

A THERMAL DECOMPOSITION STUDY OF INDIVIDUAL AND CO-PRECIPIATED Y, Ba AND Cu OXALATES

Chung-King Hsu¹ and Jinn-Shing Lee^{1,2,3}

¹Department of Material and Mineral Resources Engineering, National Taipei University of Technology, Taipei, 10643 Taiwan

²Department of Chemistry, Chung-Yuan Christian University, Chung-Li, Taiwan 32023

³Chung-Shan Institute of Science and Technology, Lung-Tan, P.O. Box 90008-15-9, Taiwan 32526, R.O.C.

Abstract

Y–Ba–Cu oxalate powder with a presumed Y:Ba:Cu molar ratio of 1:2:4 was prepared by a modified co-precipitation method and its solid-phase thermal decomposition was studied from 25 to 1000°C, the major evolved gases being H₂O and CO₂. The air-dried powder contained residual moisture. It required isothermal heat treatment for elimination of the evolved gases. The melting point of the co-precipitation Y–Ba–Cu oxalate powder, determined by DSC at a heating rate of 10°C min⁻¹ was approximately 882°C in N₂, 949°C in air and about 979°C in O₂. The dependence of the sintering properties of this material upon the atmosphere and the temperature is considered.

Keywords: co-precipitation, metal oxalates, thermal decomposition study

Introduction

Modified co-precipitation is one method of synthesizing superconductor precursor powders [1–13]. It is important, in order to enhance the superconductivity, to subject the precursor powders to heat treatment in an O₂ atmosphere. In previous works [14], the thermal stability of YBa₂Cu₄O₈ was found to be better than that of YBa₂Cu₃O₇ when the temperature was lower than 820°C, owing to the structure of YBa₂Cu₄O₈ possessing a double bond between copper and oxygen. On the other hand, there is no need to heat the precursor of YBa₂Cu₄O₈ from room temperature to 500°C in an O₂ atmosphere, and maintain it at that temperature for about 1 h [15].

Thermoanalytical methods such as TG, DTA, DSC and TMA are employed to investigate the thermal properties of materials in the liquid or solid state at elevated temperatures. These techniques involve the continuous measurement of changes in the physical properties. The aim of the present work is to investigate the thermal behaviour of the individual Y, Ba and Cu oxalates and of co-precipitated Y–Ba–Cu oxalate powder with a presumed Y:Ba:Cu molar ratio of 1:2:4. The thermal decomposition properties of these materials were investigated by means of TG, DTA/DSC, TG-FTIR and X-ray. From the thermal decomposition data, the optimum heat treat-

ment procedure can be determined, which is very important for the preparation of a good superconductor.

Experimental

The experimental conditions used in the preparation of the individual Y, Ba and Cu oxalates and the co-precipitated Y–Ba–Cu oxalate powder are listed in Table 1. The co-precipitated Y–Ba–Cu oxalate powder was pre-dried in an oven at 120°C for 2 h until constant mass was achieved, and the powder was then crushed to fine grains with an agate mortar and pestle.

Table 1 Experimental conditions* of preparation of the three individual metal oxalates and co-precipitated Y–Ba–Cu oxalate

Initial salt	Precipitate	Precipitating agent	Final composition	Yield/%
Copper nitrate (0.10 M; 100 ml)	Copper oxalate	H ₂ C ₂ O ₄ (0.20 M; 150 ml)	Cu(C ₂ O ₄)·0.5H ₂ O	97.24
Barium nitrate (0.050 M; 100 ml)	Barium oxalate	H ₂ C ₂ O ₄ (0.20 M; 150 ml)	Ba(C ₂ O ₄)·0.5H ₂ O	97.19
Yttrium nitrate (0.025 M; 100 ml)	Yttrium oxalate	H ₂ C ₂ O ₄ (0.20 M; 150 ml)	Y ₂ (C ₂ O ₄) ₃ ·H ₂ O	96.36
Mixed nitrates	Mixed oxalates	H ₂ C ₂ O ₄	Y:Ba:Cu= 1:2.13:4.40**	

* – Precipitations were carried out in aqueous medium (pH=2.32±0.20) at room temperature

** – determined by ICP-AES: Kontron, S-35 (Continuously) Germany

For the thermal investigations, approximately 10 mg of each sample was tested under N₂ at a heating rate of 10°C min⁻¹ and a N₂ flow rate of 100 ml min⁻¹, using a Seiko SSC 5200 thermoanalyzer (model 220 TG/DTA) connected to a Bio-Rad FTS-7 FTIR Spectrometer. A Netzsch-Gerätebau GmbH DSC 404 was used to determine the melting point of the co-precipitated oxalate after heat treatment for 4 h at 750°C. A Philips X-ray diffraction analyzer was also utilized.

Results and discussion

Copper oxalate

The TG, DTG and DTA curves of copper oxalate under a N₂ atmosphere at a heating rate of 10°C min⁻¹ are shown in Fig. 1. It is clear that the loss in mass of the air-dried copper oxalate precipitate begins at ambient temperature: it contains residual moisture. From ambient temperature up to 250°C, the crystal water of the copper oxalate is lost. Table 2 shows the losses in mass within certain temperature regions. The average loss in mass up to 250°C is 5.4%, which is close to the theoretical value of 5.6% for 0.5 mole of H₂O.

Table 2 TG loss in mass, and possible reaction within the given temperature region

$T_{\text{range}}/^{\circ}\text{C}$	Possible reaction	Theoretical mass loss/%	TG mass loss/%				Error/%	
			$5^{\circ}\text{C min}^{-1}$	$10^{\circ}\text{C min}^{-1}$	$20^{\circ}\text{C min}^{-1}$	$50^{\circ}\text{C min}^{-1}$		
20-250	$\text{CuC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$ = $\text{CuC}_2\text{O}_4 + 0.5\text{H}_2\text{O}$	5.6	5.0	5.4	5.5	5.7	5.4	-3.57
250-320	$\text{CuC}_2\text{O}_4 = \text{CuO} + \text{CO} + \text{CO}_2$ $2\text{CuO} = \text{Cu}_2\text{O} + 0.5\text{O}_2$	47.5	53.4	52.0	48.5	51.3	51.0	+7.37
320-800	$\text{Cu}_2\text{O} + 0.5\text{O}_2$ = 2CuO	10.1	2.5	6.1	6.2	3.2	6.83	
25-200	$\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$ = $\text{Y}_2(\text{C}_2\text{O}_4)_3 + \text{H}_2\text{O}$	3.9	4.0	4.5	4.2	4.3	4.25	+9.0
200-800	$\text{Y}_2(\text{C}_2\text{O}_4)_3$ = $\text{Y}_2\text{O}_3 + 3\text{CO}_2 + 3\text{CO}$	48.9	49.0	47.3	47.8	47.4	47.9	-2.0
25-200	$\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$ = $\text{BaC}_2\text{O}_4 + 0.5\text{H}_2\text{O}$	3.84	4.2	3.4	3.3	3.4	3.6	-6.25
200-600	BaC_2O_4 = $\text{BaCO}_3 + \text{CO}$	12.4	13.1	10.6	11.5	11.4	11.65	-6.0

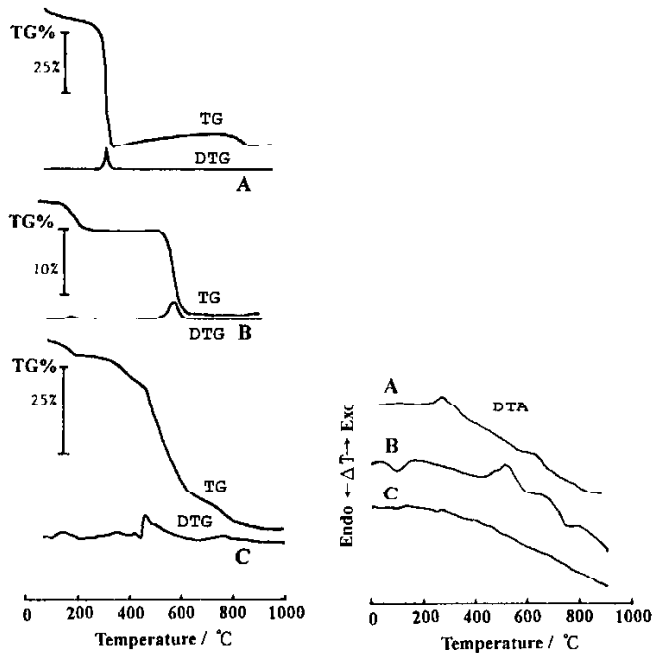


Fig. 1 TG, DTG and DTA curves of copper oxalate, barium oxalate, yttrium oxalate and coprecipitated Y–Ba–Cu oxalate under a N_2 atmosphere at a heating rate of $10^\circ C \text{ min}^{-1}$. A – copper oxalate; B – barium oxalate; C – yttrium oxalate

After the loss of the crystal water, the decomposition of anhydrous CuC_2O_4 takes place, the rate of decomposition being maximum at $290^\circ C$. The DTA curve of $CuC_2O_4 \cdot 0.5H_2O$ also shows an exothermic peak near $290^\circ C$. Although the reactions $M(COO)_2 \rightarrow MCO_3 + CO$ and $MCO_3 \rightarrow MO + CO_2$ are endothermic, the CO formed in the decomposition is partly burned in the furnace, releasing energy, because the nitrogen is not pure enough, the DTA curve then giving an exothermic peak [16]. In the stage from 250 to $320^\circ C$, the average loss in mass is 51%, close to the theoretical value of 47.5%. The TG-FTIR spectrum of copper oxalate showed that the gas evolved between 250 and $310^\circ C$ is CO_2 , the retention time matches the heating time. This result sustains the assumption of the oxidation of CO. Simultaneously, the CO plays a reducing role: the CuO is reduced to a lower oxide or to Cu. As the temperature is raised from 310 to $800^\circ C$, there is an increase in mass, owing to the oxidation of these back to CuO.

Table 3 shows the X-ray diffraction patterns for the heating of copper oxalate from room temperature up to $1000^\circ C$. At temperatures below $200^\circ C$, the phase is $CuC_2O_4 \cdot 0.5H_2O$. In the interval 200 – $300^\circ C$, the $CuC_2O_4 \cdot 0.5H_2O$ decomposed. At temperatures above $600^\circ C$, CuO appeared, but this too disappeared above $900^\circ C$.

The XRD analysis furnished the same result as the TG analysis: anhydrous CuC_2O_4 decomposed to CuO in a single step, without intermediate carbonate formation.

Table 3 HT X-ray patterns of oxalates

Temperature/ °C	HT X-ray pattern		
	Copper oxalate	Barium oxalate	Yttrium oxalate
room temperature	$\text{CuC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$	$\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$	$\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$
100	$\text{CuC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$	$\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$	$\text{Y}_2(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{O}$
200	$\text{CuC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$	BaC_2O_4	$\text{Y}_2(\text{C}_2\text{O}_4)_3$
300		BaC_2O_3	
400		BaC_2O_4	
500	CuO	BaCO_3	
600	CuO	BaCO_3	
700	CuO	BaCO_3	
800	CuO	BaCO_3	Y_2O_3
900	CuO		Y_2O_3
1000		BaO	Y_2O_3

Barium oxalate

The TG, DTG and DTA curves of barium oxalate under a N_2 atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$ are shown in Fig. 1. Barium oxalate undergoes no loss in mass up to 100°C , i.e. the air-dried material contains no residual moisture. Between 100 and 250°C , the crystal water is lost, the average loss being 3.6%. This is close to the theoretical loss of 3.84% for 0.5 mole of H_2O . Between 250 and 470°C , there was no indication of a loss in mass in the TG curve, but the anhydrous BaC_2O_4 subsequently decomposed, the maximum decomposition rate being found at 575°C . In this stage, the average loss in mass was 11.65%, which is close to the theoretical 12.4%. This shows that 1 mole of CO was evolved from the BaC_2O_4 .

The TG-FTIR spectrum of BaC_2O_4 revealed the evolution of CO_2 between 470 and 610°C , and the retention time was the same as the heating time. The DTA curve in Fig. 1 demonstrates an exothermic peak from 470 to 610°C . Above 800°C , there are two endothermic peaks in the DTA curve. That at around 825°C corresponds to a phase transition of BaCO_3 from rhombic to hexagonal, while that at around 980°C reflects the phase transition of BaCO_3 from hexagonal to cubic [17]. Table 3 relates to the X-ray diffraction patterns observed when barium oxalate is heated from room temperature to 1000°C . The phase below 100°C is $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$; at higher temperatures, BaC_2O_4 appears. The characteristic XRD intensity of BaCO_3 was observed until the temperature was above 600°C . The phase then changed again be-

tween 800 and 900°C, and between 900 and 1000°C, in harmony with the TG analysis results.

Yttrium oxalate

Yttrium oxalate decreased in mass when the temperature was elevated above ambient temperature. TG, DTG and DTA curves of yttrium oxalate in a N₂ atmosphere for a heating rate of 10°C min⁻¹ are illustrated in Fig. 1: the air-dried yttrium oxalate contained residual moisture. Up to 200°C, the average loss in mass was 4.25% which approximates to the theoretical 3.9% for 1 mole of H₂O (Table 2). After the loss of the crystal water, the anhydrous salt decomposed, the average loss between 200 and 800°C being 47.9%, close to the theoretical 48.9% for 3 moles of CO and 3 moles of CO₂. The TG/DTG curves revealed decomposition in several steps, the maximum decomposition rate occurring at 432°C.

The dynamic TG-FTIR spectrum of yttrium oxalate indicated the evolution of CO₂ between 400 and 500°C; the retention time was the same as the heating time. Table 3 reflects the X-ray diffraction patterns when yttrium oxalate is heated from room temperature to 1000°C. The phase below 200°C is Y₃(C₂O₄)₃·H₂O. At higher temperature, the phase progressively changes to Y₂(C₂O₄)₃. The phase changes again when the temperature exceeds 400°C. The characteristic intensity of Y₂O₃ becomes clearer as the temperature rises to 800°C. These results agree with those of TG analysis.

Co-precipitated Y–Ba–Cu oxalate powder

Gallagher [18] reported that the melting point of YBa₂Cu₃O_x is dependent upon the furnace atmosphere, due to the pronounced change in *x* at the melting temperature. The melting point ranges from about 975°C in N₂ to 1035°C in O₂. This reflects a strong dependence of the sintering properties upon the furnace atmosphere. In the present study, the precursor of YBa₂Cu₃O₈ was prepared by a modified co-precipitation method, and the Y:Ba:Cu molar ratio of 1:2:4 was examined by ICP-AES (Table 1). The morphology of the particles of the co-precipitated Y–Ba–Cu oxalate was demonstrated by TEM. The particle size distribution was quite uniform, and the average particle size was approximately 0.25 μm. Before the DSC run, the co-precipitated Y–Ba–Cu oxalate powder was sintered at 750°C for 4 h. The DSC curves were then recorded under N₂, air and O₂ atmospheres at a heating rate of 10°C min⁻¹ (Fig. 2). The melting points were 882°C in N₂, 949°C in air and 979°C in O₂. The variation in the melting temperature of the precursor YBa₂Cu₄O₈ in the DSC curves under different atmospheres resembles that for YBa₂Cu₃O_x, but the value is 56–93°C lower than that for YBa₂Cu₃O_x. This result agrees with the finding of Gallagher [15].

The air-dried co-precipitated Y–Ba–Cu oxalate lost mass when the temperature was raised above room temperature; i.e. it contained residual moisture. The TG curve of the powder under a N₂ atmosphere at a heating rate of 10°C min⁻¹ is shown in Fig. 2. Up to 200°C, the average loss in mass was 10% (up to 200°C, the losses for the individual salts were 3.2% for CuC₂O₄·0.5H₂O, 3.9% for Y₂(C₂O₄)₃·H₂O and

3.84% for $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$), this value being close to the theoretical loss of crystal water for the co-precipitated Y–Ba–Cu oxalate powder. Thereafter, the anhydrous powder decomposed, the loss in mass between 200 and 500°C being 49%. In this temperature range, there were two mass loss stages, with maximum decomposition rates at 266 and at 420°C. This reflected the thermal decomposition of the oxalates. Another loss in mass appeared above 700°C, with maximum rate at 771°C. The TG results indicated that isothermal heat treatment procedures are needed before sintering of the precursor of the superconductor, in order to eliminate the gases evolved from the co-precipitated Y–Ba–Cu oxalate powder. However, the TG curve of the co-precipitated $\text{YBa}_2\text{Cu}_4\text{O}_8$ powder continued to fall slowly up to 700°C, and the loss up to 1000°C was only 11%.

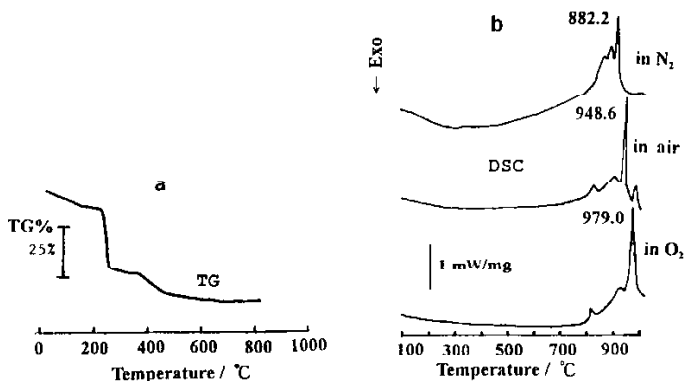


Fig. 2 a – TG curve of co-precipitated Y–Ba–Cu oxalate under a N_2 atmosphere at a heating rate of $10^\circ\text{C min}^{-1}$; b – DSC curves for co-precipitated Y–Ba–Cu oxalate powder after heat treatment for 4 h at 750°C

Conclusions

When co-precipitated Y–Ba–Cu oxalate powder is prepared under suitable conditions, the average particle size is $0.25\ \mu\text{m}$, and it has been verified that the powder is the precursor of a superconductor. The coprecipitated Y–Ba–Cu air-dried oxalate powder loses residual moisture up to 100°C . The crystal water is lost up to 250°C . At higher temperature, CO and CO_2 are evolved. Although the reactions $\text{M}(\text{COO})_2 \rightarrow \text{MCO}_3 + \text{CO}$ and $\text{MCO}_3 \rightarrow \text{MO} + \text{CO}_2$ are endothermic, the CO formed is partly burned in the furnace and yields an exothermic peak in the DTA curve if there is any oxygen in the heating atmosphere. Isothermal heat treatment is required to eliminate the gases evolved from the co-precipitated powder. The melting points of the powder are 882°C in N_2 , 949°C in air and 979°C in O_2 . This reflects that the sintering properties are dependent upon the atmosphere under which the preparation is performed.

References

- 1 A. D. Shartua, R. N. Basu and H. S. Maiti, *J. Mat. Sci. Lett.*, 11 (1992) 122.
- 2 G. Marbach and H. Passing, *Electrocramics*, (1988) 253.
- 3 F. H. Chen and T. Y. Tseng, *J. Am. Ceram. Soc.*, 73 (1990) 889.
- 4 A. Neigishi, Y. Takahashi, R. Sakamoto, M. Kamimoto and T. Ozawa, *Thermochim. Acta*, 132 (1989) 15.
- 5 J. Sestak, T. Hanslik, M. Nevriua, E. Pollert and A. Triska, *J. Thermal Anal.*, 33 (1988) 947.
- 6 M. Kamimoto, *Thermochim. Acta*, 174 (1991) 153.
- 7 G. Braun, G. Schuster, H. Ullmann, W. Matz and K. Henkel, *Thermochim. Acta*, 165 (1990) 261.
- 8 J. Sestak and N. Koga, *Thermochim. Acta*, 203 (1992) 321.
- 9 P. K. Gallagher, *Thermochim. Acta*, 148 (1989) 229.
- 10 T. Ozawa, *Thermochim. Acta*, 133 (1988) 11.
- 11 J. Sestak, *Pure and Appl. Chem.*, 64 (1992) 125.
- 12 A. M. Gadalla and T. Hegg, *Thermochim. Acta*, 145 (1989) 149.
- 13 T. Kawai and M. Kanai, *Japanese J. Appl. Phys.*, 26 (1987) L736.
- 14 J. Karpinski, S. Rusieck, E. Kaldis, B. Bucher and E. Jilek, *Physica C*, 160 (1989) 449.
- 15 P. K. Gallagher, *Adv. Ceram. Mater.*, 2 (1987) 632.
- 16 L. Erdey, G. Liptay, G. Svehla and F. Paulik, *Talanta*, 99 (1962) 489.
- 17 G. Liptay, 'Atlas of Thermoanalytical Curves', Heyden, London 1975, p. 286.
- 18 P. K. Gallagher, *Thermochim. Acta*, 174 (1991) 85.