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THERMOANALYTICAL INVESTIGATION OF $YBa_2Cu_3O_{7-y}$ SUPERCONDUCTOR. IV. MECHANISM OF PEROVSKITE FORMATION FROM VARIOUS STARTING MATERIALS

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ABSTRACT

Thermogravimetry (TG) at various heating rates was applied to perovskite formations of $YBa_2Cu_3O_{7-y}$ prepared from coprecipitated carbonates of yttrium, barium and copper, and from a physical mixture of yttrium oxide, barium carbonate and copper oxide. Kinetic analyses of TG data were made for the two starting materials. Mechanisms of perovskite formation are discussed in comparison with other starting materials: mixed 2-ethylhexanoates and coprecipitated oxalate.

INTRODUCTION

Various starting materials for preparation of the high temperature superconductor, $YBa_2Cu_3O_{7-y}$ (YBCO), have been proposed [1–5]. Temperature conditions and the time of heat treatment are of great importance in the preparation of high quality superconductors. The authors have investigated perovskite formation from coprecipitated oxalate [6,7] and from mixed 2-ethylhexanoates of yttrium, barium and copper [8] by TG–DTA and TG. Both starting materials begin by changing to precursors consisting of barium carbonate and oxides of yttrium and copper. When the precursors were heated at a constant heating rate by TG, the perovskite formation from the mixed 2-ethylhexanoates precursor started at a lower temperature compared with that from the coprecipitated oxalate precursor. This difference seems to arise from a difference in the mechanisms of perovskite formation for the two different starting materials.

The mechanism for the coprecipitated oxalate was found to be a phase-boundary-controlled contracting interface reaction [7]. In the present study, TG with various heating rates was applied to two other starting materials: coprecipitated carbonate and physical mixture of yttrium oxide, barium carbonate and copper oxide. Kinetic analysis of TG data is made for all the starting materials, and the reaction mechanisms are discussed in relation to particle size, crystalline state and the homogeneity of the components.

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EXPERIMENTAL

Sample

The coprecipitated carbonate of yttrium, barium, and copper was prepared as follows. An aqueous nitrate solution of yttrium, barium and copper with a 1 : 2 : 3 composition was first prepared and adjusted to pH 7–8 by adding 2.70 mol solution of KOH. Subsequently, K_2CO_3 solution was added to this nitrate solution and a light blue coprecipitate appeared in the solution. The coprecipitate was washed several times and dried in air for 8 h at 393 K. The size of the obtained particles was 0.2–0.3 μm in diameter.

Another starting material, the 1 : 2 : 3 mixture of yttrium oxide, barium carbonate and copper oxide of chemical reagent grade purchased from Wako Pure Chemical Co. Ltd., was ground and used for TG. The size of each particle of ground powder was a few μm in diameter.

Apparatus

TG–DTA, X-ray diffractometry and chemical analysis by energy dispersion X-ray analysis (EDX), together with scanning electron microscopy, were applied; the apparatuses used have been described elsewhere [6].

Procedure of TG at different heating rates

Before the TG measurements, both the coprecipitated carbonate and the mixture of yttrium oxide, barium carbonate and copper oxide were kept at 500 °C for one hour. A series of TG measurements were made on the precursors thus obtained up to 1000 °C in air at various heating rates from 1 to 16 °C $\min^{-1}$. Sample pans made of platinum were used.

RESULTS AND DISCUSSION

Results of TG

Typical weight loss curves at heating rates of 2 °C $\min^{-1}$ and 8 °C $\min^{-1}$ are shown for both starting materials in Fig. 1. The weight loss curves for coprecipitated oxalate and those for the mixed 2-ethylhexanoates are also shown in the figure. The weight losses are plotted as a function of the conversion C of the reaction forming the perovskite in order to compare the processes among the different starting materials.

All the weight loss curves reach a constant value above 900 °C, and then further weight loss takes place. The latter weight loss seems to be due to loss of oxygen from the perovskite formed because the weight loss is recovered

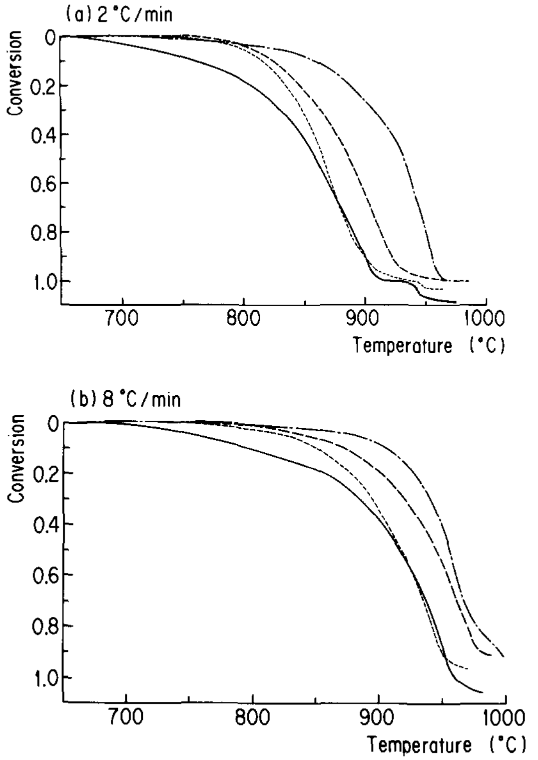

Fig. 1. Typical weight loss curves for different starting materials of the YBCO at (a) 2 °C min^{-1} and (b) 8 °C min^{-1}: ······, coprecipitated carbonate (present study); ·—·—·, mixture of Y_2O_3, $BaCO_3$ and CuO (present study); ------, coprecipitated oxalate; ———, mixed 2-ethylhexanoates.

by cooling the sample down to room temperature. As can be seen, the weight loss starts at lower temperatures for the mixed 2-ethylhexanoates. However, the weight loss of the mixture of yttrium oxide, barium carbonate and copper oxide occurs at much higher temperatures. The heating rates, except for the physical mixture, were selected in the range 2–16 °C min^{-1}; those for the mixture were chosen to be between 1 and 8 °C min^{-1}, because, in this case, only 20% of the weight loss reaction occured below the temperature of partial melting (above 960 °C) at a heating rate of 16 °C min^{-1}.

The perovskite formation from the coprecipitated carbonate proceeds faster than that from the coprecipitated oxalate. It is expected from Fig. 1 that the reaction from the coprecipitated carbonate proceeds faster than the reaction from the mixed 2-ethylhexanoates at higher temperatures i.e. at higher conversions. Reaction speed from the different starting materials can be quantitatively discussed in terms of a kinetic analysis of TG data obtained at different heating rates.

X-ray diffraction and EDX

Figure 2 shows X-ray diffraction patterns observed at room temperature for the coprecipitated carbonate precursors following one hour of heating at 500 ° C, 800 ° C and 850 ° C.

In the diffraction pattern for the sample heated at 500 ° C, peaks corresponding to $BaCO_3$ and many diffuse peaks corresponding to oxides are seen. The perovskite structure characterized by 32–33° diffraction is clearly seen in the pattern for the sample heated at 850 ° C. This pattern is the same as the patterns for the coprecipitated oxalate and the mixed 2-ethylhexanoates heated at the same temperature for 1 h. However, the coprecipitated carbonate sample heated at 800 ° C for 1 h shows rather small peaks of the perovskite with other peaks of the precursor; therefore, one hour of heating is not enough for the perovskite formation from the coprecipitated carbonate at this temperature.

Kinetic analysis of TG data

Kinetic analysis similar to those in previous papers [7,8] was made using the TG data at different heating rates. First, a plot was made for the estimation of the activation energy, the so-called Ozawa plot, proposed by Ozawa [9]. The logarithm of the heating rate was plotted against reciprocal absolute temperature at a given weight loss, as shown in Figs. 3 and 4 for the coprecipitated carbonate and the mixture of yttrium oxide, barium carbonate and copper oxide respectively. The plots obtained for the different weight losses were linear, and the activation energies were estimated from the slope of the linear lines by the least-squares method.

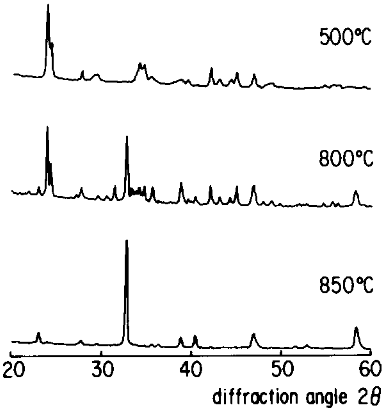

Fig. 2. X-ray diffraction patterns for the coprecipitated carbonate precursors after one hour of heating at 500 ° C, 800 ° C and 850 ° C.

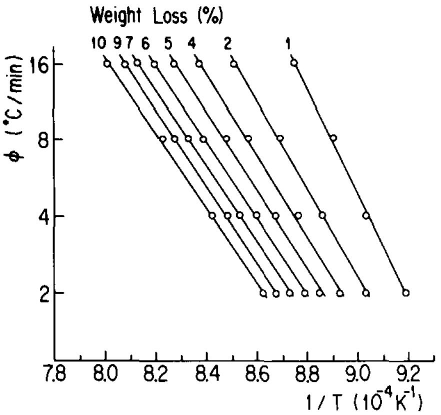

Fig. 3. Logarithm of heating rate versus reciprocal absolute temperature at different percentages of weight loss for the coprecipitated carbonate. T and ϕ are the temperature and the heating rate respectively.

The slope changes with temperature for the mixture of yttrium oxide, barium carbonate and copper oxide. This was also observed in another TG experiment for the mixture, and, moreover, the slopes were not reproducible. This means that the perovskite formation reaction consists of many different processes, probably due to the inhomogeneous distribution of the component materials and to the rather large particle size of the starting mixture. According to additional TG–DTA experiments on the mixtures of two components, weight loss occurs above 800 °C for $BaCO_3$–CuO and Y_2O_3–CuO mixtures; the two-component reactions, therefore, could take place together with the three-component perovskite formation in the similar temperature range.

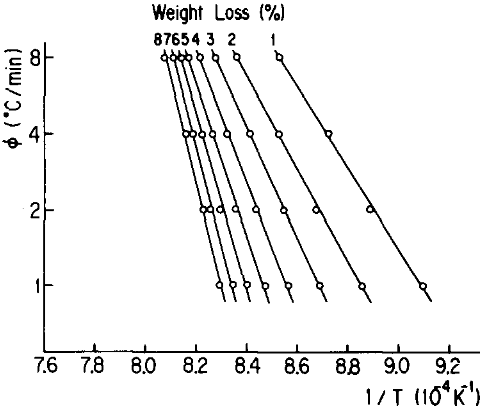

Fig. 4. Logarithm of heating rate versus reciprocal absolute temperature at different percentages of weight loss for the mixture of Y_2O_3, $BaCO_3$ and CuO. T and ϕ are the temperature and the heating rate respectively.

Table 1
Activation energy and reduced time

Weight loss (%)	Activation energy (kJ mol^{-1})	Reduced time (10^{-13} min)
2	314	9.58
4	293	13.01
5	283	16.92
6	273	20.93
7	272	25.91
9	274	31.78
10	267	37.40
Average	282 ± 16 [a]	

[a] Standard deviation.

In contrast, the slopes for the coprecipitated carbonate were almost the same for all the given weight losses. The perovskite formation in this case proceeds homogeneously on an atomic scale. The activation energies estimated are listed in Table 1 for the coprecipitated carbonate only, because they are meaningless for the mixture. The average activation energies are 282 ± 16 kJ mol^{-1}, 263 ± 13 kJ mol^{-1} [7] and 269 ± 16 kJ mol^{-1} [8] for the coprecipitated carbonate, coprecipitated oxalate and the mixed 2-ethylhexanoates respectively.

By using the average activation energy E in Table 1, we can calculate a reduced time [10], θ $(= \int \exp(-E/RT)\,dt)$, generalized for the process of weight loss/perovskite formation. The θ values calculated are also listed in the Table. The reduced time is a hypothetical time for this process, assumed

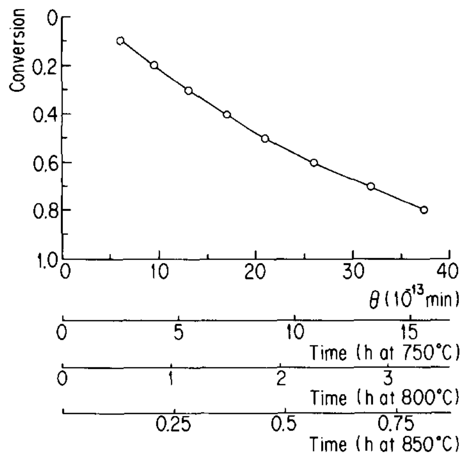

Fig. 5. Weight loss versus reduced time for perovskite formation from the coprecipitated carbonate precursor.

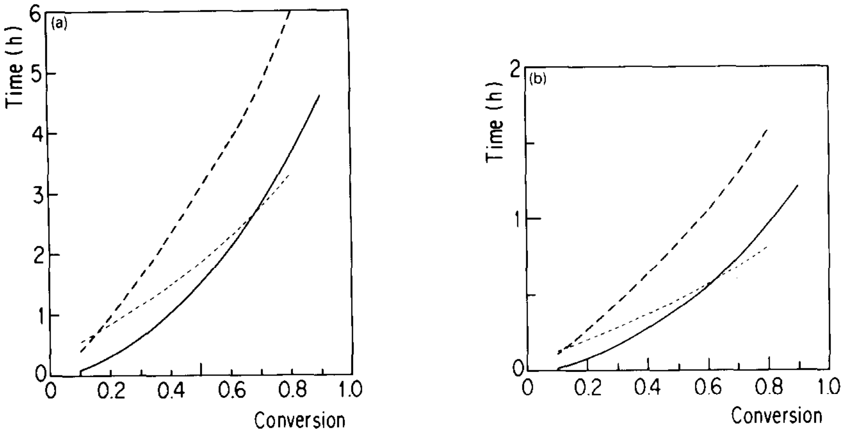

Fig. 6. Plots of the time needed for the perovskite formation from three kinds of starting materials against the conversion at (a) 800 °C and (b) 850 °C: ······, coprecipitated carbonate (present study); - - - - - -, coprecipitated oxalate; ———, mixed 2-ethylhexanoates.

to proceed at infinite temperatures and proportional to the actual time for the isothermal process. The weight loss is plotted against the reduced time in Fig. 5. For prediction, the actual times for this process occurring at 750, 800 and 850 °C are calculated from the reduced time and are also shown in this figure.

Plots of the time required for the perovskite formation against the conversion at 800 and 850 °C are shown in Fig. 6. Such relations for the reactions from the coprecipitated oxalate and from the mixed 2-ethylhexanoates were obtained from the figures in the previous papers [7,8] and also plotted in Fig. 6. As already noted, this kind of plot was not possible for the mixture of yttrium oxide, barium carbonate and copper oxide, because the perovskite formation from this mixture did not show a constant activation energy value. It should be noted that the time required for the reaction from the mixed 2-ethylhexanoates increases with increasing conversion at a greater rate than that for the reaction from the coprecipitated carbonate.

Mechanisms of perovskite formation

The differences in the time versus conversion curves observed for different starting materials is considered to reflect differences in the mechanism of perovskite formation. Mechanisms of the reactions can be determined by finding a best-fit function of the conversion C against the reduced time. In the present study, the following functions were considered

(1) $\theta = -\ln(1 - C)$, first-order reaction;

(2) $\theta = C^2$, diffusion-controlled reaction in an infinite slab;

Table 2
Standard deviation of the curve-fit for determination of reaction mechanisms (%)

Eqn. [a]	Oxalate	Carbonate	Mixed 2-ethylhexanoates
(1)	8.0	8.5	14.2
(2)	10.8	10.0	1.9
(3)	1.8	1.4	4.5
(4)	2.9	2.9	4.4
(5)	30.6	30.9	36.0
(6)	18.9	18.4	13.2

[a] (1) $\theta=-\ln(1-C)$; (2) $\theta=C^2$; (3) $\theta=1-(1-C)^{1/2}$; (4) $\theta=1-(1-C)^{1/3}$; (5) $\theta=[1-(1-C)^{1/3}]^2$; (6) $\theta=(1-C)\ln(1-C)+C$.

(3) $\theta=1-(1-C)^{1/2}$, phase-boundary-controlled contracting interface reaction (cylindrical);

(4) $\theta=1-(1-C)^{1/3}$, phase-boundary-controlled contracting interface reaction (spherical);

(5) $\theta=[1-(1-C)^{1/3}]^2$, diffusion-controlled contracting reaction (spherical); and

(6) $\theta=(1-C)\ln(1-C)+C$, diffusion-controlled contracting reaction (cylindrical).

Table 2 shows the standard deviations of the curve-fit in %. From the Table, it is concluded that the perovskite formation from the coprecipitated carbonate is a phase-boundary-controlled contracting interface reaction, as is that from the coprecipitated oxalate. On the other hand, the reaction from the mixed 2-ethylhexanoates seems to be a diffusion-controlled reaction in an infinite slab. In Figs. 7 and 8, the best-fit function versus the reduced time curves are shown for the coprecipitated carbonate and for the mixed

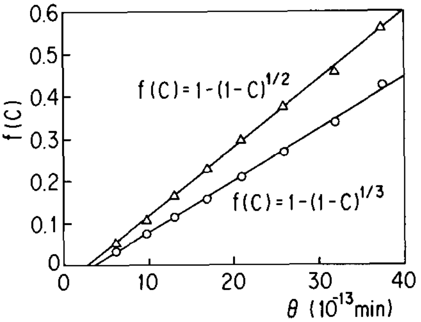

Fig. 7. $1-(1-C)^{1/3}-\theta$ and $1-(1-C)^{1/2}-\theta$ plots for the weight loss process of the coprecipitated carbonate. C is the conversion.

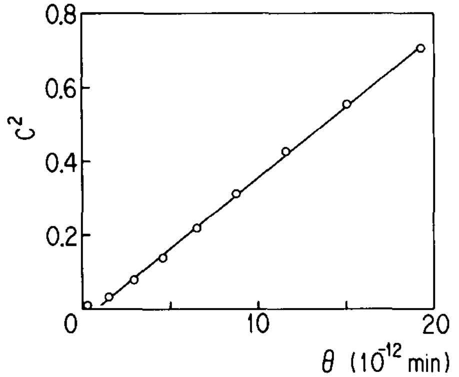

Fig. 8. $C^2 - \theta$ plot for the weight loss process of the mixed 2-ethylhexanoates. C is the conversion.

2-ethylhexanoates respectively. Other functions failed to show a linear relation with θ, even in a limited range of θ.

A phase-boundary-controlled contracting interface reaction usually shifts to a diffusion controlled reaction as the reaction proceeds. In the present case, the particle size of the coprecipitated carbonate and oxalate was much less than 1 μm, and the components were homogeneously distributed, especially in the coprecipitated carbonate. The reaction from starting materials is, therefore, almost completed before the diffusion becomes a rate-determining step. The YBCO superconductor made from the coprecipitated carbonate had an onset critical temperature of 110 K and an end point of 96 K.

The precursor obtained from the mixed 2-ethylhexanoates, on the other hand, has a 3-dimensionally inhomogeneous distribution of the component materials, as was observed using EDX [8]. This could be a consequence of the preparation of the precursor, which was made by pyrolysing a flaky sample, being several tenths to a few hundred μm in thickness, obtained by evaporating the solvent from the mixed solution of yttrium, barium and copper 2-ethylhexanoates in a glass dish. The X-ray diffraction peaks of the precursor obtained from the mixed 2-ethylhexanoates are also different from those of the coprecipitated oxalate and the coprecipitated carbonate; the peaks of the coprecipitates are most diffuse (not well-crystallized). These experimental facts are considered to be closely related to the difference in the reaction mechanisms of the formation of the mixed 2-ethylhexanoates precursor and the coprecipitate precursors.

CONCLUSIONS

Thermogravimetry at various heating rates was applied to perovskite formations of $YBa_2Cu_3O_{7-y}$ from the coprecipitated carbonate of yttrium, barium and copper, and from a physical mixture of yttrium oxide, barium carbonate and copper oxide. Kinetic analyses of TG data were made for the various starting materials.

Mechanisms of the perovskite formation depend on the starting materials; a phase-boundary-controlled contracting interface reaction proceeds for the precursors obtained from coprecipitated carbonate and the coprecipitated oxalate, which are fine homogeneous particles; a diffusion controlled reaction in an infinite slab occurs for the flaky precursor obtained from the mixed 2-ethylhexanoates; the reaction of the mixture of yttrium oxide, barium carbonate and copper oxide consists of many different processes due to the inhomogeneous distribution of the component materials and the rather large particle size.

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