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SYNTHESIS AND THERMAL DECOMPOSITION OF ANTIMONY(III) OXIDE HYDROXIDE NITRATE

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Abstract

The thermal decomposition of the only known antimony nitrate antimony(III) oxide hydroxide nitrate $Sb_4O_4(OH)_2(NO_3)_2$, whose synthesis routes were reviewed and optimized was followed by TG-DTA under an argon flow, from room temperature up to 750°C. Chemical analysis (for hydrogen and nitrogen) performed on samples treated at different temperatures showed that an amorphous oxide hydroxide nitrate appeared first at 175°C, and decomposed into an amorphous oxide nitrate above 500°C. Above 700°C, Sb_6O_{13} and traces of α-Sb_2O_4 crystallized.

Keywords: antimony oxides, antimony(III) oxide hydroxide nitrate, thermal decomposition, X-ray diffraction

Introduction

Although many bismuth nitrates, more precisely oxide nitrates, hydroxide nitrates and oxide hydroxide nitrates, have been mentioned and characterized in the literature [1–5], only one oxide hydroxide nitrate is known for antimony, a close element whose metallic character is less pronounced: $Sb_4O_4(OH)_2(NO_3)_2$. Cited in Gmelin's Handbook under the dualistic formula $2Sb_2O_3{\cdot}N_2O_5{\cdot}H_2O$ [6], it has been the subject of two studies:

– in 1974, Bovin established its crystalline structure and confirmed its formula as an oxide hydroxide nitrate. This crystallographic study was performed on crystals synthesized by a nitric acid attack of Sb_2O_3, followed by very slow cooling [7].

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– in 1984, Berry and Brett obtained a white solid by the attack of metallic antimony powder by HNO_3. This solid was proved to be a mixture of orthorhombic Sb_2O_3 and $Sb_4O_4(OH)_2(NO_3)_2$. The products of its thermal decomposition *in air* were identified by X-ray diffraction: Sb_2O_3 existing from 135°C to 360°C, and α-Sb_2O_4 from 360 to 735°C [8].

No other study was performed on the thermal behaviour of $Sb_4O_4(OH)_2(NO_3)_2$ (designated hereafter by Sb(III)OHN). We have tried to clarify the synthesis route required to obtain a pure product, and to present a complete study of its thermal decomposition in an inert atmosphere, from room temperature up to 750°C.

Experimental

Materials

HNO_3 (69%) and Sb_2O_3 were supplied by Prolabo. X-ray diffraction analysis of Sb_2O_3 showed that both orthorhombic and cubic varieties of this oxide were present.

Methods

The products synthesized in this study were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), differential thermal analysis (DTA), thermogravimetric analysis (TG), and chemical analysis (for nitrogen and hydrogen).

XRD spectra were recorded with a Philips powder diffractometer (Philips PW1830), using $CuK_{\alpha 1}$ radiation (1.5418 Å).

The micrographs of the powders were obtained with a Streoscan 120.

Thermal decompositions were followed with a Setaram TG-DTA 92 unit. The measurements were carried out under an argon flow (100 ml/min), using Pt crucibles and α-Al_2O_3 as a reference material. A heating rate of 5 deg·min^{-1} was used.

Chemical analyses were performed by the CNRS regional service of microanalysis, attached to Université P. et M. Curie. After a flash combustion of the sample, the H_2O and NO_2 produced were converted into CO_2 and N_2, respectively. CO_2 was measured by coulometry and N_2 by catharometry. No carbon was previously detected in the samples.

Results

Synthesis and characterization of Sb(III)OHN

Syntheses

The first preparation route followed Bovin's method [7]. Sb_2O_3 was suspended in a dilute nitric acid solution (2 g oxide/l of solution). The suspension was stirred for a few hours, then filtered on a glass-frit (porosity 4), and washed with water. The powder was dried for five days over P_2O_5. The final product was a very fine, white, pearly powder.

Three parameters of this procedure were varied:

- HNO_3 concentration
- reaction temperature
- reaction time.

The synthesis conditions of the main samples are given in Table 1 (Samples A to J). The yield of the reaction was 75% referred to the initial Sb_2O_3.

Table 1 Conditions of preparation of various samples

Sample	Concentration of HNO_3 / mol·L^{-1}	Temperature / °C	Reaction time / h
A	0.1	25	2
B	0.1	80	2
C	1	80	2
D	1	105	2
E	6	25	2
F	6	25	3
G	6	25	4
H	6	80	2
I	6	120	2
J	6	120	4

The second preparation route to Sb(III)OHN was developed by Berry and Brett [8]. Metallic antimony powder was attacked by concentrated HNO_3 (69–71%) (3 g Sb in 600 ml acid). At room temperature, the reaction between the metal and the acid was exothermic and accompanied by evolution of nitrogen oxide fumes. When the fumes began to disappear, the temperature was increased to 80°C. The Sb(III)OHN precipitated during cooling. It was filtered off, washed and dried as in the first method (Sample K). The yield was about as high as in first synthesis.

Crystallinity of the samples

A first classification of the samples can be made by XRD and SEM. It can be noted, that during preliminary experiments with varying Sb_2O_3/HNO_3 ratios no other oxide hydroxide nitrate than $Sb_4O_4(OH)_2(NO_3)_2$ was detected by XRD.

Samples A to J

– When the acid was very dilute (samples A and B), no reaction occurred and Sb_2O_3 remained intact.

– When the reaction took place in 1 mol/l HNO_3 (samples C and D), the characteristic lines of Sb(III)OHN appeared, as mentioned by Bovin (Fig. 1a).

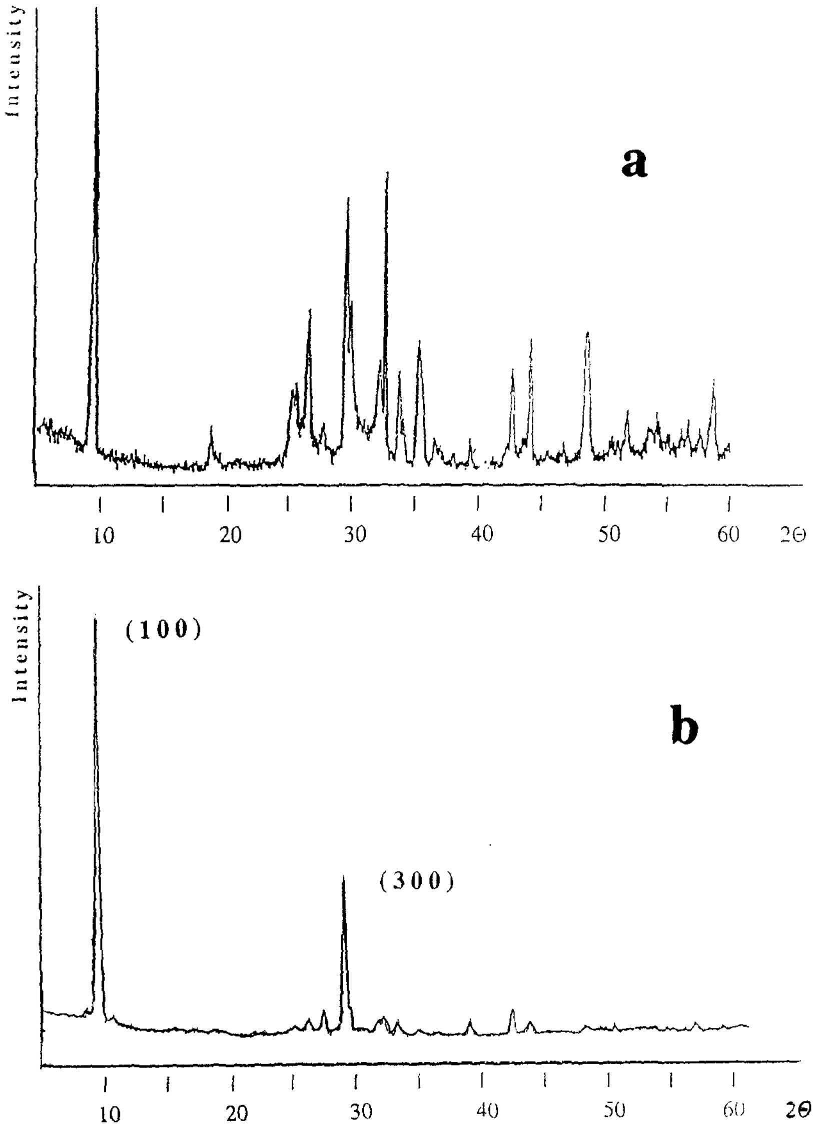

Fig. 1 XRD patterns of: a) Sample C (1 mol/l HNO_3, 80°C); b) Sample E (6 mol/l HNO_3, 25°C);

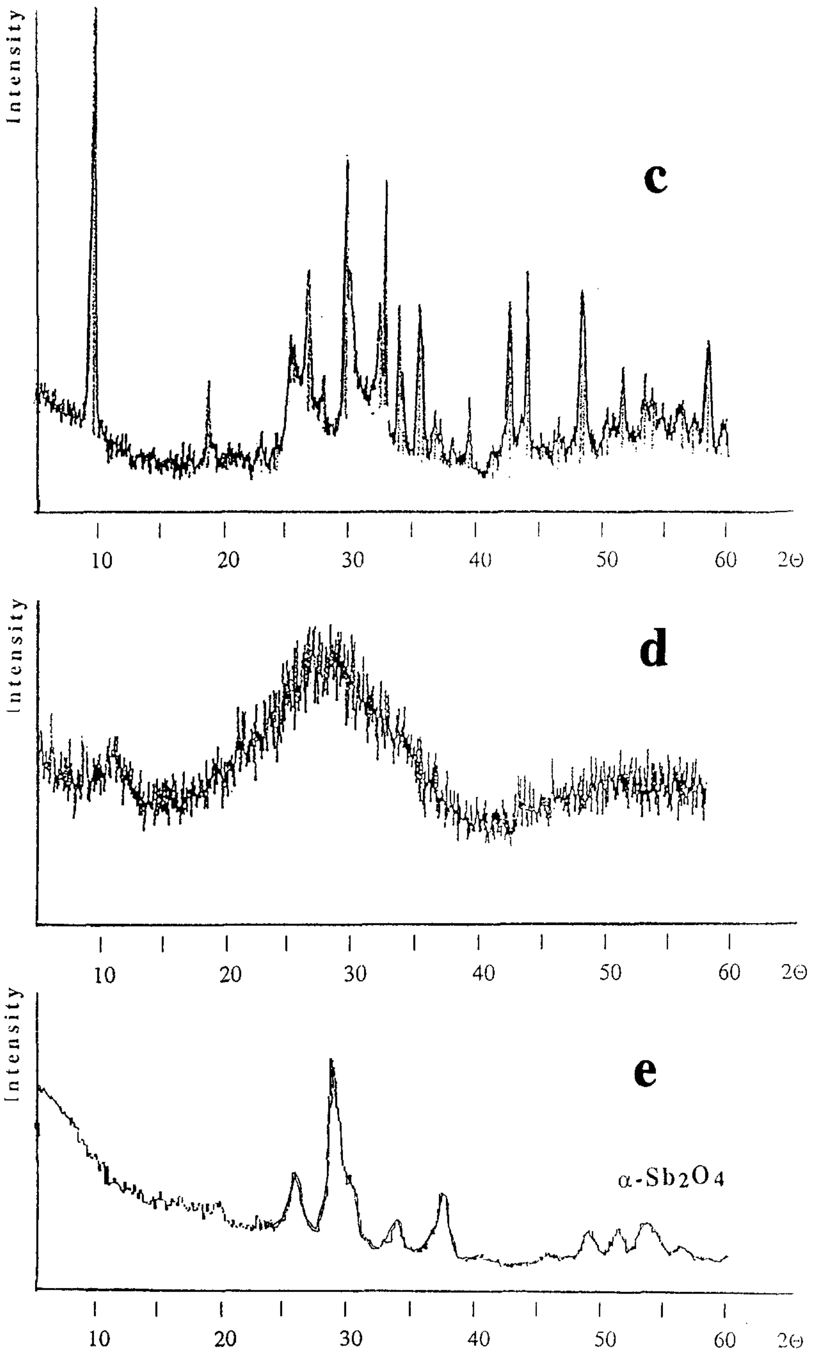

Fig. 1 XRD patterns of: c) Sample synthesized in 7 mol/l HNO_3, 50°C; d) Sample I (6 mol/l HNO_3, 120°C, 2 h); e) Sample J (6 mol/l HNO_3, 120°C, 4h)

– When Sb_2O_3 was suspended in 6 mol/l HNO_3, a sharper XRD spectrum of Sb(III)OHN (samples E to H) was obtained.

As shown by SEM, the products obtained at room temperature (E to G) crystallized in long-shaped platelets with angular facies (Fig. 2a); their degrees of crystallization increased when the reaction time increased. (100) and (300) XRD lines were found to be very strong. This was due to the layered structure of the product and to the growth of platelets in the *yz* plane (Fig. 1b). Further experiments carried out in 7 mol/l HNO_3 at 50°C led to microcrystals (Fig. 2b), whose XRD pattern was closer to Bovin's results, but still with a few differences in the intensities (Fig. 1c).

Micrographs of sample H ($T=$ 80°C) showed a mixture of a crystallized phase (platelets) and a probably amorphous phase, constituted of rough round-shaped particles (Fig. 2c).

Sample I (120°C, 2 h) gave an X-ray pattern characteristic of an amorphous product, as confirmed by SEM (Fig. 1d). If the reaction was continued at this temperature (sample J), the XRD spectrum of the product was ill-defined, but exhibited analogies with α-Sb_2O_4 (Fig. 1e).

Sample K

Sample K gave results similar to samples C to G.

Chemical analyses

Weight percentages of hydrogen and nitrogen in samples C to H and K were compared with the percentages calculated from the formula $Sb_4O_4(OH)_2(NO_3)_2$ (N = 3.95%, H = 0.28%). Samples D and H were found to be slightly degraded (loss of nitrogen, relative excess of hydrogen).

Conclusions

The only sets of conditions leading to pure Sb(III)OHN correspond to samples C, E to G and K. The analysis and the characterization of Sb(III)OHN degradation products in nitric acid medium will be described in a later paper [9].

Thermal decomposition of $Sb_4O_4(OH)_2(NO_3)_2$

One of the samples E to G was selected in order to study its decomposition by TG coupled with DTA, by XRD and by chemical analysis for hydrogen and nitrogen, up to 750°C.

The TG and DTA curves are given in Fig. 3. They were obtained under an argon flow, to avoid oxidation of the products in case of contact with air.

A significant loss in mass, associated with a strongly exothermic effect (6.5%) was observed at 175°C. The resulting product was amorphous (Fig. 4a),

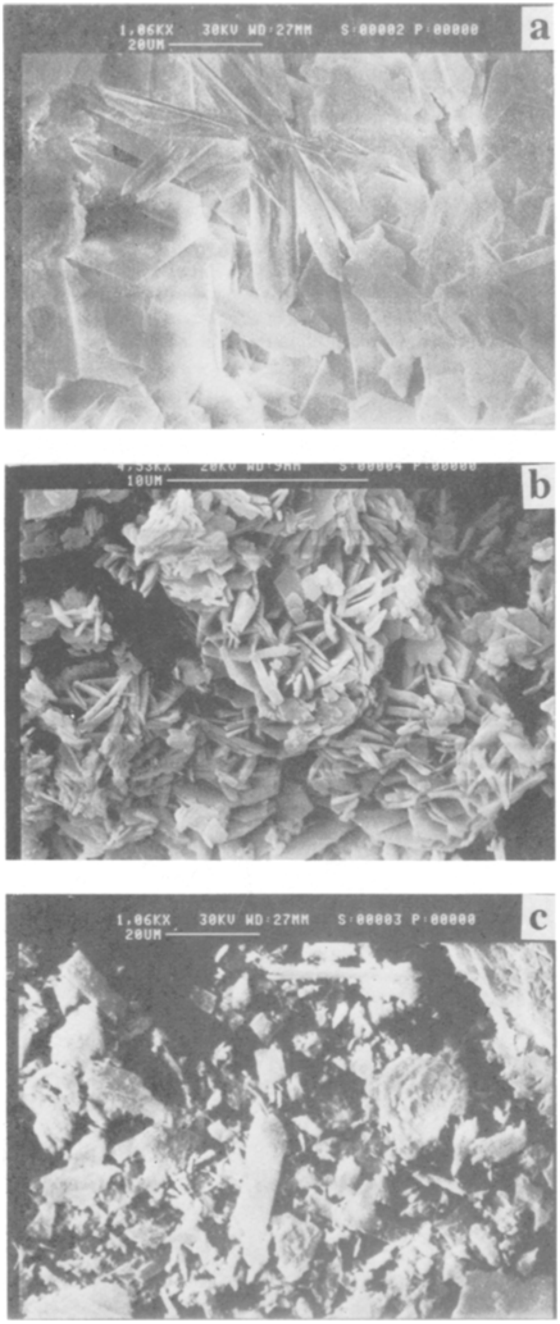

Fig. 2 SEM micrographs of: a) Sample E (6 mol/l HNO_3, 25°C); b) Sample synthesized in 7 mol/l HNO_3 50°C; c) Sample H (6 mol/l HNO_3, 80°C)

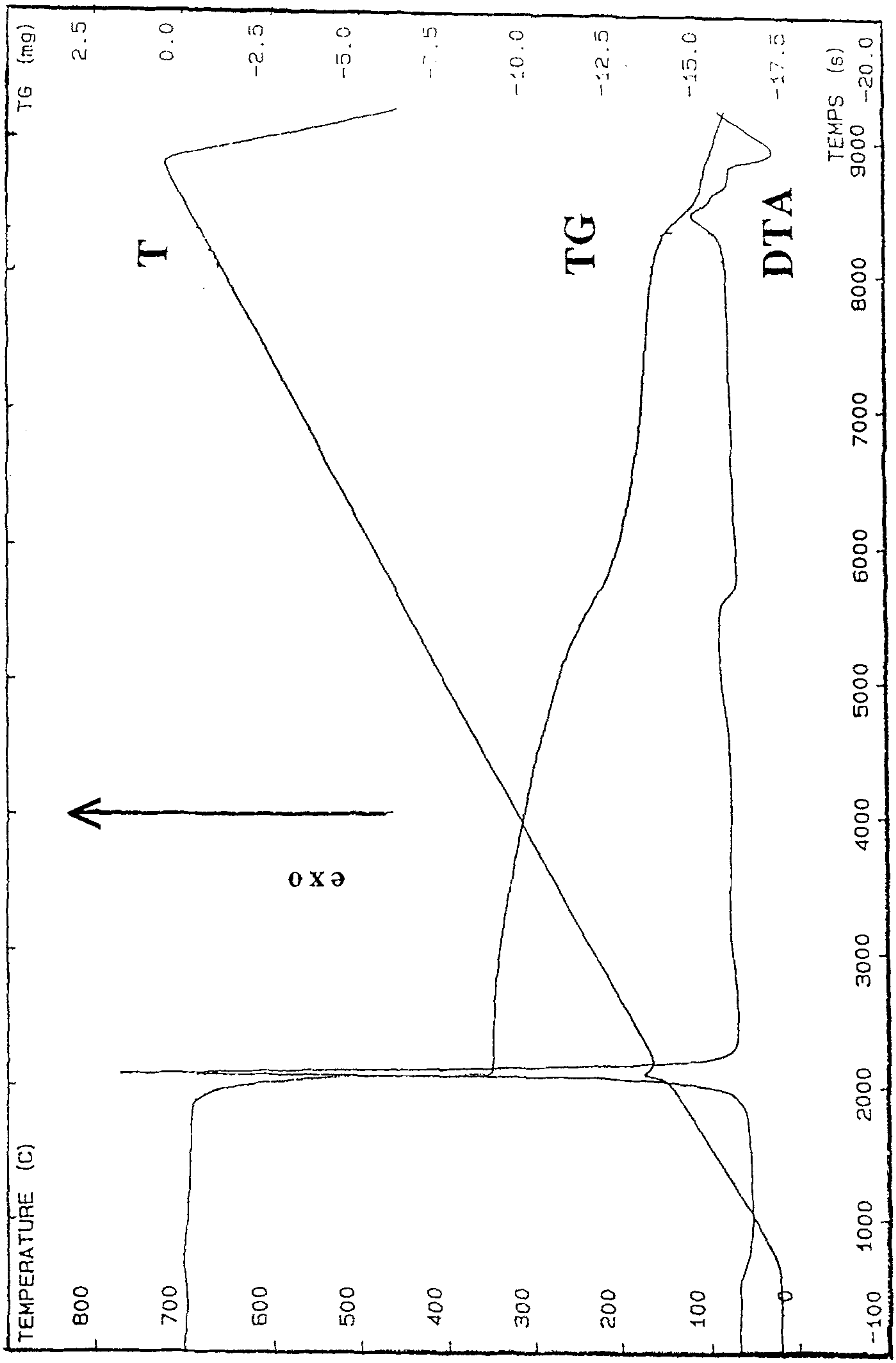

Fig. 3 TG and DTA curves of the $Sb_4O_4(OH)_2(NO_3)_2$ (sample weight = 139 mg)

and so were the decomposition products up to 700°C. The loss in mass went on continuously up to 750°C, with two inflexions, between 400 and 450°C, and around 700°C. They were accompanied by two slightly exothermic effects. At

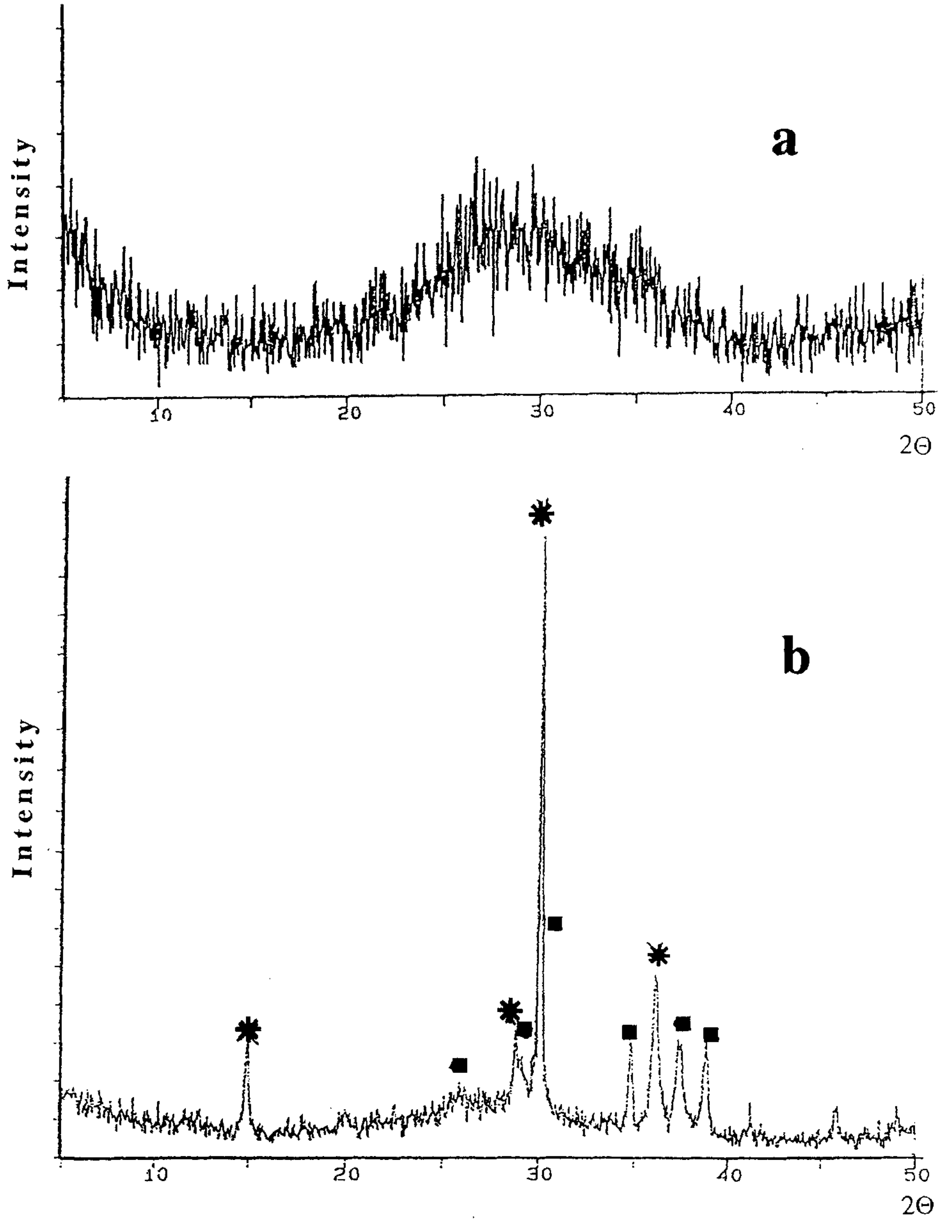

Fig. 4 XRD patterns of products of decomposition of $Sb_4O_4(OH)_2(NO_3)_2$: a) after treatment under an argon flow at 175°C; b) after treatment under an argon flow at 700°C (∗: Sb_6O_{13}; ■ α-Sb_2O_4)

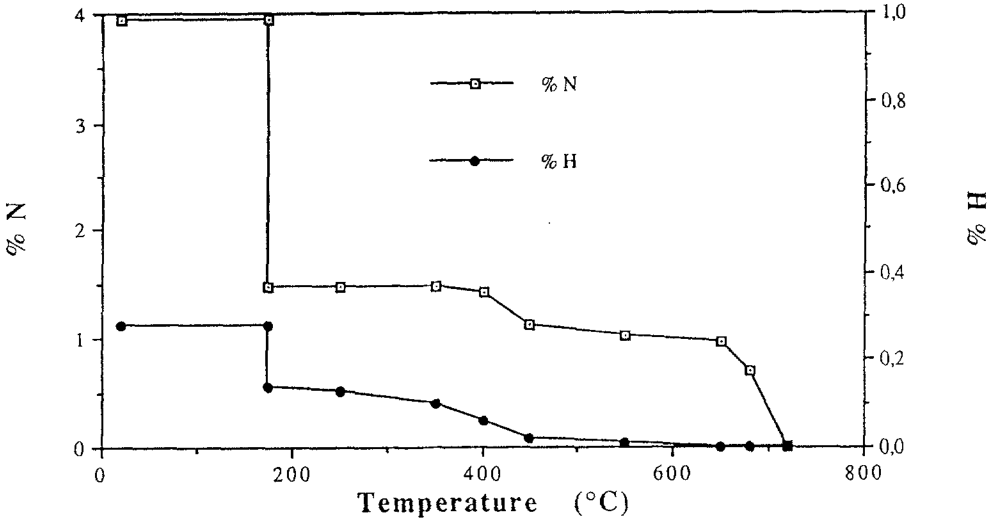

Fig. 5 Change in hydrogen and nitrogen contents during calcination of $Sb_4O_4(OH)_2(NO_3)_2$

700°C, the exothermic peak coincided with the crystallization of the oxides Sb_6O_{13} and α-Sb_2O_4, as shown by the XRD pattern (Fig. 4b). The total loss in mass amounted to 10.5% at 700°C.

In order to determine the mechanism of the decomposition, chemical analyses were performed at several temperatures (Fig. 5).

Even after the destruction of the crystalline network of Sb(III)OHN at 175°C, nitrogen and hydrogen still existed in the solid. Hydrogen progressively disappeared between 175 and 480°C, its rate of elimination increasing between 350 and 450°C. A drop in nitrogen content was observed over the same period. The nitrogen content of the resulting oxide nitrate then remained roughly constant and dropped to zero in the temperature interval between 550 and 700°C.

Between 175 and 700°C, an amorphous phase of oxide hydroxide nitrate, then of oxide nitrate, exists. Above 700°C, the slight exothermic effect recorded corresponds to the crystallization of Sb_6O_{13} (with traces of α-Sb_2O_4), as already mentioned by Berry and Brett [8].

Conclusions

The synthesis of $Sb_4O_4(OH)_2(NO_3)_2$ from Sb_2O_3 in HNO_3 can only be done under mild conditions. Too high a temperature for a given acid concentration leads to a degraded product. On the other hand, our synthesis from metallic Sb only produces pure $Sb_4O_4(OH)_2(NO_3)_2$.

The thermal decomposition of pure $Sb_4O_4(OH)_2(NO_3)_2$ in an inert atmosphere involves three steps, two of which are different from what Berry and Brett observed:

- between 175 and 480°C, amorphous oxide hydroxide nitrate
- between 480 and 700°C, amorphous oxide nitrate
- above 700°C, crystallized Sb_6O_{13} and α-Sb_2O_4 are formed.

The compositions of the amorphous phases vary with temperature, and so probably does the oxidation state of antimony (from only Sb(III) to Sb(V)/Sb(III) in a 4/2 ratio), depending on the concentration of the oxidizing species, i.e. nitrate ions. The relationships between the structure of these compounds, the oxidation state of antimony and the oxidative part played by nitrate ions will be the subject of a later paper [9].

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