffractometry were also used to observe phase changes of the superconductor. The final process in the formation of the superconductor has been elucidated and a phase transition accompanied by oxygen sorption was observed in addition to fusion. The equilibrium content of the oxygen sorption was measured by isothermal TG.

INTRODUCTION

Since the recent discovery of the Y–Ba–Cu–O superconductor [1], tremendous effort has been devoted to investigation of this substance, because it shows superconductivity above the temperature of liquid nitrogen. Many reports were presented in historical ad hoc meetings held in New York [2], Nagoya [3] and Tokyo [4]. However, these reports are inconsistent with each other, especially with regard to the synthetic methods, such as the heat treatment [5]. We have thus carried out a thermoanalytical investigation of the synthetic processes and phase changes by simultaneous thermogravimetry and differential thermal analysis (TG–DTA), DTA, X-ray diffractometry and high-temperature microscopy; the results are reported herein.

EXPERIMENTAL

Samples

The superconductor, $(YBa_2)_2Cu_6O_y$, was made by the following processes. A mixture of $BaCO_3$, Y_2O_3 and CuO in the above atomic ratio was ground

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in a mortar and the powder was sintered at 930 °C for several hours. This process was repeated. Pellets of the sintered sample were annealed at 900 °C for several hours. Then, they were cooled in the furnace to ambient temperature to obtain the superconductor. The superconductor sample used for thermal analysis was taken from a batch whose superconductivity had been demonstrated. The sintered sample without annealing was also used, but it is a powder and its superconductivity was not tested. To observe the reactions forming the superconductor, a TG–DTA study was made for an oxalate of yttrium, barium and copper, which was made by co-precipitation [6]; i.e., addition of oxalic acid solution to a solution containing nitrates of yttrium, barium and copper in the above atomic ratio. The precipitate was washed with water, so that it is probably oxalic acid free.

Apparatus

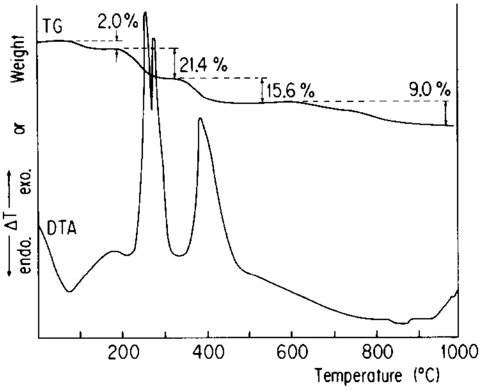
A TG–DTA apparatus made by Rigaku Denki Co., Ltd. was used with a platinum open shallow pan (2 mm depth and 5 mm diameter) for the decomposition of the oxalate and with a platinum open container (5 mm depth and 5 mm diameter) for the other experiments. A Perkin–Elmer DTA 1700 was also used in the differential scanning calorimetry (DSC) mode with a platinum container (7 mm depth and 5 mm diameter). High-temperature X-ray diffraction apparatus (JDX-10PA manufactured by JEOL, Ltd.) was applied with Cu K_α to confirmation of the phase transitions. Observation by high-temperature microscopy with an infrared heating hot stage (Shinku Riko Co., Ltd. Superoven SO-100) was applied to the process forming the superconductor from the oxalate, and chemical analysis of the products was made by energy dispersion X-ray analysis (EDX) together with scanning electron microscopy (EDAX International, Inc.).

RESULTS AND DISCUSSION

Thermal decomposition of oxalate by TG–DTA

Typical results of the TG–DTA study of thermal decomposition of the oxalate at 15 °C min^{-1} under oxygen flow are shown in Fig. 1. A little weight loss (2% of the initial sample weight) around 100 °C is presumably due to dehydration. Two stages of decomposition with 21.4% weight loss were observed in the temperature range 250–320 °C, and one stage weight loss of 15.6% was observed in the temperature range 380–430 °C. These three reactions are considered to be thermal decomposition of the oxalate, because they are all exothermic reactions due to combustion of volatilized carbon monoxide to carbon dioxide. Assuming that the original sample is neutral oxalate, $Y_2Ba_4Cu_6(C_2O_4)_{13}$, and the product is $Y_2Ba_4Cu_6O_{14}$, the

(a) overview



(b) high temperature range

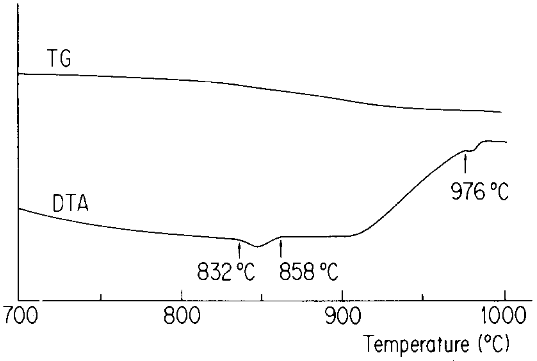


Fig. 1. A typical TG–DTA curve of thermal decomposition of oxalate of Y, Ba and Cu (atomic ratio 1 : 2 : 3): (a) overview; (b) high temperature range.

ratio of the product to the original sample is about 59%. Otherwise, oxy-oxalates and/or hydroxy-oxalates are contained in the oxalate sample, and the ratio is more than 59%. On the other hand, the observed ratio is 62% and roughly in accordance with the above ratio. Therefore, it is concluded that the product is almost oxide, which may contain some carbonate, especially thermally stable barium and yttrium carbonates, and the three stage exothermic decomposition is direct thermal decomposition from the oxalate to the oxide.

Thus, the thermal decomposition of this oxalate is quite different from thermal decompositions of ordinary oxalates, such as barium oxalate hemihydrate [7–10] and calcium oxalate monohydrate [11,12]. These latter two compounds undergo three stages of endothermic decomposition; i.e., dehydration, decomposition of the oxalate to the carbonate and its decomposition to the oxide. Thermal decomposition of yttrium oxalate is also a multistage decomposition [13]. On the other hand, copper oxalate is decomposed directly to copper oxide in one stage [7,14].

Changes in high temperature range

In the higher temperature range 800–990 °C, 9.0% of the initial sample weight was volatilized. The mechanism of this process is not clear. However, on the basis of the above we suggest that it is partly volatilization of the metallic components from the oxide.

A broad endothermic peak from 823 to 858 °C without a distinctive corresponding weight loss is also unexplained from the above experiments alone, and it does not appear reproducibly on repeated heating and cooling, or on keeping the sample at 790 °C for about one day. This process will be discussed below together with other experimental results.

In the final stage of TG–DTA of the oxalate sample, a small sharp endothermic peak was observed at 976 °C, as shown in Fig. 1. This peak is not accompanied by weight loss, and it is reproducible on repeated heating and cooling. On cooling, double peaks were observed in a lower temperature range. Therefore, it can be assigned to a phase change.

In the high-temperature microscopy study, a change in appearance was observed for the oxalate in an oxygen flow at a heating rate of 50 °C min^{-1}. Blackening of the oxalate, began abruptly at about 270 °C, and the volume of the sample decreased to 3/4 of the initial volume. Then, the blackening and the shrinkage of the sample continued gradually up to 900 °C. Finally, the volume decreased to 1/10 with weight loss of 47%, and some greenish black particles were observed, presumably due to formation of an insulating phase [5], although the main phase is the black phase.

High-temperature microscopic observation was also done by keeping the oxalate sample at 762–774 °C for about 5 h and at 866–876 °C for 5 h. In both cases, the same black products were obtained and the weight losses (48%) are also the same as the TG results and the above dynamic observation. However, when the sample was kept at 966–975 °C, the product became partly transparent, and some of the transparent product crept up the wall of the platinum container and flowed out. Chemical analysis with scanning electron microscopy (EDX) was applied to the product, and its barium content was found to be increased in the transparent part, while the yttrium content was increased in the black part. These facts suggest that melting and decomposition of the superconductor occur in this temperature range.

Formation of perovskite structure

The superconductor sample and the other sample without the annealing were both investigated by TG–DTA at 15 °C min^{-1} in ambient atmosphere; typical results are reproduced in Fig. 2. A peak was observed around 800 °C for both samples, and it is similar to the broad peak around 840 °C observed for the decomposition product of the oxalate. These peaks can be observed

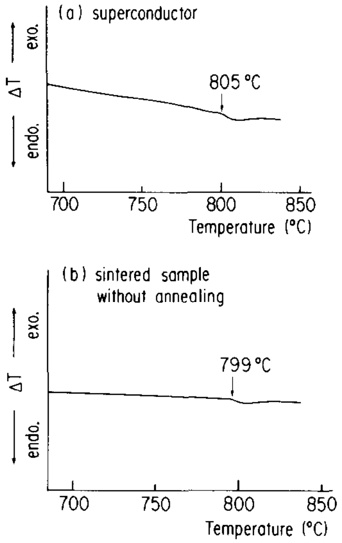


Fig. 2. DTA curves of superconductor sample and sintered sample without annealing.

only at the first heating and cannot be observed in repeated heating and cooling. After keeping the sample below this temperature range for about one day, it was heated at a rate of 15 °C min^{-1}, but the peak was not observed. The process seems irreversible. Moreover, the peak of the superconductor sample is the smallest, while the peak of the decomposition product from the oxalate is the largest. Furthermore, this process did not accompany distinctive corresponding weight loss in the temperature range of the DTA peak, and appreciable weight change was not observed after the experiments except for the oxalate sample, for which the weight loss began before the DTA endothermic peak and continued after the peak. It is deduced that this endothermic peak is related to the reaction forming the superconductor, i.e., the ordered perovskite crystal, from the precursor oxide.

DTA observation of this endothermic peak is considered to be a powerful tool for characterization and quality control in the future production of this material, because the peak area becomes small with increase in the conversion. To elucidate the kinetics of this reaction, such as the activation energy, further investigation is required, for instance by DSC at different heating rates [11,15].

It is also interesting to note that 9.0% weight loss was observed for the decomposition product of the oxalate, while little weight loss was detected for either the superconductor sample or the sintered sample. Thus, it may be concluded that the superconductor is much more thermally stable, both in physical structure and in chemical composition, than the precursor oxide, for which weight loss occurred, presumably due to volatilization of the metallic component.

Phase transition of perovskite crystal

In the above experiments, it was noticed that the low weight loss occurred reversibly for the superconductor sample and the sintered sample, and the weight was not changed after the experiments, so this process appears reversible. The weight difference between 800 ° C and ambient temperature is roughly 1.1–1.2%, which corresponds to approximately one oxygen atom per $(YBa_2)_2Cu_6O_{14}$. To confirm this, TG experiments were made in stepwise heating and cooling mode. The results are shown in Fig. 3. As clearly shown in this figure, the sample weight is constant in the isothermal part of the experiments. The weight loss of the sample from the initial weight was measured at the end point of the isothermal observation, and it is plotted against the temperature in Fig. 4.

The weight loss by stepwise heating is in agreement with the weight gain by stepwise cooling. Therefore, this process is thought to be reversible oxygen absorption, and the weight plotted in this figure is considered to be the equilibrium weight, but the equilibrium oxygen content cannot be calculated, because the exact original oxygen content was not known. As is clearly seen in Fig. 4, the temperature dependence of the oxygen content can be divided into three regions; constant oxygen content below about 445 ° C, linear temperature dependence above 520 ° C, and curved temperature dependence between them. Thermodynamic data, such as the partial free energy of oxygen, will be obtained by precise TG under controlled oxygen partial pressure [16].

In the DTA curve of the superconductor sample, a thermal change, such as change in heat capacity, was observed at 431 ° C on heating, and also a similar change at 619 ° C on cooling (both at 5 ° C $\min^{-1}$): they are shown in

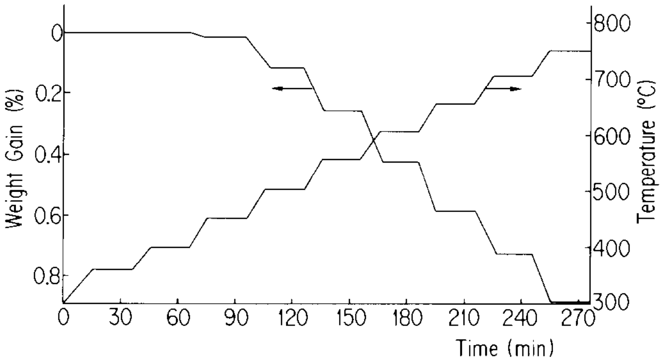


Fig. 3. A TG curve of superconductor sample by stepwise heating and cooling.

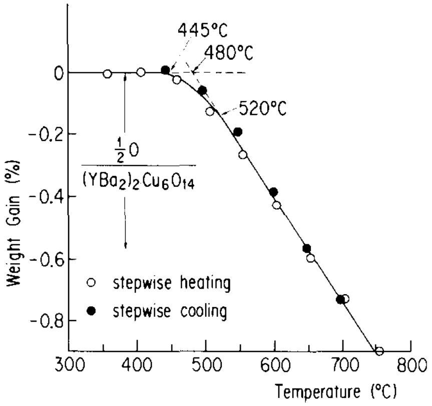


Fig. 4. Oxygen sorption of superconductor sample at different temperatures by stepwise temperature increase (○) and decrease (●). The ordinate is the weight change from that at ambient temperature.

Fig. 5. To elucidate this process, high-temperature X-ray diffraction was obtained in this temperature range by stepwise heating. The results are shown in Fig. 6. As clearly seen in Fig. 6, especially in the diffraction around 22, 33, 46 and 58°, crystalline structure gradually changes in the temperature range 400–600 °C. This change was observed to be reversible when the sample was cooled by a similar stepwise mode. The temperature range of this crystalline transition corresponds to that of the curved dependence of

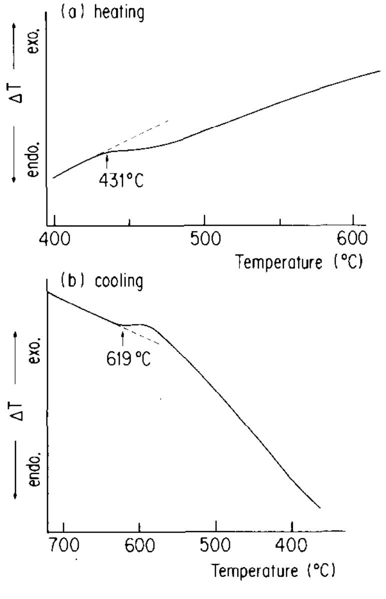
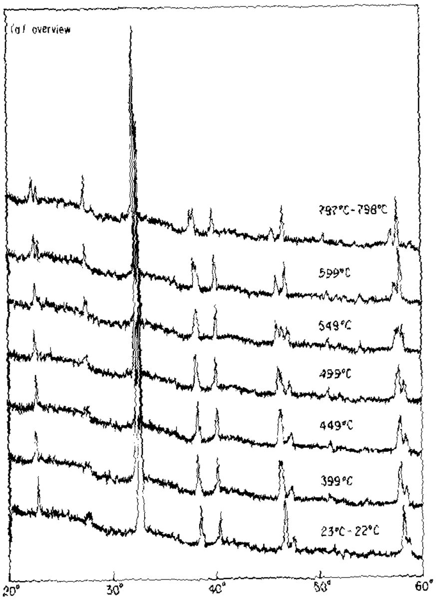


Fig. 5. DTA curves of superconductor sample and sintered sample without annealing.


(a) overview

(b) diffraction between 30° and 35°

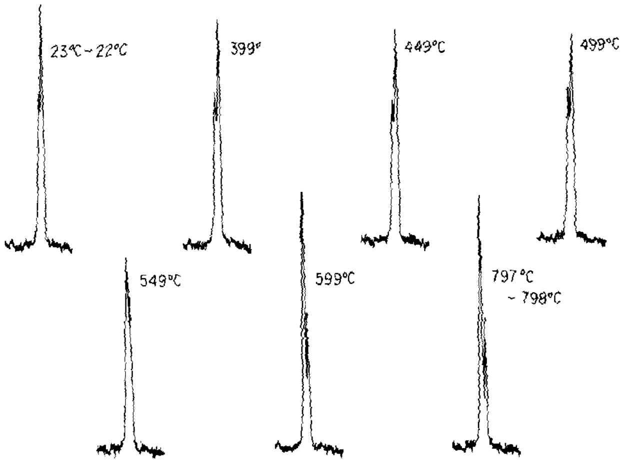


Fig. 6. X-ray diffraction at different indicated temperatures: (a) overview; (b) diffraction between 30 and 35°.

oxygen content in Fig. 4 and the thermal changes in Fig. 5. Thus on heating, the high temperature crystalline phase is formed by losing roughly half of one oxygen atom per $(YBa_2)_2Cu_6O_{14}$. For this superconductor, polymorphism of the tetragonal and orthorhombic forms has been reported [17]. This phase transition is considered to be a transition between the tetragonal form and the orthorhombic form. Exact assignment needs further detailed crystallographic investigation.

CONCLUSIONS

The processes forming the superconductor have been elucidated. On heating the oxalate, the precursor oxide is first formed around 500 °C and it then converts to the perovskite crystal with the endothermic process at a temperature around 800 °C. Around 970 °C this crystal melts, and decomposition and phase separation occur above this temperature. Because there is a phase change between 400 and 600 °C with oxygen sorption for the perovskite crystal, either crystalline form is the superconductor.

Thus, the following points were made clear for reproducible production of the superconductor.

(1) The sintering should be made below 960 °C. Heating above 960 °C may cause decomposition and phase separation accompanied with melting.

(2) Formation of the superconductor, i.e., the ordered perovskite crystal, proceeds at a temperature around 800 °C. Therefore, the heat treatment at about this temperature is essential. However, conversion of this process depends on the temperature and the duration of the heat treatment, so that kinetic investigation is required.

(3) Because the volatilization of metallic components from the precursor oxide seems also to proceed competitively in the same temperature range, further investigation, including kinetic analysis, is required to minimize the composition change due to this volatilization.

(4) The DTA endothermic peak observed at about the above temperature can be utilized for characterization and quality control. When it is observed, further sintering seems necessary to form high quality superconductor.

(5) The phase change from the high-temperature crystalline form to the low-temperature crystalline form occurs in the temperature range 620–430 °C with oxygen absorption and it is reversible.

(6) Provided that the low temperature crystalline form is the superconducting phase, slow cooling from 620 to 430 °C and/or annealing around 400 °C in enough oxygen is necessary to obtain high quality superconductor. Otherwise, quenching from 620 °C without oxygen is needed, and air and oxygen may have a harmful influence on superconductivity, so that some protective film on the material surface is essential for practical applications. In both cases, control of oxygen partial pressure is important, and non-stoichiometric investigation is required.

NOTE ADDED IN PROOF

After the acceptance of this paper, the authors re-examined the weight loss described herein, having regard to critical comment by Dr. Patrick K. Gallagher (AT&T Bell Laboratories, Murray Hill, NJ, U.S.A.) on the process causing the weight loss. The results and discussion are described in the following papers of this series to be submitted to this journal.

The authors express their sincere appreciation to Dr. Gallagher for his courtesy.

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