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KINETIC STUDY OF Y, Ba, Cu OXALATES AND COPRECIPITATED Y–Ba–Cu OXALATE

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Abstract

The kinetics of the decomposition of Y, Ba and Cu oxalates and coprecipitanted Y–Ba–Cu oxalate was investigated under a nitrogen atmosphere on the basis of dynamic thermogravimetric data, the average activation energies of the decomposition of Y, Ba and Cu oxalates were obtained from the slopes of the T. Ozawa plot.

The average activation energies for the dehydration of these oxalate and coprecipitated Y–Ba–Cu oxalate were also evaluated from the thermogravimetric curves.

Keywords: coprecipitated Y–Ba–Cu oxalate, kinetic study, thermal decomposition, thermal dehydration, Y, Ba and Cu oxalates

Introduction

Since the discovery of high-temperature superconductivity in the Y–Ba–Cu–O system [1–4], methods of synthesis of Y–Ba–Cu–O system materials have been investigated, such as solid-state reaction [5, 6], modified coprecipitation [7, 8], citrate [9], and sol-gel method [10]. In order to have good superconducting properties, a widely accepted technique is to coprecipitate the metal ions as oxalates from a mixed salt solution.

Thermoanalytical methods such as TG, DSC and DTA are widely employed to investigate thermal properties in both the liquid and solid states at elevated temperatures; usually changes in a chosen physical property are measured continuously at a predetermined heating rate. The thermal decomposition behaviour of the oxalates has been investigated by Hsu *et al.* [11]. The average activation energies of dehydration and decomposition for these oxalates and coprecipitated Y–Ba–Cu oxalates were evaluated by means of thermal analysis technique.

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Experimentals

Calculated amounts of Y, Ba and Cu nitrates were dissolved in de-ionized water and 0.5 mol l^{-1} oxalic acid solution was prepared. The pH in the above solutions was measured with a pH meter and the equivalent amounts of each metal nitrate solution and the mixed metal nitrate solutions were titrated with oxalic acid solution. During the titration the pH was adjusted by using Et_3N or nitrate solution, and the pH was controlled within ±0.02. The precipitates were dried at 120°C in a drying oven for two hours to constant weight and then the powders were crushed to fine grains in an agate mortar.

For studying the thermal properties, approximately 10 mg samples were measured using a Seiko SSC5200 thermoanalyzer (model 220 TG/DTA) at a heating rate of 5 to 50°C min^{-1} and a N_2 flow rate of 100 ml min^{-1}.

Results and discussion

Figure 1 shows the TG and DTA curves of Y, Ba and Cu oxalates in a N_2 atmosphere, at a heating rate of 10 K min^{-1}. The decomposition of copper oxalate

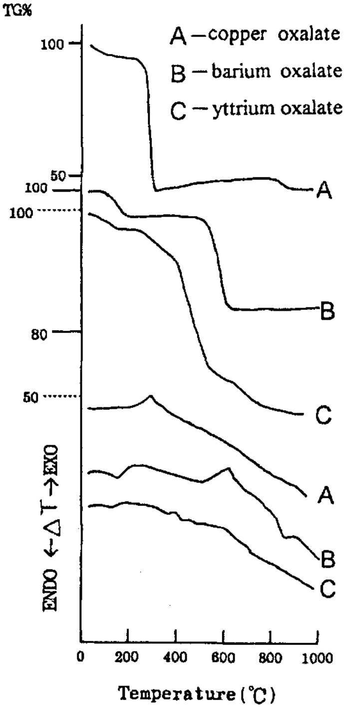

Fig. 1 TG and DTA curves for Y, Ba and Cu oxalate at a heating rate of 10°C min^{-1} in a N_2 atmosphere

Table 1 TG mass loss of Y, Ba and Cu oxalate and possible reactions within various temperature regions

Temperature/°C	Possible reaction	Theoretical mass loss/%	TG mass loss/%					Error/%
			5°C $\min^{-1}$	10°C $\min^{-1}$	20°C $\min^{-1}$	50°C $\min^{-1}$	average	
25~250	$CuC_2O_4 \cdot 1/2H_2O$ $=CuC_2O_4+1/2H_2O$	5.6	5.0	5.4	5.5	5.7	5.4	-.3.57
250~320	$CuC_2O_4=CuO+CO+CO_2$ $2CuO=Cu_2O+1/2O_2$	47.5	53.4	52.0	48.5	51.3	51.0	+7.37
320~800	$Cu_2O+1/2O_2$ $=2CuO$	10.1	2.5	6.1	6.2	8.2	6.83	
25~200	$Y_2(C_2O_4)_3 \cdot H_2O$ $=Y_2(C_2O_4)_3+H_2O$	3.9	4.0	4.5	4.2	4.3	4.25	+9.0
200~800	$Y_2(C_2O_4)_3$ $=Y_2O_3+3CO_2+3CO$	48.9	49.0	47.3	47.8	47.4	47.9	-2.0
25~200	$BaC_2O_4 \cdot 1/2H_2O$ $=BaC_2O_4+1/2H_2O$	3.84	4.2	3.4	3.3	3.4	3.6	-6.25
200~600	$BaC_2O_4=BaCO_3+CO$	12.4	13.1	10.6	11.5	11.4	11.65	-6.0

and yttrium oxalate starts immediately as the temperature begins to increase (i.e. the air-cooled precipitate contains moisture). Barium oxalate shows no mass loss up to 100°C, while in the temperature range between 100 and 200°C the crystal water is lost. Table 1 shows the possible percent mass loss in the reaction within the given temperature regions. After the loss of water is accomplished, the decomposition of the three anhydrous oxalates takes place, the peaks (endothermic or exothermic) in the DTA curves correspond to the decomposition stages appearing in the TG curves. The decomposition of CuC_2O_4 occur in a single step with the maximum rate of decomposition attained at 290°C. $Y_2(C_2O_4)_3$ decomposes in several steps with the maximum decomposition rate at 432°C. The thermal decomposition of BaC_2O_4 proceeds in several steps, the maximum decomposition rate occurring at 575°C. These results are close to those presented by G. Braun [12] (6 K min^{-1} heating rate).

The TG and DTA curves of coprecipitated Y–Ba–Cu oxalate in a N_2 atmosphere, at a heating rate of 10 K min^{-1} are shown in Fig. 2. The coprecipitated Y–Ba–Cu oxalates exhibited a mass loss as soon as the temperature rose above room temperature, i.e., the air-cooled precipitated Y–Ba–Cu oxalate contains residual moisture.

The average mass loss up to 200°C is 10%, a value close to the theoretical mass loss corresponding to the departure of crystal water from the coprecipitated Y–Ba–Cu oxalate. Thereafter, the anhydrous coprecipitated Y–Ba–Cu oxalate decomposes and the percent mass loss between 200 and 500°C is 49%. There are two mass loss stages, the maximum decomposition rate of stage 1 occurs at 266°C and that of stage 2 at 420°C. Above 700°C another mass loss stage appears and the maximum decomposition rate occurs at 771°C. According to the TG curve, this is due to the release of gases produced during the decomposition of coprecipitated Y–Ba–Cu oxalate.

According to Gallagher's [13] investigations the melting point of $YBa_2Cu_3O_x$ is dependent on the furnace atmosphere, due to the pronounced change in x at the melting temperature. The melting point varies from about 975°C in N_2 to 1035°C in O_2, which reflects a strong dependence of the stoichiometry of the product on the furnace atmosphere and is in agreement with phase diagram studies [14]. In this study, the precursor of $YBa_2Cu_4O_8$ was prepared using a modified coprecipitation method, the melting points of coprecipitated Y–Ba–Cu oxalate were detected at 860°C in N_2, 953°C in air and 965°C in O_2, respectively (Fig. 2).

Ozawa [15] Flynn and Wall [16] and Dolye [17] have shown that the activation energy of a thermal decomposition process can be determined directly from a series of DTA and TG curves obtained at different heating rates. The method developed by Flynn *et al.* was a quick, simple method for determining activation energies directly from mass loss *vs.* temperature data at several heating rates. It is not to be expected that any single kinetic expression would be applicable to the wide range of decomposition process. A kinetic analysis method based on the as-

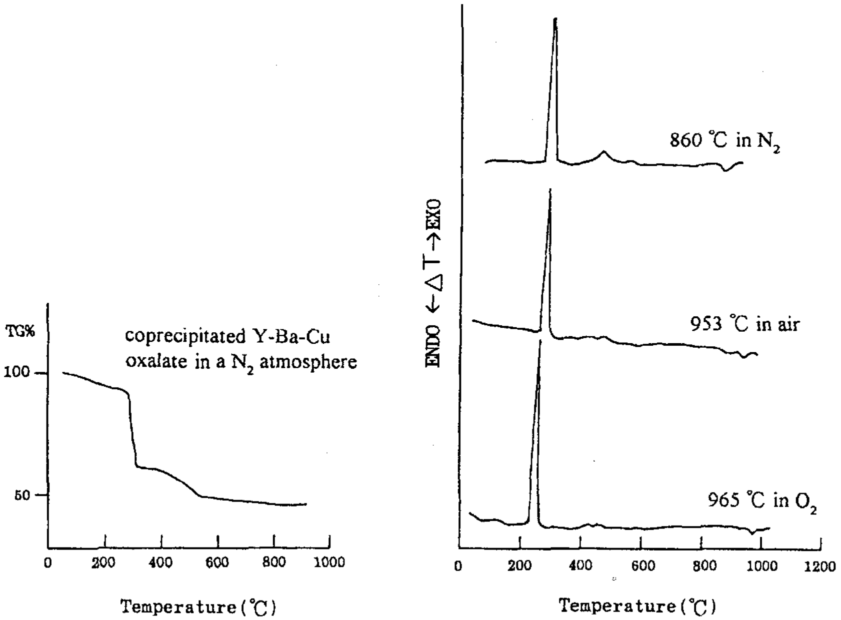

Fig. 2 TG and DTA curves for coprecipitated Y–Ba–Cu oxalate at a heating rate 10°C min^{-1}

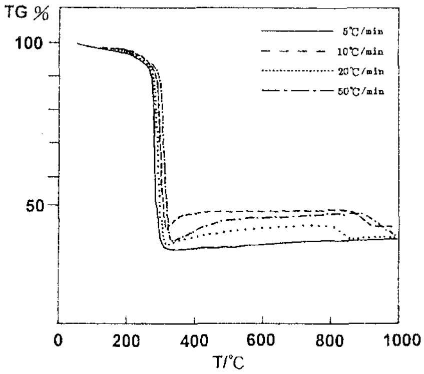

Fig. 3 Dynamic TG curves for the thermal decomposition of copper oxalate, at heating rates (5–50°C min^{-1}) in a N_2 atmosphere

sumption that the decomposition obeys first-order kinetics was later generalized. The assumption that the calculated activation energy is independent of the reaction mechanism does not hold for the later stages and should be used with caution, an upper limit of 10% decomposition is suggested, although 20% is justified in certain cases. It is strongly advised that calculations be made at several different levels of decomposition, for example, 5, 10, 15 and 20% [18]. The Arr-

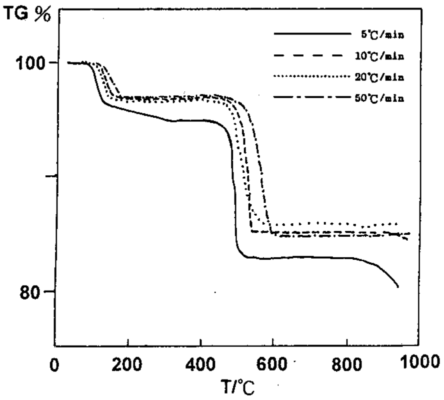

Fig. 4 Dynamic TG curves for the thermal decomposition of barium oxalate, at different heating rates (5–50°C min^{-1}) in a N_2 atmosphere

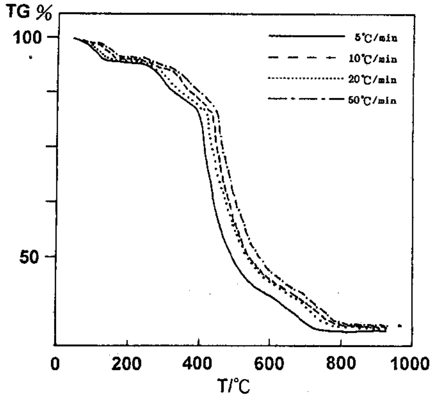

Fig. 5 Dynamic TG curves for the thermal decomposition of yttrium oxalate, at different heating rates (5–50°C min^{-1}) in a N_2 atmosphere

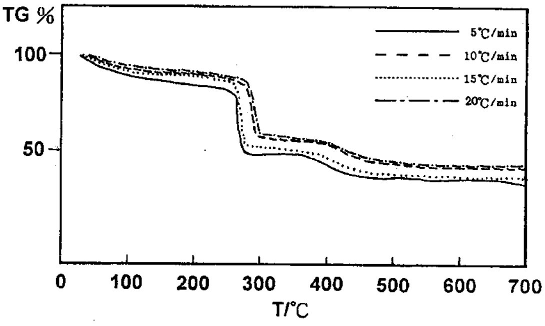

Fig. 6 Dynamic TG curves for the thermal decomposition of coprecipitated Y–Ba–Cu oxalate, at different heating rates (5–20°C min^{-1}) in a N_2 atmosphere

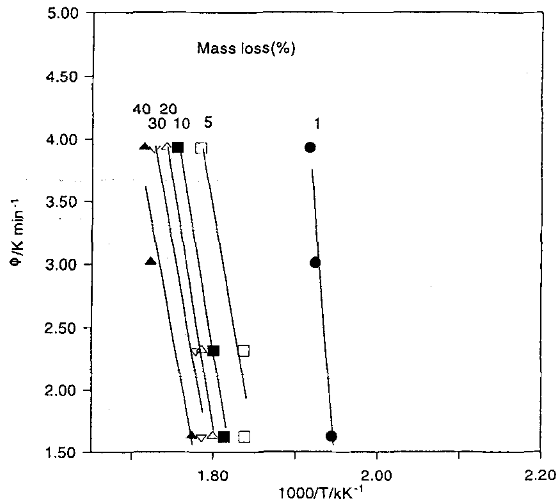

Fig. 7 Heating rate (natural logarithmic scale) *vs.* reciprocal absolute temperature at different percent mass losses for copper oxalate

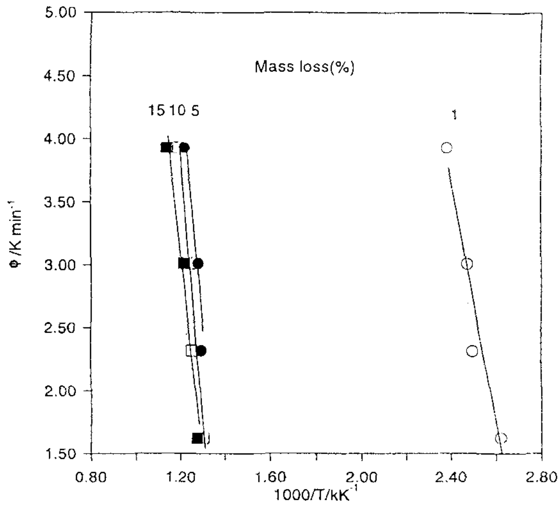

Fig. 8 Heating rate (natural logarithmic scale) *vs.* reciprocal absolute temperature at different percent mass losses for barium oxalate

henius activation energy is determined from a plot of the logarithm of heating rate *vs.* the reciprocal of the absolute temperature at constant conversion level.

The TG curves of the thermal decomposition of Y, Ba, Cu oxalates and coprecipitated Y–Ba–Cu oxalate in a N_2 atmosphere, at heating rates between 5 and

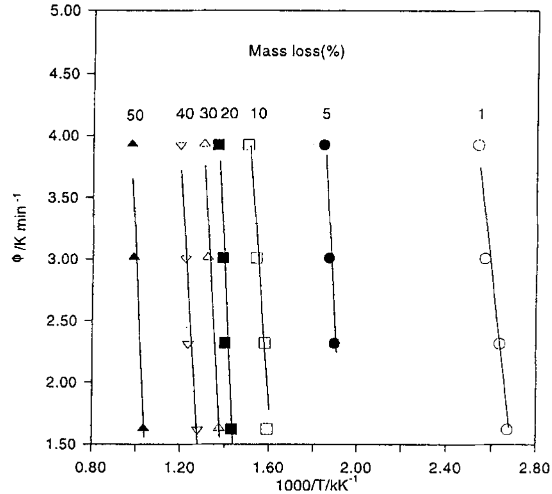

Fig. 9 Heating rate (natural logarithmic scale) *vs.* reciprocal absolute temperature at different percent mass losses for yttrium oxalate

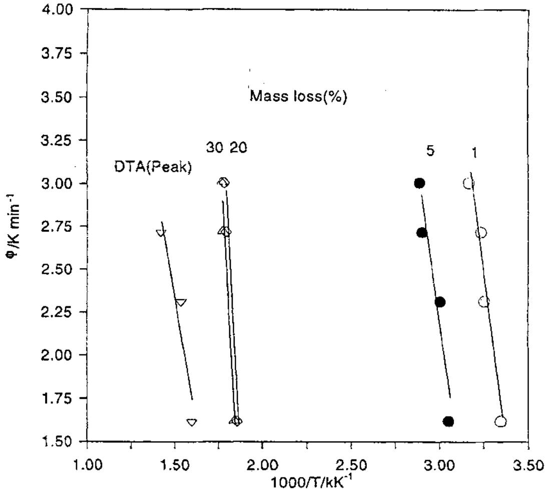

Fig. 10 Heating rate (natural logarithmic scale) *vs.* reciprocal absolute temperature at different percent mass losses for the precursor of $YBa_2Cu_4O_8$ superconductor

50°C min^{-1} are shown in Figs 3 to 6. A plot proposed by Ozawa [19] was used for the estimation of the activation energy. The logarithm of the heating rate was plotted against the reciprocal of the absolute temperature at a given mass loss, as shown in Figs 7 to 10.

Table 2 Activation energies of dehydration and decomposition for Y, Ba and Cu oxalate and coprecipitated Y–Ba–Cu oxalate under nitrogen

	Average activation energy of dehydration/kJ mol^{-1}	Correlation coefficient	Average activation energy of decomposition/kJ mol^{-1}	Correlation coefficient
Copper oxalate	233.6	0.9875	682.0	0.9952
Barium oxalate	185.7	0.9760	356.1	0.9966
Yttrium oxalate	193.4	0.9821	593.6	0.9963
Coprecipitated Y–Ba–Cu oxalate	134.8	0.9891	338.2	0.9971

The average activation energies for the decomposition and for the dehydration in a N_2 atmosphere of Y, Ba, Cu oxalate evaluated by dynamic TG method are listed in Table 2. Copper oxalate has the highest average activation energy of dehydration (233.6 and 208 kJ mol^{-1} from non-isothermal DTA measurements), and the average activation energy of dehydration for barium oxalate was the lowest (185.7 kJ mol^{-1}). The difference is insignificant between these results and those given by Mu [20]. The average activation energies of decomposition for Y, Ba and Cu oxalates range from 356 to 682 kJ mol^{-1}. These values are similar to the results of Mu [20] (665.2 kJ mol^{-1} for CuC_2O_4 in nitrogen, but 400 kJ mol^{-1} in air) and the result of Nair [21] [566 kJ mol^{-1} for $Y_2(C_2O_4)_3$ in an atmosphere of static air].

The average activation energy of decomposition for the coprecipitated Y–Ba–Cu oxalate in a N_2 atmosphere evaluated by dynamic TG method is also listed in Table 2. When the percent mass loss is lower than 10%, the average activation energy of dehydration for the coprecipitated Y–Ba–Cu oxalate is 134.8 kJ mol^{-1}, but the average activation energy of decomposition has a higher value (338.2 kJ mol^{-1}), and the average activation energy of decomposition for the coprecipitated $YBa_2Cu_3O_7$ [22] is 236 kJ mol^{-1}.

Conclusions

The water of crystallization is released from metal oxalates below 250°C when the precipitate is heated. At a higher temperature CO and CO_2 evolve. The powder of the coprecipitated Y–Ba–Cu oxalate shows a mass loss up to 100°C, i.e., the air-cooled coprecipitated powder contains residual humidity, the weight at 100°C is to be taken as the 'precipitate weight'. Three stages of isothermal heat treatment are needed before sintering in order to release the gases by thermal decomposition of the coprecipitated powder. The melting points of coprecipitated Y–Ba–Cu oxalate are detected at 860°C in N_2, 953°C in air and at 965°C in O_2, which reflects that the sintering properties (its stoichiometry) are dependent on the furnace atmosphere. The average activation energy of decomposition for Y, Ba and Cu oxalate range from 356 to 682 kJ mol^{-1} and the average activation energy of dehydration of the coprecipitated Y–Ba–Cu oxalate is 134.8 kJ mol^{-1} and the average activation energy of decomposition for coprecipitated Y–Ba–Cu oxalate is 338.2 kJ mol^{-1}. Our kinetic data on the oxalates are in agreement with the results of previous studies (e.g., CuC_2O_4 [19] and $Y_2(C_2O_4)_3$ [20]).

References

1 Gillson and A. W. Sleight and J. L. P. E. Bierstedt, Solid State Commun., 17 (1975) 27.
2 J. G. Bednorz and K. A. Muller, Z. Phys. B, 64 (1986) 189.

3 T. Kawai and M. Kanai, Japanese, J. Appl. Phys., 26 (1987) L736–L737.
4 M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang and C. W. Chu, Phys. Rev. Lett, 58 (1987) 908.
5 G. Marbach and H. Passing, Electroceramics, (1988) 253.
6 A. M. Gadalla and T. Hegg., Thermochim. Acta., 145 (1989) 149.
7 D. Pandey, V. S. Tiwari, A. K. Singh and S. C. Pramana, J. Phys., 30 (1988) L251.
8 J.Šesták, T. Hanslik, M. Nevriva, D. Zemanova, E. Pollert, A. Triska and J. Tlakal, J. Thermal Anal., 33 (1988) 947.
9 D. H. A. Blank, H. Kruidhof and J. J. Flokstra, J. Phys., D21 (1988) 226.
10 J. M. Tarascon, P. Bardoux, B. G. Bagley, L. H. Greene, W. R. Mckinnon and G. W. Hull, ACS Symp. ser., (1987) 351.
11 C. K. Hsu, J. S. Lee and C. W. Huang, Thermochim Acta., (Sumbitted).
12 G. Braun, G. Schuster, H. Ullmann, W. Matz and K. Henkel, Thermochim. Acta., 165 (1990) 261.
13 P. K. Gallagher, Adv. Ceram. Mat., 2 (1987) 632.
14 J. Šesták, Pure Appl. Chem., 64 (1992) 125.
15 T. Ozawa, J. Thermal Anal., 7 (1975) 601.
16 J. H. Flynn and L. A. Wall, Polymer Letter, 4 (1966) 323.
17 C. D. Doyle, J. Appl. Polym Sci., 6 (1962) 639.
18 ASTM Designation: E 1641–94, 1033–1037.
19 T. Ozawa, Thermochim. Acta., 133 (1988) 11.
20 J. Mu and D. D. Permutter, Thermochim. Acta., (1981) 207.
21 K. G. Nair, V. V. Sreerajan and V. S. V. Nayar, Thermochim. Acta, 39 (1980) 253.
22 A. Negishi, Y. Takahashi, R. Sakamoto, M. Kamimoto and T. Ozawa, Thermochim. Acta., 132 (1988) 15.