

## **SYNTHESIS OF BISMUTH (III) OXIDE FROM OXALATE: A STUDY BY CONTROLLED TRANSFORMATION RATE THERMAL ANALYSIS (CRTA)**

E. Diez, O. Monnereau, L. Tortet, G. Vacquier, P. Llewellyn, F. Rouquerol

Lab. MADIREL, UMR UP-CNRS n° 6121 – Saint-Charles Centre (Case 26)  
3, Place V. Hugo – 13331 MARSEILLE Cedex 3 – France

This study presents recent results on thermal decomposition of an hydrated bismuth oxalate by the use of the Controlled transformation Rate Thermal Analysis (CRTA) under vacuum and in air. The precipitate of  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$  presents an unknown XRD diagram. Its decomposition proceeds in two steps, either under vacuum or in air atmosphere. Under vacuum, the decomposition leads to Bi between 200 and 300°C. In air, the controlled decomposition leads to obtain the metastable  $\beta\text{-Bi}_2\text{O}_3$  phase around 270°C. This last result demonstrates the possibility to stabilise new or metastable phases by CRTA routines.

*Keywords:* Bismuth oxalate, Bismuth oxide, Thermal analysis, CRTA

### **1. Introduction**

Chemical routes have been intensively investigated during the last decade in connection with the development of high-Tc superconducting ceramics because these chemical techniques improve the homogeneity of the final product [1]. The oxide powders prepared this way have high specific surface area and readily undergo solid-state reaction and sintering [2]. Bi-based superconducting ceramics have been widely obtained by using the oxalate coprecipitation techniques [3,4]. A better knowledge in the decomposition process of the relevant metal oxalates allow to a better control in the elaboration of these oxides. For this objective, we have started a study of the thermal decomposition of the hydrated bismuth oxalate by the use of an original thermal technique, so-called Controlled transformation Rate Thermal Analysis (CRTA) [5].

Only Polla et al [6] give information on bismuth oxalates, possible starting compounds for the obtaining of bismuth oxide by chemical routes. They have clearly characterised two different varieties:  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$  and  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{C}_2\text{O}_4$ . Cell parameters have been proposed (ICCD files 38-548 and 38-549) and thermal behaviour of these compounds has been studied by means of thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC).  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$  presents a first weight loss at about 38°C which corresponds to 4 H<sub>2</sub>O per formula unit and another one between 86 and 105°C which corresponds to 3 H<sub>2</sub>O. For the  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot \text{H}_2\text{C}_2\text{O}_4$  compound, all the oxalic acid is lost at 100°C and the residue remains stable up to 224°C.

An older study on the decomposition of a bismuth oxalate has been made by Dollimore et al [7], but their starting compound was not clearly defined. Under O<sub>2</sub>, they observe an endothermic decomposition around 243-274°C allowed by a little endothermic peak at 718°C. At 800°C, the oxidation of Bi during the air entrance leads to a large exothermic peak. An exothermic decomposition is observed around 230-265°C under N<sub>2</sub> and an endothermic peak is observed around 691-704°C.

Recently, Popa et al [8] used oxalates to synthesise high-Tc Bi-based superconducting oxides. They propose some results corresponding to a new bismuth oxalate, but its structure is not shown.

In this paper, we present new results on the thermal decomposition of a bismuth oxalate with the use of the CRTA, an original technique initially developed by Rouquerol in 70's [9]. This method authorises a finer approach of the thermal decomposition. CRTA experiments have been carried out under vacuum and in air at atmospheric pressure.

## 2. Synthesis of bismuth oxalate

Bismuth nitrate (0,2 M) in nitric acid (1 M) and oxalic acid (0,3 M) solutions are starting reactants. Both solutions are progressively mixed with constant stirring. The white precipitate is filtered, carefully washed with water, then dried at ambient temperature. The obtained oxalate is maintained at 5°C to avoid partial dehydration. Products are characterised by X-ray powder diffraction (XRD, Siemens D5000), scanning electron microscopy (SEM, Philips XL30 ESEM) and Fourier transform infrared spectroscopy (FTIR, Nicolet 630). The obtained XRD diagram (Fig. 1a) corresponds neither to known ICDD files nor to Popa's diagram (precipitation realised at pH = 3.5 [8]). The FTIR spectrum is displayed on fig. 1b: between 3300 and 3600 cm<sup>-1</sup> the bands correspond to the  $\nu_{(O-H)}$  vibration modes and characteristic bands of oxalate group vibrations are evidenced at 1450-1600 ( $\nu_{(C=O)}$ ), 1380 ( $\nu_{(C-O)}$ ;  $\nu_{(C-C)}$ ), 1300 ( $\nu_{(C-O)}$ ;  $\delta_{(O-C-O)}$ ), and 790 cm<sup>-1</sup> ( $\nu_{(Bi-O)}$ ;  $\delta_{(O-C-O)}$ ) [10].

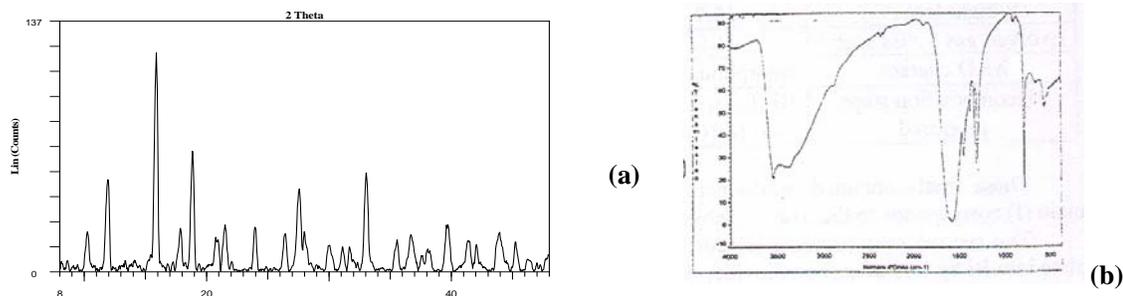


Fig. 1. XRD diagram (a) and FTIR spectrum (b) of hydrated bismuth oxalate.

SEM observations can verify the morphologic and granulometric homogeneity of the obtained product. The gravimetric analysis (and thermal analysis presented hereafter) agrees with the stoichiometry  $Bi_2(C_2O_4)_3 \cdot 7H_2O$ .

## 3. Controlled transformation Rate Thermal Analysis (CRTA) of bismuth oxalate

### 3.1. CRTA under vacuum

Bismuth oxalate has been first investigated under vacuum, between -16°C and different final temperatures. Oxalate powder ( $\approx 80$  mg) is introduced in a silica cell into a furnace. To avoid a partial decomposition of the precursor, the initial temperature of the experiment has been fixed around -16°C. After slowly degassing of the cell to secondary vacuum, the investigation can begin when the system is stable. An automatic system permits the pressure control and the temperature calibration in order to keep a constant pressure of 5 mbar above the sample. When the final temperature is reached, the sample weight loss is controlled and its characterisation is realised by XRD and FTIR. Fig. 2 presents the CRTA curve obtained between -16 and 300°C and the corresponding results are reported in Table 1.

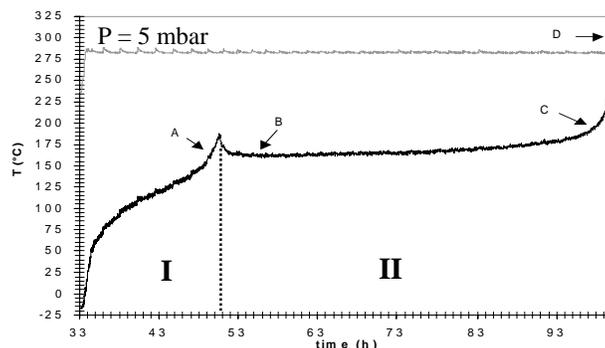


Fig. 2. CRTA curve corresponding to the thermal decomposition under vacuum of bismuth oxalate between -16 and 300°C.

Fig. 2 reveals the critical decomposition temperatures and the two different decomposition domains (I and II). To understand the decomposition mechanism, it is necessary to exactly repeat the same experiment and stop it at the different critical temperatures values. Four points have been studied corresponding to 170°C, 165°C (but 22 h after starting, i.e. just after the temperature peak), 205°C and 300°C. The evolved gases are analysed by a mass spectrometer situated at the exit of the sample cell.

Table 1. Results of the thermal decomposition of  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$  studied by vacuum CRTA.

Experiment (domain)	A (I)	B (II)	C (II)	D (II)
Constant pressure	5 mbar	5 mbar	5 mbar	5 mbar
Initial temp.	-16°C	-16°C	-16°C	-16°C
Final temp.	170°C	165°C (after 22h)	205°C	300°C
Weight loss (%)	15.7 <sub>5</sub>	25.5	49.0	54.1
Evolved gas (mass spec.)	$\text{H}_2\text{O}$	$\text{CO}_2$	$\text{CO}_2$	
XRD charact.	amorphous phase	am. phase + $\epsilon$ Bi	pure Bi	Bi
Decomposition steps proposed	$\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O} \rightarrow \text{Bi}_2(\text{C}_2\text{O}_4)_3$	$\text{Bi}_2(\text{C}_2\text{O}_4)_3 \rightarrow \text{Bi}_2(\text{C}_2\text{O}_4)_3 + \text{Bi}$	$\text{Bi}_2(\text{C}_2\text{O}_4)_3 + \text{Bi} \rightarrow \text{Bi}$	Bi sublimation

These firstly obtained results permit to propose a thermal decomposition in two steps. The domain (I) corresponds to the oxalate dehydration:  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O} \rightarrow \text{Bi}_2(\text{C}_2\text{O}_4)_3 + 7 \text{H}_2\text{O}_{(g)}$ .

The second step (domain II) corresponds to the gradual transformation of the dehydrated oxalate into Bi by loss of carbon dioxide:  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \rightarrow 2 \text{Bi} + 6 \text{CO}_{2(g)}$ .

### 3.2. CRTA under air atmospheric pressure

Under air the thermal decomposition mechanism will be quite different because  $\text{O}_2$  is a reactive gas. A more complex CRTA apparatus able to work under corrosive gases has been built by Gilardi and Fulconis [11] in our Lab. As for the classical CRTA, the basic idea is to control the sample temperature so as to keep constant a parameter related to the decomposition rate. Since a reactive gas is introduced into the cell, the controlled parameter has to be a  $\Delta P$  between test and sample cells. The experiment performed between 10 and 270°C is presented on Fig. 3. The number of experiments carried out up to now are insufficient to propose a complete thermal decomposition mechanism: only three temperatures have been studied and characterisation results are reported in Table 2. These primary results permit to suppose a thermal decomposition in two steps:

- in the domain (I), FTIR analysis at 215°C (E point) shows the presence of water and oxalate molecules. Dehydration seems not complete and we suppose this first domain corresponds with the oxalate dehydration:  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O} \rightarrow \text{Bi}_2(\text{C}_2\text{O}_4)_3 + 7 \text{H}_2\text{O}_{(g)}$ . Different steps clearly appear in this domain and could reveal the presence of different sorts of water molecules.

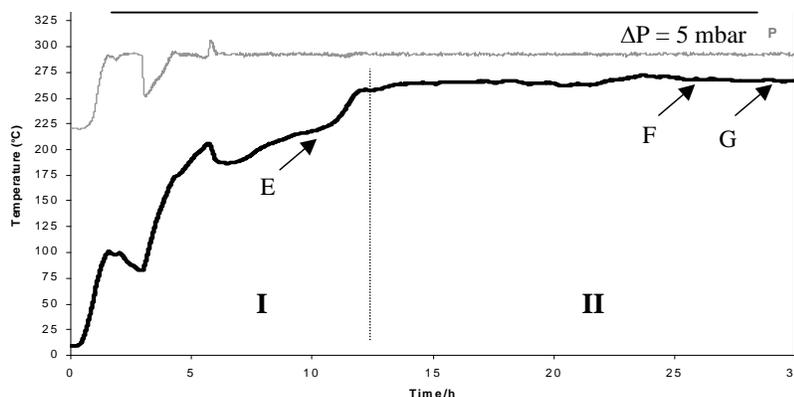


Fig. 3. CRTA curve corresponding to the thermal decomposition of the bismuth oxalate between 10°C and 270°C under air.

Table 2. Results of the  $\text{Bi}_2(\text{C}_2\text{O}_4)_3 \cdot 7\text{H}_2\text{O}$  thermal decomposition studied by CRTA under air.

Experiment (domain)	E (I)	F (II)	G (II)
$\Delta P$	5 mbar	5 mbar	5 mbar
Initial temperature	10°C	10°C	10°C
Final temperature	225°C	268°C (after 27 h)	269°C (after 30 h)
Weight loss (%)	?	41.2	42.8
XRD	amorphous phase	$\beta\text{-Bi}_2\text{O}_3 + \text{Bi}_2\text{O}_2\text{CO}_3$	$\beta\text{-Bi}_2\text{O}_3$
FTIR vibration modes	$\text{H}_2\text{O} + \text{Bi}_2(\text{C}_2\text{O}_4)_3$	$\text{Bi-O} + \text{CO}_3^{2-}$	$\text{Bi-O}$

- in the domain (II), only one step appears and  $\beta\text{-Bi}_2\text{O}_3$  [12,13] is obtained at 269°C after 30 h (G point). At 268°C and after 27 h (F point), the FTIR spectrum (Fig. 4b) reveals the presence of (Bi-O) and ( $\text{CO}_3^{2-}$ ) vibration modes at 574 and 1460-1395-8446  $\text{cm}^{-1}$ , resp. [14]. The XRD diagram (Fig 4a) corresponds with ICCD files of the oxide  $\beta\text{-Bi}_2\text{O}_3$  [12] and of the oxycarbonate  $\text{Bi}_2\text{O}_2\text{CO}_3$ .

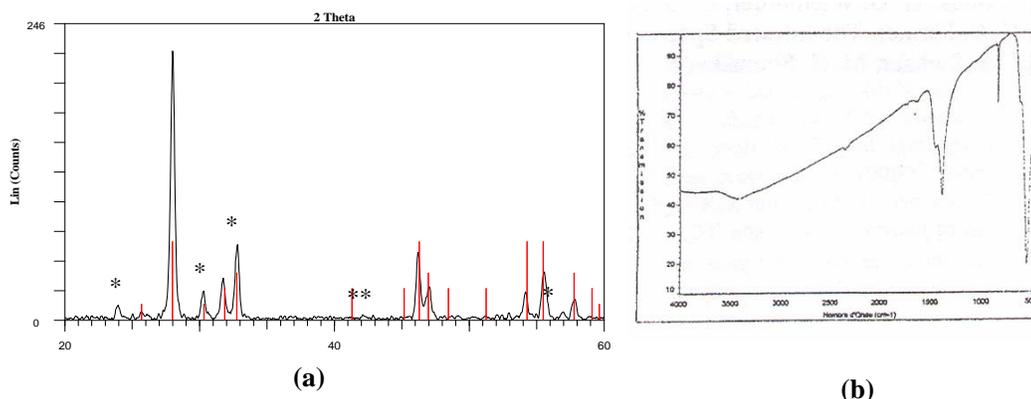


Fig. 4. XRD diagram (a) and FTIR spectrum (b) of the product obtained at 268°C in air (F point) (stars (\*) are attributed to the oxycarbonate compound).

SEM pictures of the obtained product after CRTA until 268°C in air (F point) reveals many little needles on the surface of crystals, which could be attributed to the bismuth oxycarbonate. Considering that only one step appears in the domain (II), we propose two simultaneous global decomposition reactions:

$$2 \text{Bi}_2(\text{C}_2\text{O}_4)_3 \rightarrow \text{Bi}_2\text{O}_2\text{CO}_3 + \beta\text{-Bi}_2\text{O}_3 + 11 \text{CO}_2(\text{g})$$

$$\text{Bi}_2\text{O}_2\text{CO}_3 \rightarrow \beta\text{-Bi}_2\text{O}_3 + \text{CO}_2(\text{g})$$

#### 4. Conclusion

In this work, we have demonstrated the potentiality of the CRTA technique to elucidate the different steps involved during the decomposition process of the hydrated bismuth oxalate. By a better knowledge of these steps, it is possible to finely control this process and to promote new phases or stabilise metastable ones, like  $\beta\text{-Bi}_2\text{O}_3$  in this case. Recently, Switzer et al [15] have stabilised at room temperature the fcc-form  $\delta\text{-Bi}_2\text{O}_3$  by electrodeposition on gold substrate. We want now to try to obtain this high temperature form by CRTA in air, which would make a new soft chemical route.

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