Thermal decomposition of precursors for BaBiO$_3$ prepared with amino acid complexes

S. Jaenicke, G.K. Chuah * and S.T. Khor

Department of Chemistry, National University of Singapore, Kent Ridge, Singapore 0511 (Singapore)

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Abstract

BaBiO$_3$ was prepared by several chemical and physical methods. The decomposition behaviour of the precursors was investigated using thermogravimetry, differential scanning calorimetry, evolved gas analysis, infrared spectroscopy and X-ray diffraction techniques. The self-propagating chemical decomposition (SCD) of the complexes with amino acids is compared with the decomposition of physical mixtures of barium and bismuth nitrates, with and without the addition of amino acids. Carbonate was detected as an intermediate from the IR spectra and was subsequently identified as BaCO$_3$ by XRD. No complex carboxylate, such as Ba$_2$Bi$_2$O$_5$CO$_3$, was detected. Carbonates formed by SCD required very high temperatures, in excess of 950°C, before they decomposed. Hence, the BaBiO$_3$ obtained by this method was contaminated with BaCO$_3$. The intermediate carbonates which formed in mixtures with amino acids decompose at slightly lower temperatures, <850°C. Mixtures of the pure metal nitrates gave single-phase BaBiO$_3$ at a considerably lower temperature, ≈620°C.

INTRODUCTION

Perovskite-type oxides have been reported to be catalytically active for a variety of reactions such as the oxidation of carbon monoxide, the reduction of nitrogen oxides [1] and the oxidation of ammonia [2]. Keulks et al. [3] have recently reported the use of Li-substituted BaBiO$_3$ as catalysts for the partial oxidation of methane. In the perovskite structure, Bi^{3+} and Bi^{5+} are present in a 1:1 stoichiometry. The substitution of some of the Bi ions with Li ions results in an increase in Bi^{5+} and oxide ion vacancies in the corresponding stoichiometric proportions [4]. These changes have a beneficial influence on the catalytic activity. Furthermore, substitutions at the Ba site in BaBiO$_3$ with potassium have resulted in superconductors with T_c values ranging from 13 to 30 K [5, 6].

Our interest in BaBiO$_3$ arose from its known catalytic properties. In this

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* Corresponding author.

context, a high specific surface area is essential. If carbonates are used as the starting material, very high temperatures, above 1000°C, are required to decompose the $BaCO_3$. High temperatures inevitably lead to sintering and therefore to a loss of surface area. Use of nitrates leads readily to the perovskite phase, but because the nitrate mixture melts before it decomposes to the corresponding oxides, a product with a low surface area is obtained. It was therefore hoped that by using chemical synthesis rather than conventional ceramic methods, high surface-area $BaBiO_3$ could be obtained. Kourtakis et al. [7] reported recently on a low temperature synthesis of $Ba_2YCu_3O_7$ which involved an oxidation–reduction reaction between the anions in a powder, finely mixed on an atomic scale. Ionic salts, such as nitrates, were reacted with salts of acetic acid [8] or with amino acids such as glycine, α-alanine and β-alanine, which act as reducing agents. Due to the intimate mixing in the precursor, the energy released during this redox reaction is believed to drive the decomposition to completion in a single step. The resulting mixture of metal oxides is homogeneous on an atomic scale and forms the desired mixed oxide phase more rapidly and at much lower temperatures than mixtures of oxides prepared by conventional ceramic methods. Because of the vigorous decomposition reaction, Kourtakis et al. coined the term 'self-propagating chemical decomposition' (SCD) for this process. In the earlier literature, precursors made of metal nitrates and organic polyacids, such as citric or lactic acid, have also been reported [9, 10]. A further variant of the method, which maintains the random nature of a solution in the solid phase, is the Pechini or resin-intermediate [11] process. The polycondensation reaction of a mixture of polybasic hydroxyacids with polyols at elevated temperature is utilized to trap the metal ions in a gel.

The objective of the present study was to compare some chemical and physical methods of preparing single-phase $BaBiO_3$. In order to evaluate the general applicability of the method of Kourtakis et al. [7], the self-propagating chemical decomposition method was attempted with various amino acids. Thermogravimetry (TGA), differential scanning calorimetry (DSC), evolved gas analysis (EGA), infrared spectroscopy (IR) and X-ray diffraction techniques were used to investigate the precursors and intermediates derived from the various preparative methods. An important question to be addressed was whether chemical synthesis offers an advantage over physical methods in forming the perovskite phase at lower temperatures and whether the formation occurs via carbonate intermediates.

Hennings and Mayr [12] have found that during the pyrolysis of barium titanium citrate, $BaCO_3$ and TiO_2 were present as intermediate compounds. In another study, it was suggested that a carbonate complex $(Ba_2Ti_2O_5CO_3)$ formed when barium titanyl oxalate was the starting material [13]. Cho et al. [11] have studied the thermal decomposition of (Sr, Ti) organic

precursors prepared by the Pechini process. Their results eliminate $SrCO_3$ and TiO_2 phases as intermediates. Instead, they propose the carboxylate complex ($Sr_2Ti_2O_5CO_3$) as an intermediate in the formation of $SrTiO_3$. Any extended $BaCO_3$ phase would decompose to BaO and CO_2 only above 1000°C. The lower decomposition temperature observed in several studies may also be due to nanocrystal formation or other morphological factors which facilitate the exothermic solid state reaction yielding the perovskite.

EXPERIMENTAL

Preparation procedure

Self-propagating chemical decomposition method

Aqueous 1 N solutions of $Ba(NO_3)_2$ (Riedel-de Haen, p.a.), $Bi(NO_3)_3$ · $5H_2O$, glycine ($CH_2(NH_2)COOH$), α-alanine ($CH_3CH(NH_2)COOH$), β-alanine ($H_2NCH_2CH_2COOH$), α-amino butyric acid ($CH_3CH_2CH(NH_2)COOH$) and γ-amino butyric acid ($H_2N(CH_2)_3COOH$) (Fluka, puriss) were prepared. In the case of $Bi(NO_3)_3$ · $5H_2O$, about 5% by volume of concentrated nitric acid was added in order to prevent the hydrolysis and precipitation of bismuth oxyhydrates. Appropriate amounts of these solutions were mixed so that the metal ions were in a 1:1 ratio and the total equivalents of metal ions were equal to the gram equivalents of amino acid. The mixed solution was evaporated to dryness in a rotary evaporator. The temperature was maintained below 70°C because initial tests had indicated that above this temperature, decomposition with evolution of nitrous gases occurs. Further drying was carried out under vacuum (10^{-3} mbar). The glycine, α-alanine and α-amino butyric acid precursors were obtained as solids, but β-alanine and γ-amino butyric acid precursors separated into a liquid and solid phase during subsequent drying.

Physical mixing method

Weighed amounts of $Ba(NO_3)_2$ and $Bi(NO_3)_3$ · $5H_2O$ were mixed and ground to a fine powder. Mixtures of these salts were also ground together with equivalent amounts of one of the amino acids used in the self-propagating chemical decomposition preparation. A slurry resulted which was dried under vacuum (10^{-3} mbar). All mixtures, except for the one with β-alanine, could be dried to a solid form. In the latter case, a viscous oil was formed.

The complexes and mixtures derived were calcined in air at various temperatures up to 1000°C. The SCD complexes decomposed via a vigorous exothermic reaction at about 250°C. These preparations were therefore performed in a deep dish inside a closed fume hood. As an additional precaution, the sample size was reduced in view of the potentially explosive interactions involved.

Analysis procedures

The thermal decomposition of the salts was monitored by thermo-gravimetric analysis (TGA) in air and by differential scanning calorimetry (DSC) in a nitrogen atmosphere using a Du Pont 9900 thermal analysis system. For TGA, an air flow of $75\,cm^3\,min^{-1}$ and a heating rate of $10°C\,min^{-1}$ was normally chosen. Because the Bi-containing salt reacts with platinum, quartz sample crucibles were used. The DSC analysis was carried out with a $40\,cm^3\,min^{-1}$ nitrogen flow rate and a heating rate of $10°C\,min^{-1}$. The instrument for evolved gas analysis (EGA) was home-built. It consists of a tubular quartz reactor which is inside a temperature-programmed oven. The sample tube is connected via a differentially pumped interface, made from two sampling valves, to a UHV chamber with a quadrupole mass spectrometer (Hiden HAL 200). The connections between the reactor and the quadrupole are minimized in length, and all lines were heated to avoid condensation of the products. Samples were heated at atmospheric pressure, either in a mixture of $He:O_2$ (9:1) or in pure He, at a flow rate of $100\,cm^3\,min^{-1}$. A heating rate of $5°C\,min^{-1}$ was used throughout.

Samples calcined at various temperatures were investigated by X-ray powder diffraction using a Philips PW1729 diffractometer (Cr $K\alpha$ radiation) and by infrared spectrometry (Shimadzu). The surface areas of the calcined compounds were measured by liquid nitrogen adsorption at 77 K using a Micrometrics Flowsorb 2300 (dynamic single-point determination).

RESULTS

SCD Precursors

   α-Alanine
   Figure 1 shows the TGA curve of the α-alanine precursor. A large mass loss of about 70% is observed in a single, almost vertical step at 176°C,
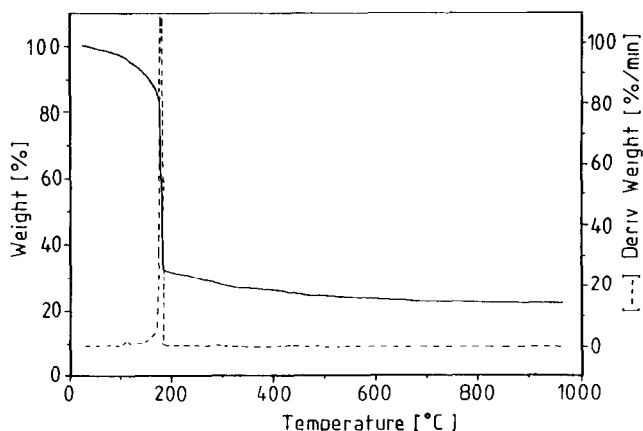

Fig. 1. TGA curve of α-alanine precursor.

which is followed by several smaller mass losses at 270, 430 and 580°C. The final mass at 950°C (22.20%) is lower than expected for $BaBiO_3$ (35.80%), which suggests that the initial precursor contained about 22 molecules of water per formula unit, despite the extensive drying under vacuum. The final mass loss of 0.0987 mg commences at about 580°C, giving a final residual mass of 1.1520 mg at 980°C. Assuming that $BaBiO_3$ is formed at this temperature, the mass loss corresponds to the loss of one molecule of CO_2 from a mixture with the composition $BaCO_3 \cdot 0.5Bi_2O_3$. If the decomposition were to occur via the carboxylate intermediate, $Ba_2Bi_2O_5CO_3$, the expected weight loss is 0.0640 mg, which is considerably less than that observed.

The EGA spectrum (Fig. 2) indicates that the first decomposition step cannot be assigned to a single reaction. H_2O, NO, N_2 (identified by the a.m.u. ratio of 28:14), CO_2 and CO are all evolved simultaneously. A closer inspection reveals that NO is lost from the complex in a broad peak from 118 to 250°C, together with water. At 176°C, a vigorous reaction occurs, which is manifested in the sharp and intense peaks of the decomposition products. This reaction is not solely an oxidation–reduction process associated with the complex but proceeds with the uptake of oxygen. More H_2O, CO and CO_2 are evolved at 270 and 430°C, showing further
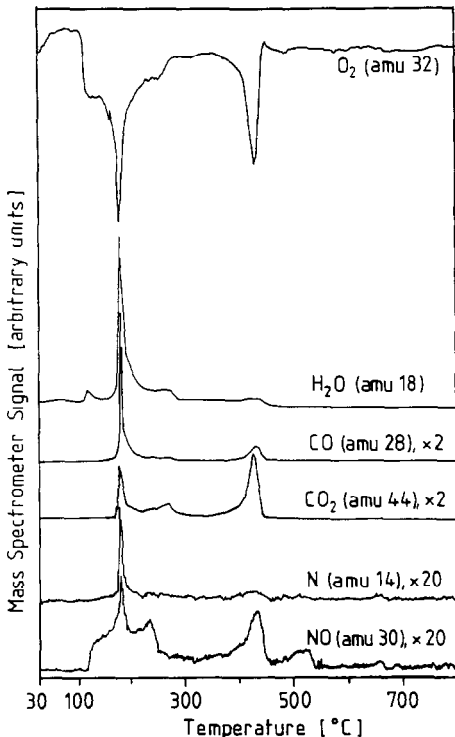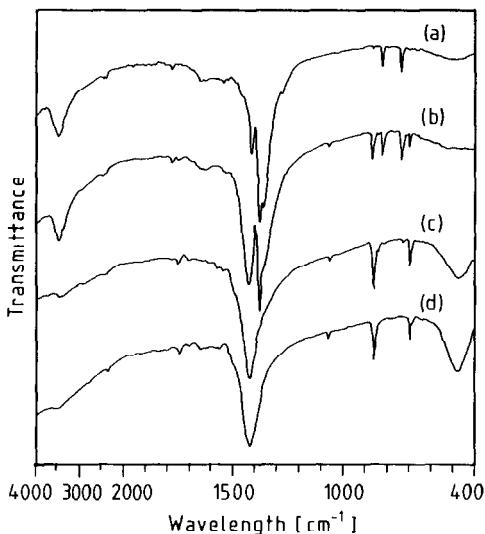

Fig. 2. EGA curve of α-alanine precursor.

Fig. 3. IR spectra of α-alanine precursor after heat treatment in air at (curve a) 250°C (curve b) 400°C (curve c) 540°C and (curve d) 780°C.

combustion of the organic part of the precursor. The remaining nitrates decompose in two steps with maxima at 430 and 530°C.

In order to analyse the structure of the solid phases involved, larger samples were prepared by calcination of the precursor at temperatures where the DSC and TGA indicated compositional or phase changes. For IR analysis, these were mixed with KBr (100:1), ground, and pressed into pellets. The IR spectra of samples treated to 250°C (Fig. 3(a)) show bands at 725, 815, 1380, 1410, 1770 and 2400 cm^{-1} that are characteristic for nitrate. After heating to 400°C (Fig. 3(b)), the absorption bands of $BaCO_3$ (690, 860, 1060, 1430 cm^{-1}) appear together with those for the nitrate. A sample heated to 540°C (Fig. 3(c)) shows only carbonate vibrations together with a broad band at 460 cm^{-1} which is indicative of the M–O–M (metal–oxygen–metal) vibration in the perovskite lattice [14]. In samples treated to successively higher temperatures, the M–O–M vibration becomes more pronounced, but the carbonate bands are still clearly visible after treatment at 780°C (Fig. 3(d)). Only after prolonged heating at 980°C is the sample completely converted to the perovskite. The carbonate therefore is not a contamination due to handling in air. Rather, the $BaCO_3$ forms by a reaction with the CO_2 produced during decomposition of the organic precursor.

Glycine, β-alanine, and α- and γ-amino butyric acid

The basic features of the decomposition of precursors made with other amino acids are similar to those described for the α-alanine complexes: a steep mass loss around 200°C, followed by a further decrease in mass until
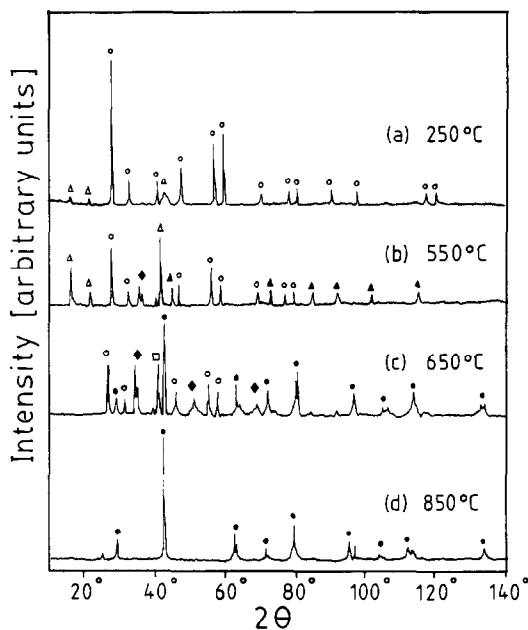
Fig. 4. XRD curves of glycine precursor following calcinations at (curve a) 250°C, 2 h (curve b) 550°C, 2 h (curve c) 650°C, 2 h and (curve d) 850°C, 10 h: ●, $BaBiO_3$; ○, $Ba(NO_3)_2$; ◆, $BaCO_3$; □, Bi_2O_3; ▲, $Bi_2O_2CO_3$; △, $Bi_6(NO_3)_4(OH)_2O_6 \cdot 2H_2O$.

the formation of the perovskite phase is completed at about 900°C. EGA shows in all cases that oxygen from the gas phase is a prerequisite for complete combustion of the organic component. As for the α-alanine precursor, NO is evolved at temperatures above 500°C. This NO probably originates from the barium nitrate that is incompletely decomposed at this temperature. The presence of $Ba(NO_3)_2$ after heating of the precursor was confirmed by IR and also by XRD.

X-ray diffraction studies correlate well with the IR results. In the glycine precursor (Fig. 4(a)–(d)), no glycine was detected after calcining at 250°C, showing that the organic component had been completely decomposed. However, not all nitrate had been decomposed, because diffraction lines of $Ba(NO_3)_2$ and of a hydroxynitrate of bismuth, $Bi_6(NO_3)_4(OH)_2O_6 \cdot 2H_2O$ (JCPDS:28-0654) were detected. Even after heating to 550°C, some nitrate was still present, together with $BaCO_3$ and $Bi_2O_2CO_3$. The perovskite phase, $BaBiO_3$, was formed at 650°C, although the $BaCO_3$ was still present. Single-phase perovskite was only obtained after 10 hours heating in air at 850°C.

The DSC curve of the amino acid precursors is dominated by a single sharp exotherm corresponding to the temperature of the steep initial mass loss (Figs. 5(a)–(c)). The peak maxima are listed in Table 1 together with the heat evolved (ΔH per mole precursor). The heat generated per mole
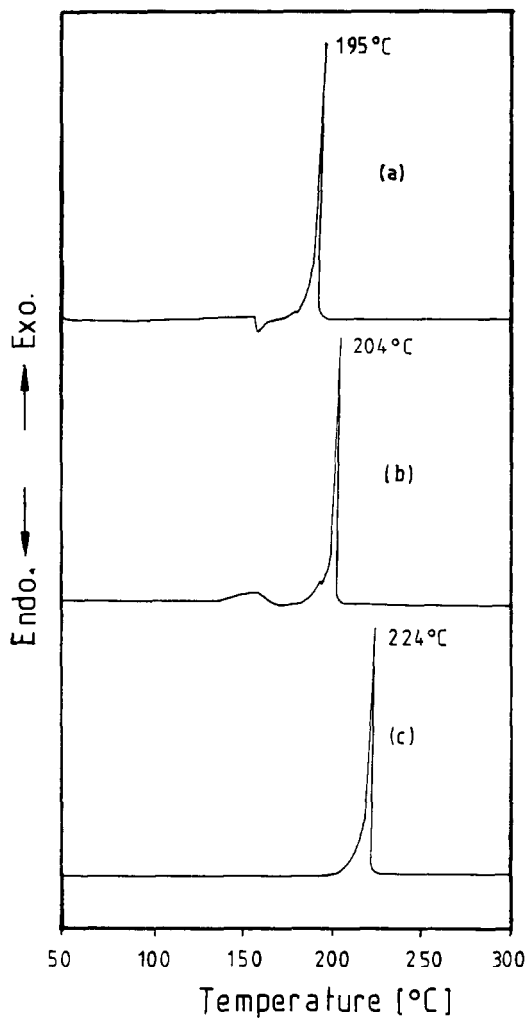
Fig. 5. DSC curves for the decomposition of (curve a) glycine (curve b) α-alanine and (curve c) γ-amino butyric acid precursors.

TABLE 1

DSC data for the decomposition of SCD precursors

Amino acid in precursor	Decomposition temperature (°C)	ΔH per mole of precursor (kJ mol^{-1})
Glycine	195	1098
α-Alanine	204	1187
β-Alanine	236	1543
α-Amino butyric acid	185	987
γ-Amino butyric acid	224	1013
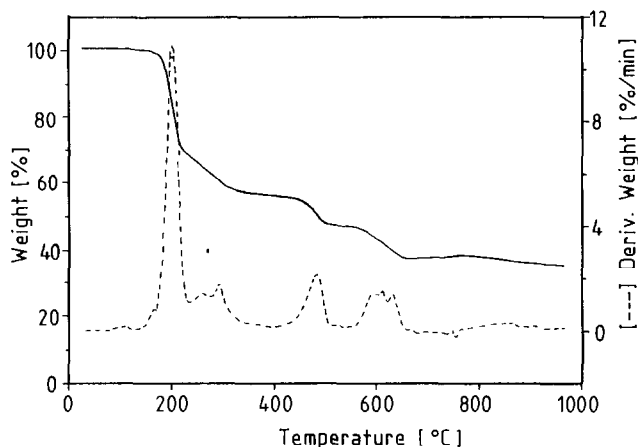
Fig. 6. TGA curve for α-alanine, $Ba(NO_3)_2$ and $Bi(NO_3)_3 \cdot 5H_2O$ mixture.

precursor is of the order of $1000 \, kJ \, mol^{-1}$. In an inert atmosphere, the main decomposition of the precursors occurs between 185 and 236°C.

Physical mixture of $Ba(NO_3)_2$, $Bi(NO_3)_3 \cdot 5H_2O$ and amino acids

To evaluate the influence of the "atomic scale mixing" which takes place in the complexes, samples were also prepared from mechanical mixtures of $Ba(NO_3)_2$, $Bi(NO_3)_3 \cdot 5H_2O$ and one of the amino acids, in the same stoichiometric ratio as for the complexes. In these physical mixtures, relatively large continuous phases of the individual constituents are present. The TGA curve of a mixture of α-alanine with barium and bismuth nitrates consists of a series of steps from 145 to 650°C (Fig. 6). The biggest mass loss occurred at 200°C, followed by smaller mass losses at 257–290, 481 and 586–628°C. In contrast, the complexed precursor showed a single big mass loss at a slighly lower temperature of 176°C. The final mass obtained in the physical mixtures is close to that expected for $BaBiO_3$, generally to within 3%. The EGA results are summarized in Table 2. The first three mass losses may be attributed to the decomposition of the amino acid and nitrates, because CO, CO_2, N_2, H_2O and NO are evolved. The final mass

TABLE 2

EGA data for the mixture of α-alanine with metal nitrates

Temperature (°C)	Gases evolved	Temperature (°C)	Gases evolved
200	H_2O, CO, CO_2, N_2, NO	481	H_2O, CO, CO_2, N_2, NO
257	NO	586–628	NO
290	H_2O, CO, CO_2		
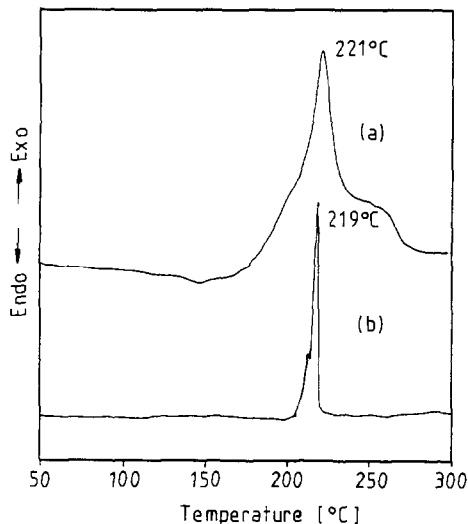
Fig. 7. DSC curves of $Ba(NO_3)_2$ and $Bi(NO_3)_3 \cdot 5H_2O$ mixtures with (curve a) α-alanine and (curve b) γ-amino butyric acid.

loss at 586–628°C is due solely to the decomposition of the remaining nitrate because only NO was detected.

DSC curves were also recorded. Mixtures with glycine, α-alanine (Fig. 7(a)) and α-amino butyric acid show a very broad exothermic peak, whereas β-alanine and γ-amino butyric acid mixtures have only one sharp exotherm (Fig. 7(b)). The peak maximum temperature was higher than in the analogous complex, with the exception of γ-amino butyric acid. The heat evolved is in the range of 700–1000 kJ per mole precursor, slightly lower than that of the SCD precursors (Table 3).

Figures 8(a)–(c) show the IR spectra of a physical mixture of the salts with glycine following heat treatment in air at various temperatures. Samples heated to 250°C show carbonate peaks at 690 and 860 cm^{-1}, together with peaks at 725, 815, 1380, 1415 and 2350 cm^{-1}, which indicate the presence of nitrates. The peak at 1270 cm^{-1} may be due to undecomposed

TABLE 3

DSC data for the decomposition of nitrate and amino acid mixtures

Amino acid in precursor	Temperature of decomposition (°C)	ΔH per mole of precursor (kJ mol^{-1})
Glycine	206, 232, 274	821
α-Alanine	221, 237, 254	712
β-Alanine	242	968
α-Amino butyric acid	189, 217, 257	827
γ-Amino butyric acid	219	787
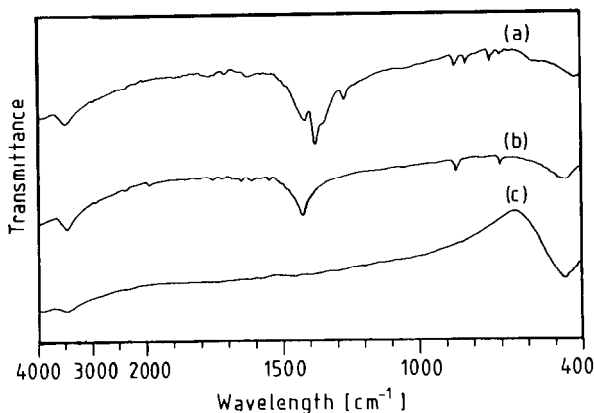
Fig. 8. IR spectra of a glycine/Ba(NO₃)₂/Bi(NO₃)₃ · 5H₂O mixture after heat treatment in air at (curve a) 250°C, 2 h (curve b) 650°C, 10 h and (curve c) 850°C, 23 h.

glycine. As the calcination temperature increases, the intensity of the carbonate peaks increases, whereas that of the nitrate peaks decreases. Metal–oxygen bands below $500 \, cm^{-1}$, which are indicative of the formation of BaBiO₃, first appeared at 650°C. At 850°C, the carbonate peaks were absent and only the metal–oxygen bands were detected. The XRD results confirm the conclusions drawn from the IR spectra and indicate that the cubic perovskite BaBiO₃ was formed at 850°C.

Physical mixture of Ba(NO₃)₂ and Bi(NO₃)₃ · 5H₂O

The TGA curve of a mixture of equal proportions of Ba(NO₃)₂ and Bi(NO₃)₃ · 5H₂O shows two major mass losses starting at 50 and 410°C respectively (Fig. 9(a)). The DTG curve shows that smaller mass losses occurred at 143, 281, 457, 582 and 605°C. Above 652°C, a slight mass increase was followed by a small mass loss of 1.27% at 800°C. The final mass at 900°C is consistent with that expected for BaBiO₃ to within 0.01%.

For comparison, the TGA curves of pure Ba(NO₃)₂ and Bi(NO₃)₃ · 5H₂O were also recorded. For Ba(NO₃)₂, decomposition commences only above 533°C (Fig. 9(b)). The DTG curve shows maxima at 624, 667, 726, 798 and 815°C. In contrast, Bi(NO₃)₃ · 5H₂O starts to decompose at comparatively low temperatures (Fig. 9(c)). Above 50°C, a very pronounced mass loss was observed with the maximum at 76°C. The corresponding DTG curve shows further mass losses at 152, 260, 469, 509 and 545°C. The residual mass is consistent with Bi₂O₃ to within 0.05%. An EGA of Bi(NO₃)₃ · 5H₂O was recorded in a mixture of He : O₂. The first low-temperature mass loss can be correlated entirely with the loss of water, whereas NO was evolved at higher temperatures together with a continuous evolution of water over the entire temperature range to 610°C.

Comparing these TGA curves, it is noted that below 572°C, the physical mixture of Ba(NO₃)₂ and Bi(NO₃)₃ · 5H₂O decomposes in a manner very
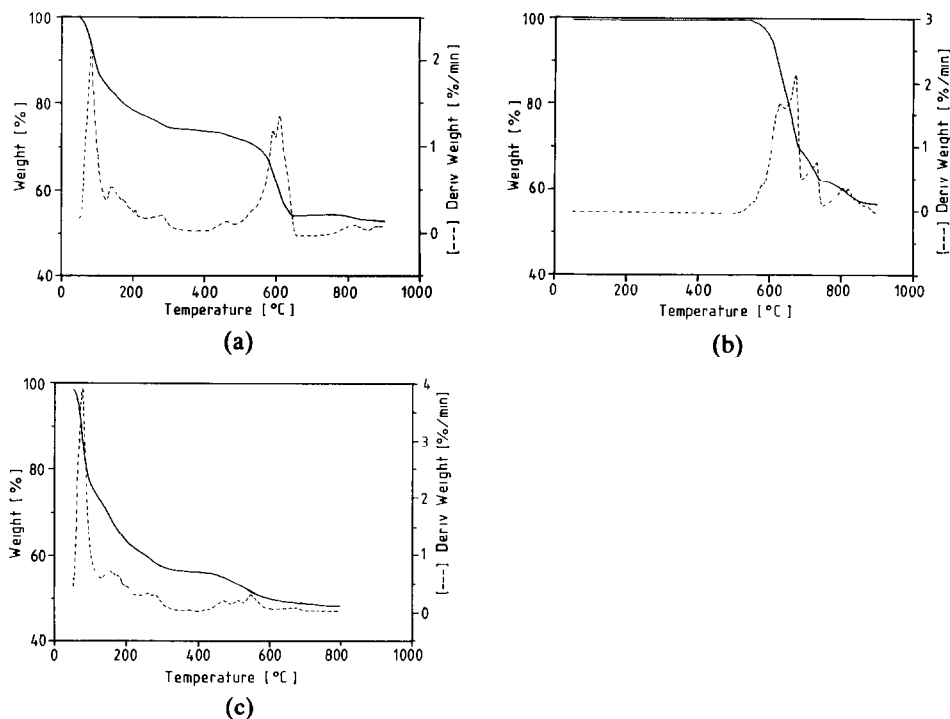
Fig. 9. TGA curves of (a) 1:1 mixture of $Ba(NO_3)_2$ and $Bi(NO_3)_3 \cdot 5H_2O$ (b) $Ba(NO_3)_2$ and (c) $Bi(NO_3)_3 \cdot 5H_2O$.

similar to that of $Bi(NO_3)_3 \cdot 5H_2O$. Above this temperature, the decomposition curve follows that of $Ba(NO_3)_2$, although the peak maxima are shifted to lower temperatures: from 624 and 667°C in $Ba(NO_3)_2$ to 582 and 605°C, respectively, in the mixture. The small mass loss at 800°C observed in the mixture was also found with $Ba(NO_3)_2$.

The IR spectrum of the mixture after treatment at 550°C reveals the presence of carbonates (695 and 858 cm^{-1}), nitrates (1375 and 1415 cm^{-1}) and oxides. The latter are identified by a broad metal–oxygen vibration band at 460 cm^{-1} (Fig. 10(a)). Following calcination at 600°C, the metal–oxygen bands become distinctive, indicating the presence of $BaBiO_3$ (Fig. 10(b)). The carbonate peaks at 695 and 858 cm^{-1} are reduced in intensity. The nitrate peak at 1415 cm^{-1} has also decreased in intensity. After heating to 650°C, carbonate and nitrate are no longer detected (Fig. 10(c)). The presence of carbonate in this mixture of pure nitrates may be due to the reaction of metal oxides with atmospheric CO_2 during calcining in air. This phase constituted only a small fraction of the bulk sample and decomposed easily at 650°C, unlike the carbonate phase formed in the SCD precursors or from physical mixtures with amino acid.

The XRD powder spectra show that some $BaBiO_3$ had formed after heating to 550°C, as well as other phases such as $Ba(NO_3)_2$, $BaCO_3$, Bi_2O_3,
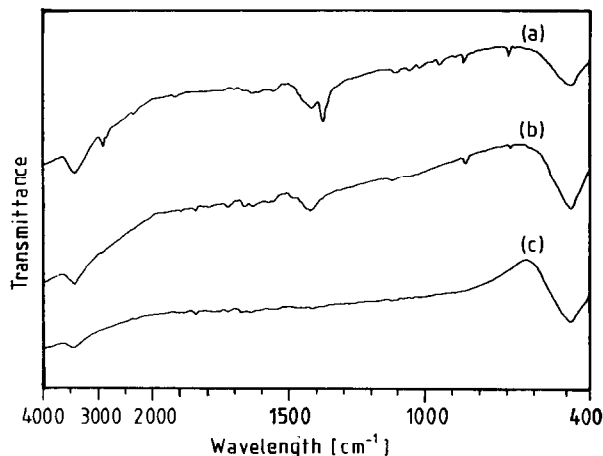
Fig. 10. IR spectra of 1:1 mixture of $Ba(NO_3)_2$ and $Bi(NO_3)_3 \cdot 5H_2O$ after heat treatment for 15 h in air at (curve a) 550°C (curve b) 600°C and (curve c) 650°C.

$Bi_2O_2CO_3$ and possibly a suboxide of bismuth nitrate, $Bi_6(NO_3)_4$-$(OH)_2O_6 \cdot 2H_2O$. Calcination at 600°C results in $BaBiO_3$ becoming the predominant phase, with only a small contamination by $BaCO_3$. One single phase, $BaBiO_3$, was detected following calcination at temperatures above 620°C.

The surface areas of the compounds prepared by SCD and by physical mixing with and without amino acids were measured using a single-point BET method. The surface areas after calcination at 850°C were always between 0.10 and 0.50 m^2g^{-1}, independent of the preparation route.

DISCUSSION

Precursors prepared by the SCD method decompose in one main step at temperatures below 230°C. The heat of decomposition is in the range of 1000 kJ per mole precursor. However, despite this large decomposition enthalpy, the metal nitrates did not decompose completely into the metal oxides. After the exothermic reaction, a compound which contains mainly nitrates together with some organic material is present. The latter is oxidized to CO_2 and H_2O in two further steps at higher temperatures. The remaining nitrates are decomposed at 650°C. The IR spectra indicate the presence of carbonates which may be $BaCO_3$ or a basic carbonate species, possibly $Ba_2Bi_2O_5CO_3$, analogous to $Ba_2Ti_2O_5CO_3$, reported by Gopalakrisnamurthy et al. [13] as a final intermediate phase in the formation of $BaTiO_3$. However, the mass loss commencing at 580°C in the TGA for α-alanine corresponds closely to the loss of one mole of CO_2 per mole of $BaBiO_3$, thereby suggesting $BaCO_3$ as an intermediate.

The XRD data also clearly indicate the presence of $BaCO_3$ (JCPDS 5-0378). Hence, the formation of $Ba_2Bi_2O_5CO_3$ as an intermediate can be

discounted. The carbon dioxide required for the formation of carbonates obviously originates from the decomposition of the amino acid. The EGA curve of α-alanine (Fig. 2) shows that large amounts of CO_2 were evolved in the highly exothermic reaction at 176°C and again at around 430°C. Nitric oxide was also detected at the same temperatures, indicating the simultaneous decomposition of the metal nitrates. In the presence of a high CO_2 partial pressure, the resulting oxides will react readily to form carbonates. Once formed, very high temperatures in excess of 1000°C are required to completely decompose the $BaCO_3$. In this case, a $BaBiO_3$ phase can only be detected after prolonged heating above 850°C.

Kourtakis et al. [7] proposed that an internal oxidation–reduction reaction takes place between the ionic nitrate and the amine group of the amino acid. They studied three amino acids, glycine, and α- and β-alanine, in their precursors for $Ba_2YCu_3O_7$ superconductors. The differences in the decomposition temperature which they observed when using different amino acids were correlated to the basicity of the amino acid amine group. The β-alanine complex shows a lower decomposition temperature than the corresponding complex with α-alanine. They postulate that the carboxylate group of the amino acid reduces the electron density at the amine group so that an α-amino acid is less basic and therefore less reactive than a β-amino acid.

However, no such trend was noted with the SCD complexes reported here. Rather, the α-amino acid precursors decompose at lower temperatures than the corresponding β- or γ-analogues (Table 1). The present complexes were formed under acidic conditions, and hence the amine function exists in the protonated form. We assume that the metal cation binds to the carboxylate ion and that the nitrate anion binds to the positively charged ammonium group, to form $RCH(NH_3^+NO_3^-)COO^-M^+$ where R is H, CH_3 or C_2H_5 and M^+ is Bi^{3+} or Ba^{2+}. Five different amino acids were studied: glycine, α- and β-alanine, and α- and γ-amino butyric acid. The organic chain in these molecules increases from 2 to 4 carbon atoms but the heat of reaction is almost constant (Table 1) with the exception of the β-alanine complex. Because the caloric value of the complexes increases with increasing hydrocarbon chain length, it is concluded from the DSC data that complete combustion and volatilization of the organic components is not achieved in a single step. This is in contrast to the results of Kourtakis et al. [7] in their study on precursors to $Ba_2YCu_3O_7$. Spray-dried glycine and metal nitrates decomposed into the metal oxides (and some $BaCO_3$) via a low temperature exothermic reaction. This discrepancy may be a consequence of the absence of catalytic activity in barium and bismuth, used in our study, compared with the known activity of copper. Courty et al. [10] observed previously that catalytically active cations can change the mechanism of the decomposition from multi-step to single-step.

By physically mixing the amino acids with the barium and bismuth nitrates, it was found that the decomposition occurred in multiple steps in the case of glycine, α-alanine and α-amino butyric acid systems. The general features are similar to those of the SCD precursors although the decomposition temperatures are increased (Table 3). Because physically mixing the amino acids with the salts does not allow close proximity between the reactants, a smaller proportion of the mixture is decomposed in successive steps, hence the heat of reaction corresponding to the first exotherm is lower (Table 3) and the steps in the TGA curve (Fig. 6) are more pronounced than for the SCD precursors. A less homogeneous mixture of oxides and nitrates can therefore be expected in this case. Following calcination of the glycine mixture at 250°C, nitrates and carbonates were detected by IR spectroscopy. The presence of carbonates shows that some of the nitrates had already decomposed at this temperature, with nitrate decomposition complete at 650°C and carbonate still present. The perovskite phase formed above 650°C but was accompanied by $BaCO_3$. Pure $BaBiO_3$ was obtained at 850°C. Compared with the SCD complexes, amino acid/metal nitrate mixtures yield a single phase perovskite $BaBiO_3$ at lower temperatures. The $BaCO_3$ formed in the process decomposes by 850°C in contrast to temperatures $>1000°C$ required for the SCD precursors.

In the absence of the amino acids, a mixture of barium and bismuth nitrates decomposes at 550°C to give $BaBiO_3$. The perovskite phase was accompanied by some $BaCO_3$ which could have formed in a reaction between the oxide and gas phase CO_2. This $BaCO_3$ was already decomposed at 600°C such that at higher temperatures, phase-pure $BaBiO_3$ was obtained.

The compounds prepared by both chemical and physical methods have very low surface areas, $<0.50 \, m^2 \, g^{-1}$, which may be due to melting of the precursors above 700°C. Pure Bi_2O_3 is known to melt at 825°C [15]. Extensive melting was noted for the SCD precursors. If $BaBiO_3$ is to be used as a catalyst for oxidative methane coupling, it is essential that the surface area is increased and sintering prevented at the operating temperature, which is usually between 700 and 800°C.

CONCLUSION

The results show that the presence of an amino acid, whether physically mixed or complexed with the metal nitrates, does not assist the formation of the perovskite $BaBiO_3$. Conversely, their presence favours the formation of carbonates which require very high temperatures for decomposition. Combustion of these amino acids leads to an increased atmosphere of CO_2 and H_2O which subsequently results in the formation of more carbonates from the oxides. The formation of $BaBiO_3$ is achieved at relatively low

temperatures from a physical mixture of the metal nitrates. This is due to the melting of Bi_2O_3 which facilitates the solid state reaction with $BaCO_3$. Unfortunately, this route leads to powders with a very low surface area.

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