

## **A THERMAL ANALYSIS EVALUATION OF THE LOW TEMPERATURE SYNTHESIS OF BaBiO<sub>3</sub>**

*G. K. Chuah, S. Jaenicke, K. S. Chan, S. T. Khor and J. O. Hill*

DEPARTMENT OF CHEMISTRY, NATIONAL UNIVERSITY OF SINGAPORE, KENT RIDGE, SINGAPORE 0511

Thermal decomposition of metal-organic precursors for the mixed oxide BaBiO<sub>3</sub> was studied using TG and EGA. Precursors produced by polyesterification of bifunctional acids with ethylene glycol (Pechini process) decomposed about 100°C higher than those without the diol. BaCO<sub>3</sub> was identified by IR and XRD as a reaction intermediate. EGA proved that the amount of BaCO<sub>3</sub> was below 10% of the total barium, and that the barium exists mainly as a nitro-compound up to 650°C. Phase-pure BaBiO<sub>3</sub> with a moderately high surface area (1.4 m<sup>2</sup>/g) could be synthesised from a citrate precursor by the Pechini process at around 850°C.

**Keywords:** BaBiO<sub>3</sub>, EGA, IR, low temperature synthesis, metal-organic precursors, TG, XRD

### **Introduction**

The perovskite phase of BaBiO<sub>3</sub> doped with Li has been proposed as a catalyst for the oxidative coupling of methane [1]. For a good heterogeneous catalyst, a high surface area is essential. Since high reaction temperatures generally lead to sintering and loss of surface area, a low-temperature route to the mixed metal oxide has to be found. Several synthetic methods are known to yield mixed metal oxides at relatively low temperature, e.g., spray-drying freeze-drying, or the Pechini process. In the Pechini process [2], the metal cations are complexed in an aqueous solution of a chelating agent, and the solution viscosity increased by addition of a gelling agent. The process described in the original patent uses a polyacid, preferentially citric acid, and a diol, normally ethylene glycol, which form a polyester resin when heated to a moderately high temperature (150–200°C). This gel can be dried and decomposed at a higher temperature. The resulting powder contains the metal oxides or carbonates in a very finely divided form. A subsequent solid-state reaction to form the mixed metal oxide will proceed at a much lower temperature and in a much faster time than that needed when starting from a mechanical mixture of the oxides or carbonates. The usefulness of the Pechini process for synthesis of a wide range of binary metal oxides and doped systems has been described by Lessing [3] and Anderson *et al.* [4]. Many

modifications of the Pechini process have been reported. Frequently, a bifunctional hydroxyacid is used both as the complexing agent and as the monomer for the polycondensation reaction [5, 6]. If nitrates are used as metal salts, the mixture contains an oxidizing compound and a reducible organic molecule. Such a mixture can spontaneously react on heating. This reaction is exothermic so that the heat of reaction will drive the decomposition to completion. During this reaction, the sample may be subjected to a far higher temperature than that of the oven; because the heat front passes the sample very fast, complete reaction can be achieved without grain growth or excessive sintering.

In barium-containing compounds, BaCO<sub>3</sub> forms readily during burning of the organic polymer. Barium carbonate normally needs very high temperatures, often in excess of 1000°C, to decompose. In this study, we investigate the mechanism of the decomposition reactions in precursor powders produced by the Pechini process with several hydroxyacids. Citric, malic, lactic, and tartaric acids were used. Polyesterification was achieved with and without ethylene glycol. The decomposition was studied by TG in air and in nitrogen, and in pure helium and helium with 10% oxygen by EGA. The results are compared with those of an earlier study on precursors with various amino acids [7].

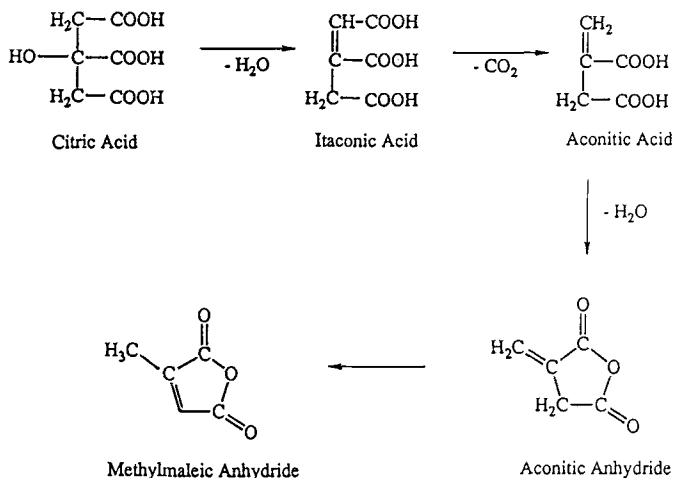


Fig. 1 Mechanism of thermal degradation of citric acid [8]

The thermal decomposition of the stoichiometric citrates, (BaTiH<sub>3</sub>)(C<sub>6</sub>O<sub>7</sub>H<sub>5</sub>)<sub>3</sub>·6H<sub>2</sub>O and (Ba<sub>2</sub>TiH)(C<sub>6</sub>O<sub>7</sub>H<sub>5</sub>)<sub>3</sub>·7H<sub>2</sub>O has been investigated by Hennings and Mayr [8]. The mechanism is shown in Fig. 1. Initially, the water of crystallization is lost. Thereafter, one molecule of water per citric acid is eliminated, leading to the aconitate. At slightly higher temperature, the aconitate decarboxylates to the itaconate, which loses another water molecule to form the anhydride. The anhydride then reacts with oxygen to carbon dioxide and water, leaving the inor-

ganic salt in the form of finely mixed oxides and carbonates. In their investigation, the presence of BaCO<sub>3</sub> with particle size >5 nm was inferred from XRD studies. The authors concluded that 'the complete mixing of barium and titanium particles at an atomic scale up to the state of formation of BaTiO<sub>3</sub> is not very probable'.

## Experimental

1M aqueous solutions of Ba(NO<sub>3</sub>)<sub>2</sub> and Bi(NO<sub>3</sub>)<sub>3</sub> were prepared. The Bi-containing solution was acidified with nitric acid to prevent basic salts from precipitating. Stoichiometric amounts of the two solutions were mixed with an aqueous solution of the hydroxyacid and ethylene glycol. The solutions were stirred vigorously at 70°C and concentrated on a rotary evaporator. A gel resulted which was charred in air at 250°C and calcined in an alumina boat at temperatures up to 850°C. Thermal analysis of the precursors was done using a TA 9900 instrument in air for TG (flow rate 75 ml/min, heating rate 10 deg·min<sup>-1</sup>) and in nitrogen for DSC (flow rate 40 ml/min, heating rate 10 deg·min<sup>-1</sup>). The instrument for evolved gas analysis (EGA) was home-built. A carrier gas flushed the evolved gases through a differentially pumped interface into the quadrupole mass separator (Hiden HAL 200). Multiple ion detection allowed for up to 16 different masses to be monitored with a sampling time of typically less than 200 ms per mass. Helium or a 10% O<sub>2</sub> in helium mixture were used as carrier gases (flow rate 50 ml/min). A heating rate of 5 deg·min<sup>-1</sup> was used throughout. Additionally, powders calcined at different temperatures were analysed by XRD, IR, and BET-surface area.

## Results and discussion

TG curves of the Pechini precursors show several weight losses occurring in very broad, overlapping steps below 300°C. Further weight losses appear around 400° and 600°C. Thermogravimetry alone does not yield enough information to determine the decomposition reactions. Even in combination with DSC, a mechanism could not be proposed. A much clearer picture emerges only when TG is combined with EGA. The example of a citric acid – Pechini precursor will be discussed in detail; results with other precursors will be summarised.

### *EGA in the presence of oxygen*

TG and EGA curves of a citrate Pechini precursor containing Ba(NO<sub>3</sub>)<sub>2</sub> and Bi(NO<sub>3</sub>)<sub>3</sub> are shown in Fig. 2. Two molecules of loosely bound water per atom of bismuth desorb in two peaks at 48° and 108°C. This is followed by simultaneous evolution of water and CO<sub>2</sub> at 167°C. The TG curve shows that the weight loss in

this range corresponds to two water and one CO<sub>2</sub> per citric acid. This is the weight loss expected for the dehydration and decarboxylation of citric acid to form a derivative of itaconic acid within the polyester chain. Additional CO<sub>2</sub> is evolved at 247°C. At 282°C, water and CO<sub>2</sub> are simultaneously evolved; this is accompanied by a corresponding uptake of oxygen. Further oxygen uptake is observed at 367°C, together with evolution of CO<sub>2</sub>, but only a small amount of water. The weight loss observed around 600°C can be attributed to decomposition of nitrates or nitrites; the evolved product is mainly NO. The decarboxylation and dehydration reactions of the citric acid Pechini polyester takes place at somewhat lower temperatures than observed for citric acid [9] or the complex with barium and titanium [8], presumably because of the catalytic action of the bismuth.

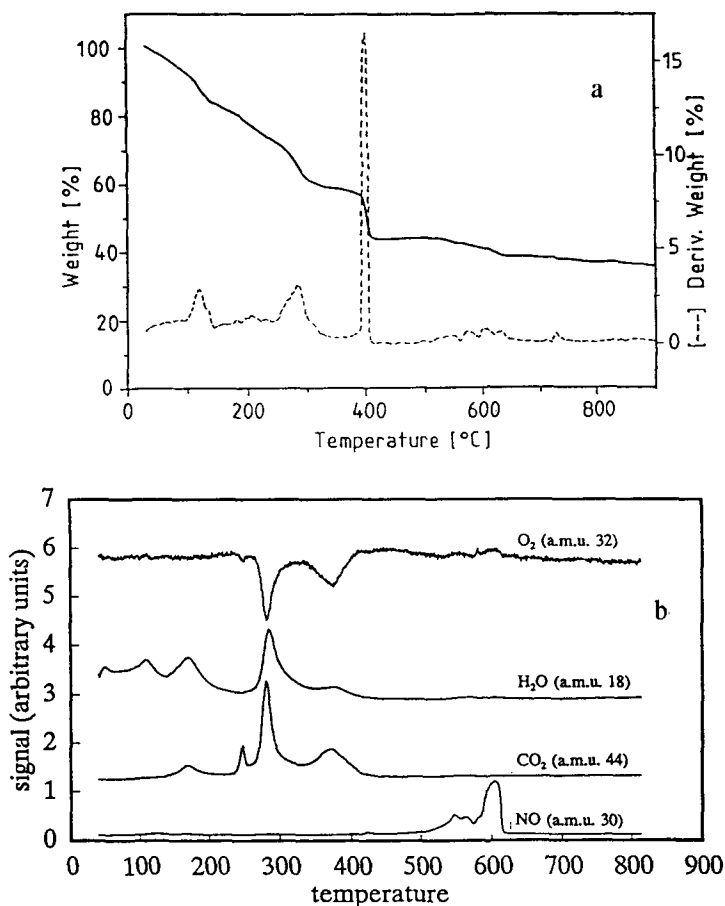


Fig. 2 (a) TG and (b) EGA of a Pechini precursor with citric acid and ethylene glycol in oxidizing atmosphere

*Decomposition without oxygen*

Decomposition of the precursor in pure helium (Fig. 3) is identical to that in an oxidizing atmosphere up to 300°C. At higher temperature, the reaction pathway changes: since no external oxidizing agent is available, an intermolecular oxidation-reduction reaction takes place with the nitrate. The reaction manifests itself in the very sharp evolution peaks of N<sub>2</sub> and CO at 552°C. Under these conditions, the nitrates are completely decomposed at about 50°C lower than in the presence of oxygen. The evolution of additional CO around 780°C indicates reduction of the metal oxides by residual carbon.

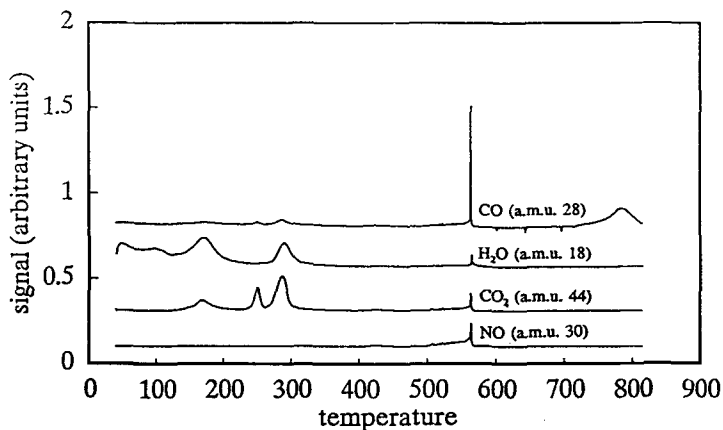


Fig. 3 EGA of a Pechini precursor with citric acid and ethylene glycol in helium

Samples for characterization by IR and powder-XRD were prepared by heating the precursors in air to different temperatures. A sequence of IR spectra for the compound calcined at increasingly higher temperatures is shown in Fig. 4. After heating to 185°C, the spectrum reveals the presence of an ester by the peaks at 1740 cm<sup>-1</sup> (C=O stretch) and 1378 cm<sup>-1</sup> (-C-O- stretch). The absorption at 1615 cm<sup>-1</sup> is assigned to a -COO<sup>-</sup> group which attaches to a metal cation in a monodentate fashion. After heating to 200°C, the IR spectrum changes. The absorption at 1740 cm<sup>-1</sup> decreases, and a shoulder appears at 1406 cm<sup>-1</sup>. Heating to 380°C leads to an IR spectrum showing characteristic features of BaCO<sub>3</sub>: two sharp absorptions at 689 and 856 cm<sup>-1</sup> and a broad band at 1424 cm<sup>-1</sup>. There is little change after heating to 450°C, but after treatment at 650°C, formation of a BaBiO<sub>3</sub> phase becomes apparent as indicated by the appearance of a band at 470 cm<sup>-1</sup>. This band becomes more intense in the sample heated to 800°C, but in this sample considerable amounts of BaCO<sub>3</sub> are still present. Only after prolonged heating at 850°C does one obtain phase-pure perovskite BaBiO<sub>3</sub>.

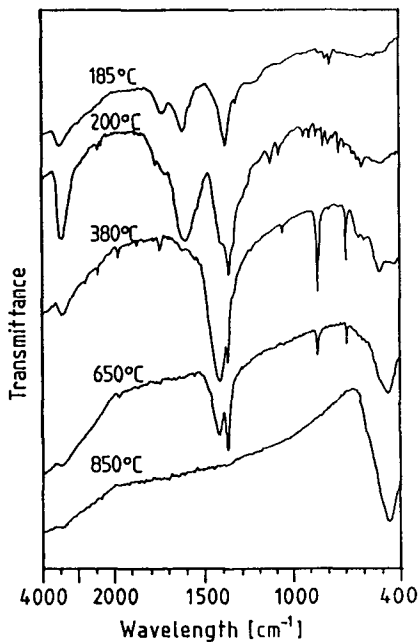


Fig. 4 IR spectra of the Pechini precursor calcined at successively higher temperatures

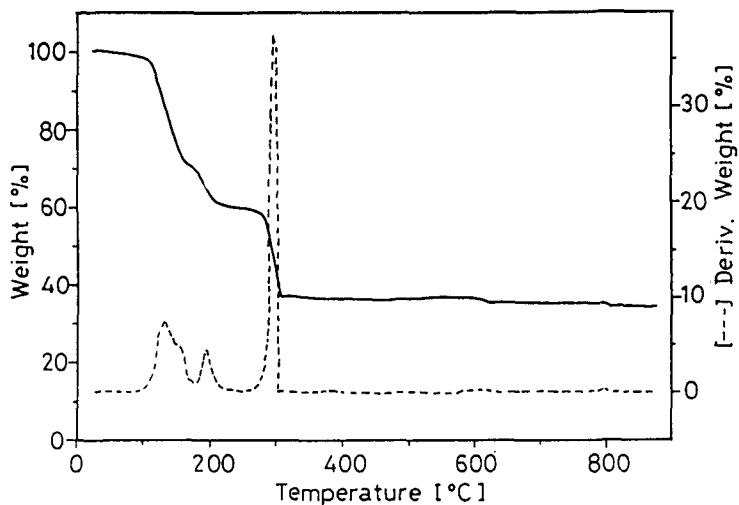


Fig. 5 TG of a precursor from citric acid without ethylene glycol

The X-ray powder patterns agreed with the conclusions drawn from the IR spectra: BaCO<sub>3</sub> could be detected from 380° to 800°C; phase-pure perovskite was obtained after prolonged heating at 850°C.

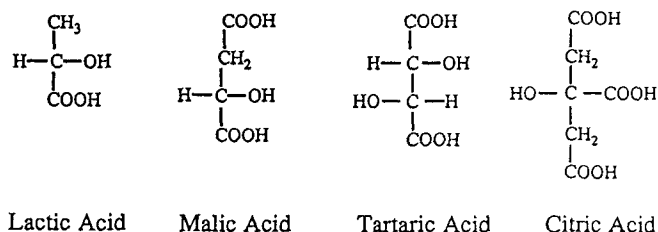


Fig. 6 Structural formulae of hydroxyacids used in this study

Precursors without ethylene glycol also gave the perovskite phase. The decomposition is similar, but because of the higher O/C ratio of the organic gel, it decomposes earlier (Fig. 5). The final evolution of NO is little affected.

Besides citric acid, the following other hydroxy-acids were tested as complexing agents for Pechini precursors: lactic, malic, and tartaric acid. Formulae of the acids are given in Fig. 6. These acids differ in the ratio of oxygen to carbon atoms in the molecule. It was therefore examined whether the different nominal oxidation state of the carbon atoms influences the decomposition pathway or the decomposition temperatures. TG curves of all four compounds were very similar, although some differences were observed in surface areas of BaBiO<sub>3</sub> obtained from the different precursors (Table 1).

Table 1 Surface area of BaBiO<sub>3</sub> from various precursors

Precursor	Surface area / m <sup>2</sup> ·g <sup>-1</sup>
Hydroacids+ethylene glycol:	
citric	1.4–1.7
malic	0.5
tartaric	0.5
lactic	0.6–1.1
Hydroxyacid w/o ethyleneglycol	
citric	0.1
Amino acids:	
α-alanine	0.2
β-alanine	0.3

## Conclusion

The Pechini-process using precursors with different hydroxyacids has been evaluated for the low-temperature synthesis of BaBiO<sub>3</sub>. Thermal analysis of the decomposition of the precursor shows that the reaction starts by loss of water of crystallization from the Bi(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O, followed by dehydration of the acids, and decarboxylation in the case of the citrate. This is followed by further oxidation of the organic matrix. In the absence of external oxygen, the oxygen for the combustion of the organic material comes from reduction of nitrate to NO. The nitrates are completely decomposed at 600°C. When calcining in air, the combustion uses external oxygen and proceeds to carbon dioxide. Under these conditions, Ba(NO<sub>3</sub>)<sub>2</sub> is stable to 650°C. Some BaCO<sub>3</sub> was formed at lower temperatures and gives rise to very prominent peaks in the IR spectra and recognizable diffraction peaks in XRD. The solid-state reaction between Bi<sub>2</sub>O<sub>3</sub> and the Ba-salt to the perovskite phase sets in at about 600°C, but is not completed until 800°C. BaBiO<sub>3</sub> synthesised from the citrate precursor shows the largest specific surface, presumably because of smaller particle size due to better complexing action of the tri-dentate citrate complex.

## References

- 1 G. W. Keulks, W. An and D. Li, 'The Use of Oxygen-Deficient Perovskite Catalysts for the Oxidative Coupling of Methane', 12th North American Meeting of the Catalysis Society, May 5-9, 1991, Lexington, Kentucky USA.
- 2 M. P. Pechini, US Patent, 3,231,328, Jan 25, 1966.; M. Pechini, US Patent, 3,330,697, July 11, 1967.
- 3 P. A. Lessing, Ceramic Bulletin, 68 (1989) 1002.
- 4 H. U. Anderson, M. J. Pennell and J. P. Guha, Advances in Ceramics Vol. 21, pp. 91-98; G. L. Messing, K. S. Mazdiyasi, J. W. McCauley and R. A. Haber (Eds), American Ceramic Society, Westerville OH 1987.
- 5 Ph. Courty, J. Ajot, Ch. Marcilly and B. Delmon, Powder Technol., 7 (1973) 21.
- 6 H. M. D. Tascón, S. Mendioroz and L. G. Tejuca, Z. Phys. Chem. N. F., 123 (1981) 109.
- 7 S. Jaenicke, G. K. Chuah and S. T. Khor, Thermochim. Acta, 216 (1993) 285.
- 8 D. Hennings and W. Mayr, J. Solid State Chem., 26 (1978) 329.
- 9 M. M. Barbooti and D. A. Al-Sammerrai, Thermochim. Acta, 98 (1986) 119.

**Zusammenfassung** — Mittels TG und EGA wurde die thermische Zersetzung der metall-organischen Vorstufen des Mischoxides BaBiO<sub>3</sub> untersucht. Die durch die Polyveresterung bifunktionaler Säuren mit Ethylenglykol (Pechini Prozeß) hergestellten Präkursoren zersetzen sich um etwa 100°C höher als die ohne Diol. Mittels IR und Röntgendiffraktion wurde als ein Reaktionszwischenprodukt BaCO<sub>3</sub> identifiziert. EGA besagt, daß der Anteil von BaCO<sub>3</sub> weniger als 10 % des Gesamtbariums ausmacht, und daß Barium bis 650°C hauptsächlich in Form einer Nitroverbindung existiert. In einem Pechini-Prozeß bei rund 850°C wurde aus einem Zitratpräkursor phasenreines BaBiO<sub>3</sub> mit einer mäßigen hohen spezifischen Oberfläche (1.4 m<sup>2</sup>/g) synthetisiert.