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THERMOANALYTICAL INVESTIGATION OF $(YBa_2)_2Cu_3O_{7-y}$ SUPERCONDUCTOR. II. PEROVSKITE FORMATION FROM COPRECIPITATED OXALATE

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ABSTRACT

Formation of the perovskite structure from the precursor was observed by high-temperature X-ray diffractometry. It proceeds in the temperature range above 750 ° C. Thermogravimetry (TG)/differential thermal analysis (DTA) was also applied to this temperature range: weight loss and an endothermic peak were observed in a higher temperature range. The endothermic peak is due only to a phase change of $BaCO_3$ in the precursor and is independent of the weight loss, which is due to evolution of CO_2 from $BaCO_3$ when perovskite formation proceeds. Kinetic analysis of these processes showed that the weight loss is a phase-boundary-controlling process.

INTRODUCTION

In a previous paper on the thermoanalytical investigation of a high-temperature superconductor $(YBa_2)_2Cu_3O_{7-y}$ [1] it was shown that coprecipitated oxalate decomposes to a precursor below 500 ° C, and then becomes a perovskite with weight loss and an endothermic peak above 800 ° C. The endothermic peak appears in the temperature region of a transition of $BaCO_3$. The present study deals with the perovskite formation from the coprecipitated oxalate in detail in relation to the weight loss and endothermic processes.

To this end, crystallographic investigation and simultaneous observation of thermogravimetry and differential thermal analysis (TG–DTA) of this process were made. Mass spectrometry of gases evolved during heating of the oxalate was also carried out. A kinetic analysis of the TG data was made to investigate the mechanism of the perovskite formation.

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EXPERIMENTAL

Sample

The precursor sample, a grayish black powder, was made from coprecipitated oxalate as previously described [1]. The size of each particle was less than 1 μm. The oxalate was heated in a crucible to 500 °C at an average rate of about 15 °C min^{-1} in ambient atmosphere and kept at that temperature for about 1 h. It was then cooled in a furnace to ambient temperature. This procedure was chosen according to the TG–DTA results from the oxalate described in ref. 1. The weight of this product was 59% of the oxalate and in accordance with the TG–DTA results of ref. 1.

Apparatus

TG–DTA and X-ray diffractometry were applied, and the apparatus used has been described [1]. The mass spectrometer used for evolved gas analysis (EGA) is a TE-600S GC–MS made by ANELVA Co.

RESULTS AND DISCUSSION

X-ray diffraction

High-temperature X-ray diffractometry was applied to the high-temperature processes. Figure 1 shows X-ray diffraction results obtained by stepwise heating of the precursor. Each diffraction procedure between 20 and 60° took about 50 min, during which the temperature was kept constant, and then the sample was heated. The measurement at 800 °C was repeated; the sample was thus kept at this temperature for about 2 h.

As is clearly seen, the diffraction pattern of the precursor is diffuse, and it is not well-crystallized. Moreover, the diffraction pattern is quite different from that of perovskite. A peak of $BaCO_3$ around 24° is seen with many other diffuse peaks due to oxides. Sharpening of the diffraction pattern of the precursor occurred in the temperature range 500–700 °C. Therefore crystal growth of the carbonate and the oxides appears to proceed in this temperature range, and it may cause phase separation from the fairly homogeneous precursor; it is undesirable for the formation of superconductor of high quality.

On the other hand, the perovskite structure was formed gradually at 750 °C, as clearly seen at 32–33° diffraction, and fully formed at 800 °C under the experimental conditions. When diffractometry was repeated at this temperature, the diffraction was the same as ordinarily observed for the superconductor.

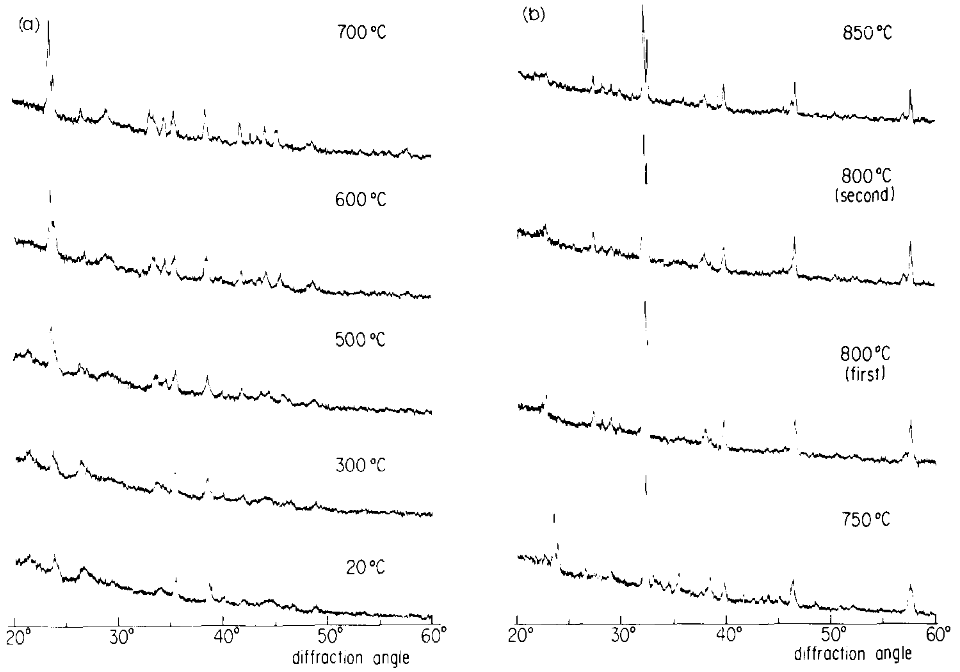

Fig. 1. X-ray diffraction patterns of precursor at the different temperatures indicated. The diffraction angle is expressed in 2θ.

TG–DTA

To elucidate kinetic aspects of the processes of the precursor, the TG–DTA study was performed at different heating rates. After the measurement up to 1000 °C, the sample was sintered to a cylinder and remarkable shrinkage was observed. Two examples of TG–DTA measurements are reproduced in Fig. 2. As may be seen the weight loss and the endothermic peak were

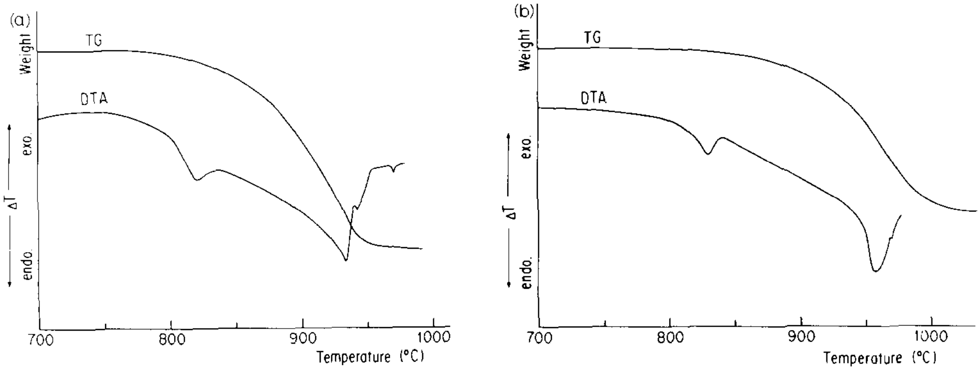

Fig. 2. TG–DTA curves of precursor at (a) 4 °C min^{-1} and (b) 16 °C min^{-1}.

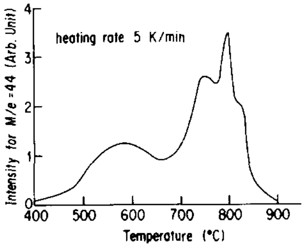

Fig. 3. EGA curve for CO_2 from precursor.

observed in the same temperature range. The weight loss was 11–13% of the precursor sample. Kinetic analysis was made for these processes, as described below.

EGA

The precursor was immediately sealed in a quartz tube to prevent the sample from absorbing CO_2 from air, and this was used for evolved gas analysis by mass spectrometry. Figure 3 shows the results obtained at a heating rate of $5\,^\circ C\ min^{-1}$ in vacuum. A considerable amount of CO_2 was evolved from the precursor above 600 °C; this process corresponds to the weight loss during heating. It can be concluded that the weight loss is due to evolution of CO_2 from $BaCO_3$ in the precursor during a reaction for perovskite formation. Although the reason is not clear, a separation of the peak was observed.

Kinetic analysis of TG data

First, a plot for estimation of the activation energy proposed by one of us (the so-called Ozawa plot) [2] was applied. The logarithm of the heating rate was plotted against reciprocal absolute temperature at a given weight loss, as shown in Fig. 4. The plots obtained for the different weight losses are linear, and the activation energy was estimated from the slope obtained by the least-squares method. The activation energies thus estimated are listed in Table 1.

The activation energy seems to be constant irrespective of the weight loss. To confirm this point, the weight loss was plotted against the reciprocal of absolute temperature. When the process proceeds by a single elementary process, the weight losses thus plotted for the different heating rates can be superposed on each other by lateral shift [2]. The superposition was made as in Fig. 5, and it can be concluded that the weight loss proceeds by a single elementary process. The difference in the logarithm of heating rate was plotted against the distance of lateral shift, i.e. the difference in the reciprocal absolute temperature in Fig. 6. The activation energy estimated from the

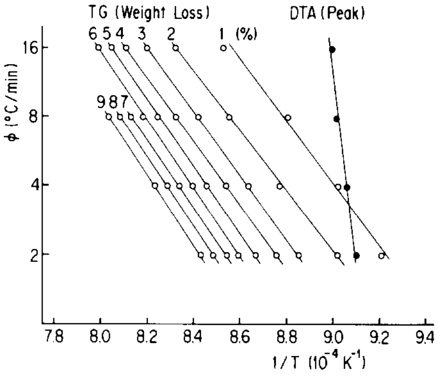

Fig. 4. Heating rate in a logarithmic scale versus reciprocal absolute temperature at different percents of weight loss and at DTA peak. T and ϕ are the temperature and the heating rate, respectively.

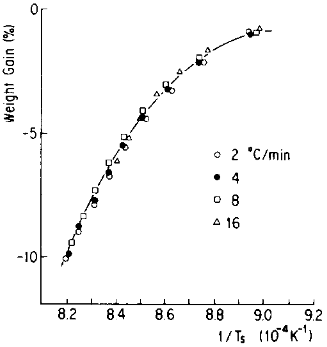

Fig. 5. Superposed weight gain curve versus reciprocal absolute temperature. The suffix s means standard curve obtained at heating rate of 4 ° C min^{-1}.

TABLE 1

Activation energy and reduced time

Weight loss (%)	Activation energy (kJ mol^{-1})	Reduced time (10^{-12} min)
1	246	3.61
2	240	7.28
3	255	12.77
4	258	18.11
5	267	24.68
6	274	31.78
7	271	37.52
8	276	45.67
9	281	55.21
Average	263 ± 3 [a]	

[a] Standard deviation.

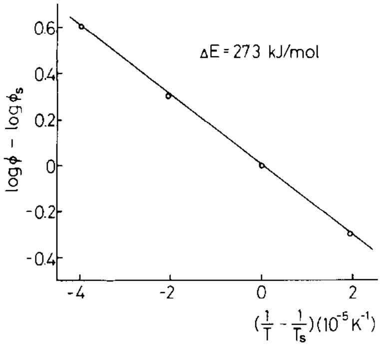

Fig. 6. Logarithm of heating rate versus lateral shift.

slope of the linear line [3] in Fig. 6 is 273 kJ mol^{-1} and was in agreement with the average value in Table 1.

Kinetic analysis of DTA data

The reciprocal absolute temperature at the maximum rate is in a linear relation with the logarithm of the heating rate similar to the above Ozawa plot [4]. Although the maximum rate is not at the DTA peak, it is fairly close to it [4]. Such a plot for the DTA peak is shown also in Fig. 4. As may be clearly seen in this figure, the endothermic process is quite different from the process of weight loss, and the slope is much greater than that of the weight loss. The heating rate dependence of the DTA curves is shown in Fig. 7, where the onset temperatures of these peaks are roughly in accordance with each other. From these facts it can be concluded that the endothermic process is due to a phase change of $BaCO_3$ only and is not related directly to the weight loss accompanied by the perovskite formation. As expected, this peak is observed only at the first heating [1].

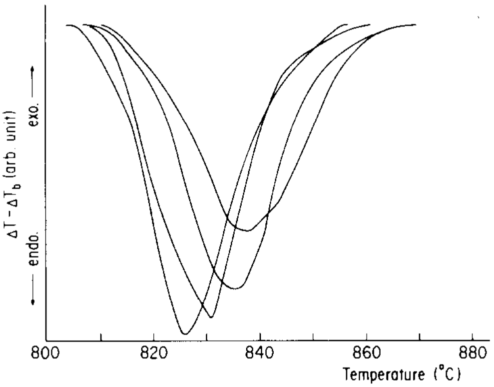

Fig. 7. Heating rate dependence of DTA peak. ΔT and ΔT_b are the temperature difference and the baseline, respectively.

Mechanism of the perovskite formation

By using the average activation energy in Table 1 and the intercept of the linear line with the abscissa in Fig. 4, we can calculate a reduced time [5], θ, generalized for the process of the weight loss: perovskite formation. The values calculated are also listed in the table. The reduced time is a hypothetical time for this process assumed to proceed at infinite temperature and proportional to the actual time for isothermal process. The weight gain is plotted against the reduced time in Fig. 8. For prediction, the actual times for this process occurring at 750, 800 and 850 °C are also shown.

A mechanism of this process was analyzed by plots of several functions of conversion C against the reduced time which are derived from certain mechanisms such as first-order and phase-boundary-controlling processes [6]. Of these functions, $1-(1-C)^{1/3}$ and $1-(1-C)^{1/2}$ showed a linear relation with the reduced time as shown in Fig. 9; furthermore, the former line passes the origin of the coordinate axes, suggesting that this process takes place at a phase boundary which proceeds from a spherical or cylindrical particle surface to inside. From the slope of the linear lines, pre-exponential factors of the rate constants were obtained as 0.458×10^{12} h^{-1} and 0.578×10^{12} h^{-1}, respectively. The relation between the conversion and the actual time can be predicted for any temperature by using the pre-exponential factor and the activation energy; the equation for the case of $A\exp(-\Delta E/R\mathrm{T})\mathrm{t} = 1-(1-C)^{1/3}$ is

$$0.458 \times 10^{12} \exp\left(-\frac{31.6 \times 10^{3}}{T}\right)t = 1-(1-C)^{1/3}$$

where T is the temperature in K and t is the actual time in h. Figure 10 shows a plot of the weight gain against the square root of the reduced time.

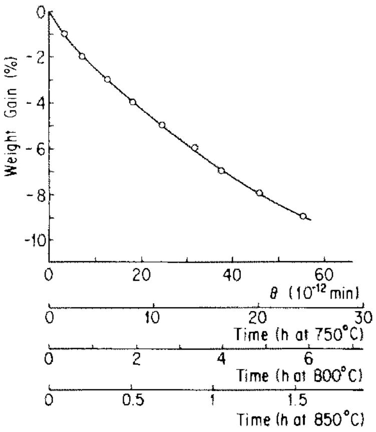

Fig. 8. Weight gain versus reduced time.

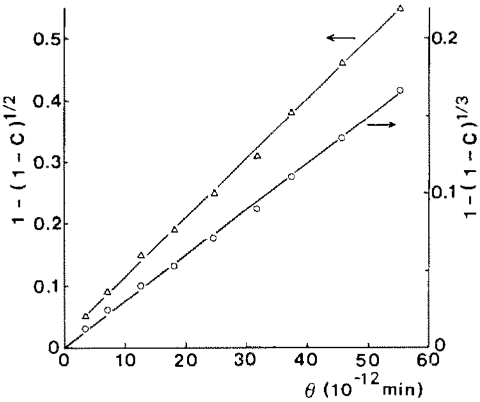

Fig. 9. $1-(1-C)^{1/3}$ versus θ and $1-(1-C)^{1/2}$ versus θ plots for the process of weight loss. C is the conversion.

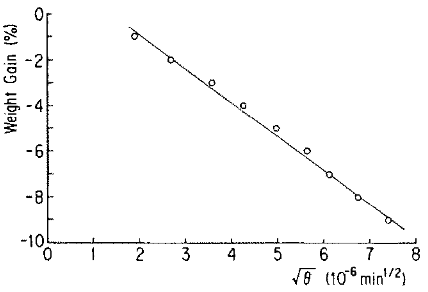

Fig. 10. Weight loss versus square root of reduced time.

As may be clearly seen, an approximately linear relation was found, so that there is also a possibility of a diffusion-controlling process. However, linearity of the plots in Fig. 9 is better than that in Fig. 10.

CONCLUSIONS

It is confirmed that the precursor is formed from the oxalate below 500 °C; the precursor is not well-crystallized at this temperature; it is converted to the perovskite crystal at temperatures above 750 °C. The crystal growth of the precursor proceeds below this temperature, and it seems undesirable because stabilization and presumably phase separation may proceed in this temperature range with decrease in homogeneity in the precursor. The process of the weight loss, i.e. the perovskite formation accompanied by CO_2 evolution, is considered to be a phase-boundary-controlling process. It was also confirmed that an endothermic DTA peak at about 810 °C is due only to a phase transition of $BaCO_3$ in the precursor.

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