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THERMOANALYTICAL INVESTIGATION OF $YBa_2Cu_3O_{7-y}$ SUPERCONDUCTOR. III. PREPARATION FROM MIXED 2-ETHYLHEXANOATES OF YTTRIUM, BARIUM AND COPPER

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ABSTRACT

The preparation of $YBa_2Cu_3O_{7-y}$ from mixtures of the 2-ethyl-hexanoates of yttrium, barium and copper has been investigated by thermogravimetry (TG), TG–DTA (differential thermal analysis), X-ray diffractometry, and energy dispersion X-ray analysis (EDX). The mixture is first transformed to a mixture of $BaCO_3$, Y_2O_3 and CuO below 500 °C and then the perovskite formation proceeds. Kinetic analysis of TG data on the perovskite formation has been performed.

INTRODUCTION

Films of the high temperature superconductor $YBa_2Cu_3O_{7-y}$ (YBCO) are required for electronic and energy devices, where films of high quality are needed. Of many processes, painted-film pyrolysis of organic acid salts, which has been used successfully in the manufacture of thin films of solid oxide electrolytes [1], has the advantage that the thin films can be made easily and inexpensively without sophisticated apparatus.

Kumagai et al. [2,3] prepared thin films of YBCO having an onset critical temperature of 90 K from barium and copper naphthenates and yttrium stearate. More recently, Nasu et al. [4] have succeeded to prepare a YBCO thin film from 2-ethylhexanoates of yttrium, barium and copper; the onset critical temperature and the end point obtained are 95 and 72 K, respectively. The critical temperature, however, is still lower than that of the bulk superconductors.

In order to improve the quality of the films prepared by such processes, investigation of the perovskite formation is useful. For this purpose, thermo-

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gravimetry (TG) and TG–DTA (differential thermal analysis) are powerful tools [5,6]. In the present study we have investigated the perovskite formation process from the 2-ethylhexanoates of yttrium, barium and copper by TG, TG–DTA, X-ray diffraction and energy dispersion X-ray analysis (EDX). Kinetic analysis of TG data has also been undertaken.

EXPERIMENTAL

Sample

Toluene solutions of the 2-ethylhexanoates of barium and yttrium, and powdered copper 2-ethylhexanoate were purchased from Nihon Kagaku Sangyo Co., Ltd. They were used to prepare samples for thermal analyses.

Apparatus

TG–DTA, X-ray diffractometry and chemical analysis by energy dispersion X-ray analysis (EDX) together with scanning electron microscopy were applied, and the apparatuses used were the same as those given in ref. 5.

Procedure

TG–DTA

A series of TG–DTA measurements were made on the 2-ethylhexanoates of yttrium, barium and copper and the 1 : 2 : 3 mixture up to 900 °C at a heating rate of 15 °C min^{-1}. The solvents used to dissolve the 2-ethylhexanoates were evaporated before TG–DTA measurements on each 2-ethylhexanoate were made; copper 2-ethylhexanoate was used as purchased; the 1 : 2 : 3 mixture was prepared by evaporating the solvents from the mixed solution.

TG at different heating rates

In order to make a kinetic analysis of the perovskite formation from the precursor, TG measurements were made from room temperature to 900 °C at various heating rates: 2, 4, 8 and 16 °C min^{-1}. The precursor samples for these experiments were prepared as follows: the solvent was evaporated from a mixed solution of 2-ethylhexanoates of yttrium, barium and copper in a glass dish; the thickness of the sample after evaporation was of the order of ~ 10–100 μm. It was then pyrolyzed in an alumina crucible at 500 °C for 1 h.

RESULTS AND DISCUSSION

TG–DTA

Figure 1 shows the TG–DTA curve for the ternary mixture of 2-ethylhexanoates; there are several exothermic peaks and large weight losses below 500 ° C. Above 800 ° C, weight loss can be seen, and an endothermic peak is also seen at around 810 ° C.

To identify these DTA peaks and weight losses, TG–DTA was performed separately on each of the 2-ethylhexanoates of yttrium, barium and copper in air and under flowing nitrogen gas. The results in air and those under nitrogen are shown in Figs. 2 and 3, respectively. As can be seen in these figures, the DTA peaks observed below 500 ° C for the experiments in air are all exothermic, while those under N_2 are all endothermic. The weight losses accompanied by these DTA peaks, except for the case of copper 2-ethylhexanoate, are independent of the atmosphere. X-ray diffraction patterns show that the products of the reactions below 500 ° C in air were Y_2O_3, $BaCO_3$, and CuO. The reaction product of copper 2-ethylhexanoate under flowing N_2 gas is considered to be a mixture of CuO and Cu_2O from its brownish color and much weight loss compared with the case in air.

It can also be seen that the reactions in air tend to take place at lower temperatures than those under N_2. The weight loss observed below 300 ° C for barium 2-ethylhexanoate is due to evaporation of residual solvent and free 2-ethylhexanoic acid; their combustion in air causes an exothermic peak shown in Fig. 2b. The endothermic peak at 810 ° C is attributed to the transition of $BaCO_3$.

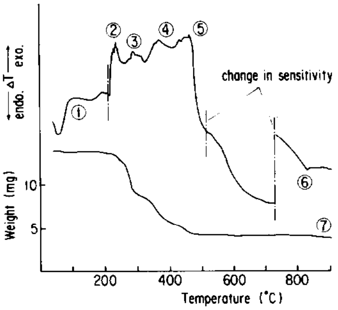

Fig. 1. TG–DTA curves of mixed 2-ethylhexanoate of yttrium, barium and copper. The features ①–⑦ are attributed to the following causes from the results of experiments on these compounds: ① combustion (oxidation) of residual solvent; ② combustion (oxidation) of free 2-ethylhexanoic acid; ③–⑤ formation of CuO, Y_2O_3 and $BaCO_3$ by pyrolysis of the 2-ethylhexanoates; ⑥ transition of $BaCO_3$ at 810 ° C; ⑦ weight loss due to the decomposition of $BaCO_3$ accompanied by perovskite formation. Heating rate, 15 ° C min^{-1}.

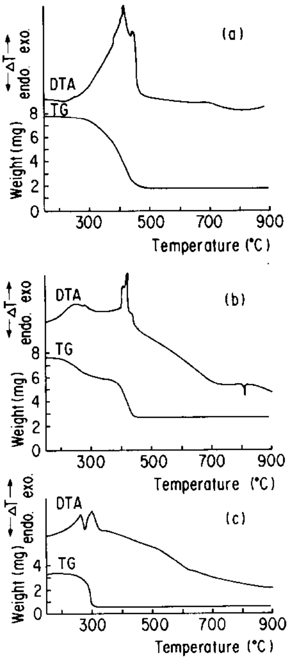

Fig. 2. TG–DTA curves of (a) yttrium 2-ethylhexanoate, (b) barium 2-ethylhexanoate, and (c) copper 2-ethylhexanoate in air. Heating rate is 15 °C min^{-1}.

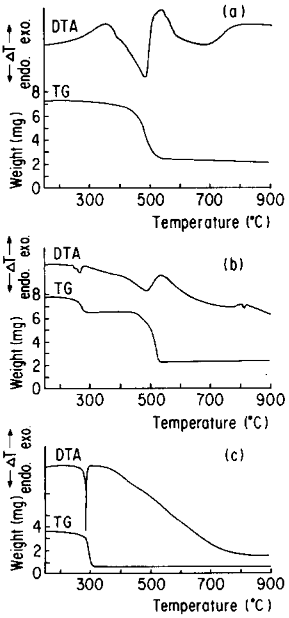

Fig. 3. TG–DTA curves of (a) yttrium 2-ethylhexanoate, (b) barium 2-ethylhexanoate, and (c) copper 2-ethylhexanoate under flowing N_2 gas. Heating rate is 15 °C min^{-1}.

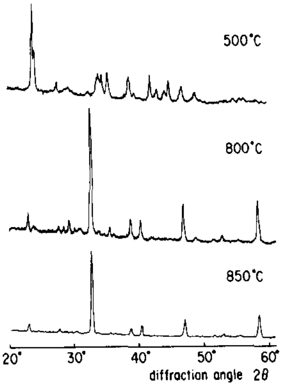

Fig. 4. X-ray diffraction patterns at room temperature for the samples obtained from the ternary mixed 2-ethylhexanoates by keeping it at 500, 800 and 850 ° C for 1 h.

The weights of the samples after evaporation of the solvents and free 2-ethylhexanoic acid were 8.00, 5.54 and 3.32 mg for the 2-ethylhexanoates of yttrium, barium and copper, respectively. The theoretical weights of the samples before pyrolysis were calculated from the final weights of the samples on the assumption that the chemical formulae of the 2-ethylhexanoates before pyrolysis were $Y(C_7H_{15}COO)_3$, $Ba(C_7H_{15}COO)_2$ and $Cu(C_7H_{15}COO)_2$. They were 7.90, 5.93 and 3.26 mg for 2-ethylhexanoates of yttrium, barium and copper, respectively; these results are close to the experimental values; thus, the chemical formulae mentioned above would seem to be reasonable.

The many peaks and weight losses observed for the mixed 2-ethylhexanoates are given in Fig. 1 (①–⑦).

X-ray diffraction and EDX

Figure 4 shows X-ray diffraction patterns observed at room temperature for the sample obtained from the ternary mixed 2-ethylhexanoate by keeping it at 500, 800 and 850 ° C for 1 h. In the diffraction pattern obtained at 500 ° C, peaks corresponding to Y_2O_3, $BaCO_3$ and CuO are seen. However, the perovskite structure is formed at 850 ° C as is clearly seen at 32–33° diffraction. Heating at 800 ° C for 1 h is not enough for perovskite formation. Thus the mixed 2-ethylhexanoate is first transformed to a mixture of Y_2O_3, $BaCO_3$ and CuO below 500 ° C and then the perovskite formation takes place.

According to the results of EDX, distributions of metallic components in the perovskite, i.e. the sample heated up to 850 ° C, are homogeneous.

Kinetic analysis of TG data

Kinetic analysis was made using the TG data at different heating rates. First, a plot for estimation of the activation energy proposed by one of the

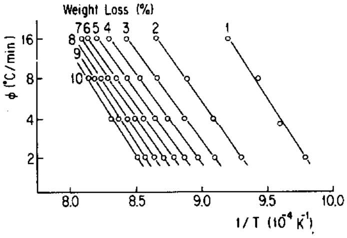

Fig. 5. Logarithm of heating rate vs. reciprocal absolute temperature at different weight losses.

authors (the so-called Ozawa plot) [7] was applied. The logarithm of the heating rate was plotted against reciprocal absolute temperature at a given weight loss, as shown in Fig. 5. The plots obtained for the different weight losses are linear, and the activation energy was estimated from the slope of the linear curves determined by the least squares method. The activation energies thus estimated are listed in Table 1.

By using the average activation energy in Table 1, we can calculate a reduced time [8], θ, for the general process of the weight loss, i.e. perovskite formation. The values thus 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 the isothermal process. The weight loss is plotted against the reduced time in Fig. 6. For prediction, the actual times for this process occurring at 750, 800 and 850 °C are calculated from the reduced time and also shown in this figure.

From a comparison of the present results with those for the perovskite formation from the coprecipitated oxalate, it is concluded that the reaction

TABLE 1

Activation energy and reduced time

Weight loss (%)	Activation energy (kJ mol^{-1})	Reduced time (10^{-12} min)
1	289	0.30
2	260	1.51
3	253	2.99
4	252	4.63
5	254	6.58
6	258	8.83
7	268	11.71
8	278	15.15
9	288	19.41
10	288	23.67
Average	269 ± 16 [a]	

[a] Standard deviation.

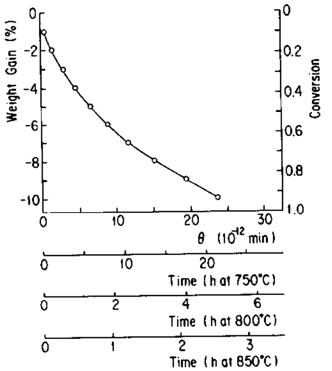

Fig. 6. Weight loss vs. reduced time.

proceeds at lower temperatures in the present case, although the reaction rate is almost the same at higher temperatures such as 850 °C. Mechanisms of perovskite formation from several starting materials, including the coprecipitated oxalate and the 2-ethylhexanoates will be discussed in the next paper of this series [9].

CONCLUSIONS

Perovskite formation from the mixed 2-ethylhexanoates of barium, yttrium, and copper was investigated by TG, TG–DTA, X-ray diffractometry and EDX. The following conclusions were obtained:

(1) The mixture is first transformed to a mixture of Y_2O_3, $BaCO_3$ and CuO below 500 °C. Perovskite formation therefore requires high temperature, as high as 800 °C.

(2) The activation energy for perovskite formation from the mixed 2-ethylhexanoates is 269 ± 16 kJ mol^{-1}.

(3) Perovskite formation by this method proceeds at lower temperatures than that from the coprecipitated oxalate.

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