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Synthesis of a New Compound, $Bi_5O_7NO_3$, by Thermal Decomposition

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Thermal decomposition of basic bismuth nitrate and bismuth nitrate pentahydrate has been studied by means of thermal analysis and mass spectrometry. On the basis of the data obtained, a new compound, $Bi_5O_7NO_3$, synthesized during the decomposition process, has been identified. The new compound was isostructural with Bi_5O_7I and its diffraction peaks were indexed on the basis of an orthorhombic cell of a = 16.280 Å, b = 5.548 Å, and c = 23.301 Å. X-ray diffraction data of $Bi_5O_7NO_3$ are listed. © 1994 Academic Press, Inc.

INTRODUCTION

Many compounds belonging to the Bi_2O_3–N_2O_5–H_2O system have been reported. They include OH or H_2O in their chemical formulae such as $4Bi(NO_3)(OH)_2 \cdot BiO(OH)$, $Bi_6O_6(OH)(NO_3)_5 \cdot 2.5H_2O$, $Bi_6O_6(OH)_2(NO_3)_4 \cdot 2H_2O$, $Bi_6O_6(OH)_3(NO_3)_3 \cdot 1.5H_2O$ (1), $Bi_6O_5(OH)_3(NO_3)_5 \cdot 3H_2O$ (2), $Bi_6O_4(OH)_4(NO_3)_6 \cdot 4H_2O$ (3), etc. On the other hand, $BiONO_3$ is reported as the only compound belonging to the Bi_2O_3–N_2O_5 system (4). However, its preparation is very difficult and even its X-ray diffraction pattern is not known.

We can find the possibility of the presence of new compounds belonging to the Bi_2O_3–N_2O_5 system in previously published papers. For example, Levin and Roth (5) studied the polymorphism of bismuth sesquioxide produced by thermal decomposition of bismuth compounds and reported that an unknown intermediate compound was produced in the early step of the thermal decomposition of bismuth nitrate pentahydrate. Then, Anand and Baxi (6) studied thermal decomposition of basic bismuth nitrate and reported that some intermediate compounds belonging to the Bi_2O_3–N_2O_5–H_2O system were formed, and these had ion exchange capacity.

In the present paper, the thermal decomposition of basic bismuth nitrate and bismuth nitrate pentahydrate is studied and then, on the basis of the obtained data, synthesis of a new compound, $Bi_5O_7NO_3$, is studied. This compound is a member of the Bi_2O_3–N_2O_5 system. Its crystal structure is also studied.

From the viewpoint of removal and immobilization of radioactive iodide ions, the new compound, $Bi_5O_7NO_3$, is very interesting, since it is reported that Bi_5O_7I is a candidate material for the immobilization of radioactive iodine, such as iodine-129 (7, 8). The composition of Bi_5O_7I and $Bi_5O_7NO_3$ can be represented by Bi_5O_7X (X is I or NO_3). If the structures of the two compounds are isostructural and ion exchange of I^- and NO_3^- in solution occurs easily, this new compound is expected to be a useful ion exchanger for the removal and solidification of radioactive iodide.

EXPERIMENTAL PROCEDURE

The preparation of $Bi_5O_7NO_3$ was carried out by thermal decomposition of basic bismuth nitrate, $4Bi(NO_3)(OH)_2 \cdot BiO(OH)$, or bismuth nitrate pentahydrate, $Bi(NO_3)_3 \cdot 5H_2O$, under controlled heating temperatures and heating times.

In order to prepare the new compound, $Bi_5O_7NO_3$, the thermal decomposition of the starting materials was initially examined in detail by means of thermal analysis and mass spectrometry. The purpose of these experiments was to evaluate the decomposition temperatures necessary for the preparation of pure $Bi_5O_7NO_3$. The thermal analysis and mass spectrometry data were obtained simultaneously on a computer-interfaced MAC & VG TG-DTA/MS system using a heating rate of 10°C/min between room temperature and 700°C in a flow of Ar gas.

Then, within the evaluated temperature range, heating temperatures and heating times for the preparation of $Bi_5O_7NO_3$ were determined as follows: The starting material (about 2 g) was charged in a platinum crucible and heated in air at a constant temperature for a constant time. After each heating, decomposed products were quenched and identified by powder X-ray diffraction analysis with Ni-filtered Cu$K\alpha$ radiation. Moreover, the NO_3 content was determined by means of thermogravimetric analysis. Thus, by incrementally changing the heating temperature

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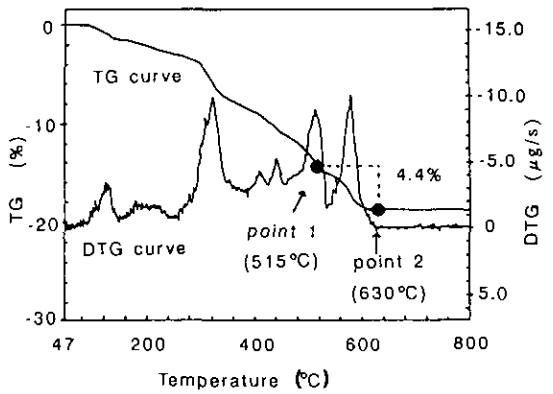

FIG. 1. TG and DTG curves of basic bismuth nitrate.

and time within the range of interest, the best conditions for synthesizing pure $Bi_5O_7NO_3$ were established.

The obtained $Bi_5O_7NO_3$ crystals were observed using an Akasi-130 scanning electron microscope.

RESULTS AND DISCUSSION

1. Synthesis from Basic Bismuth Nitrate

The experimental results of the thermal decomposition of basic bismuth nitrate observed by a thermobalance and a mass spectrometer are given in Figs. 1 and 2, respectively.

Figure 1 shows that the decomposition began near 80°C and proceeded gradually through seven steps and came to completion at 630°C. Figure 2 shows that the first two peaks and a part of the third peak observed between 80 and 350°C correspond to the release of H_2O, and all the other peaks observed above 350°C correspond to the decomposition of NO_3. All the peaks shown in Fig. 2 correspond to the respective peaks of DTG (differential thermogravimetry) curves shown in Fig. 1. It is, therefore, concluded that thermal decomposition above 350°C is suitable for preparing $Bi_5O_7NO_3$, since the decomposed products do not contain H_2O or OH.

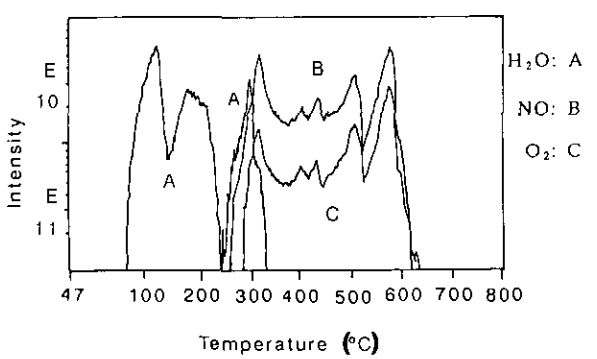

FIG. 2. The profile of ion intensity (logarithmic display) against temperature for thermal decomposition of basic bismuth nitrate.

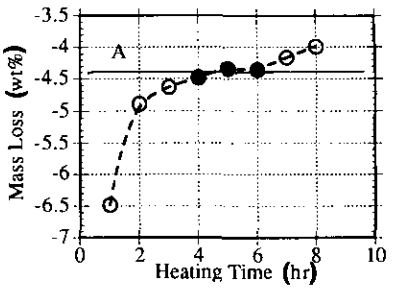

FIG. 3. The relationship of heating time of basic bismuth nitrate and mass loss of the decomposed product when it is decomposed perfectly.

In the thermal decomposition of basic bismuth nitrate, if $Bi_5O_7NO_3$ is the sole product, the thermal decomposition reaction can be written as follows:

$$4Bi(NO_3)(OH)_2 \cdot BiO(OH) \rightarrow Bi_5O_7NO_3 + 9/2H_2O + 3NO + 9/4O_2. \quad [1]$$

On the other hand, when basic bismuth nitrate is decomposed perfectly by heating, (α-)Bi_2O_3 is the final solid product. This suggests that $Bi_5O_7NO_3$ changes into Bi_2O_3 when decomposed completely by heating. The decomposition of $Bi_5O_7NO_3$ can be written as follows:

$$Bi_5O_7NO_3 \rightarrow 5/2Bi_2O_3 + NO + 3/4O_2. \quad [2]$$

It is calculated, from Eq. [2] that the decomposition of $Bi_5O_7NO_3$ into Bi_2O_3 is accompanied by the mass loss of about 4.4 wt%. In Fig. 1, the thermal decomposition from point 1 (515°C) to point 2 (630°C) was accompanied with the mass loss of 4.4 wt%, so that the compound produced near 515°C must have the average composition represented by $Bi_5O_7NO_3$. It is difficult, at a temperature above 515°C, to expect the formation of pure $Bi_5O_7NO_3$.

It was concluded from these experimental results that heating in the temperature range 350–515°C is the most suitable for the synthesis of $Bi_5O_7NO_3$ by the thermal decomposition of basic bismuth nitrate. Hence, the thermal decomposition of basic bismuth nitrate was studied in detail over the temperature range 350–500°C. Thermal decomposition was carried out at intervals of 25°C in this range. The experimental procedures were already

TABLE 1

The Successful Experimental Conditions of the Synthesis of $Bi_5O_7NO_3$ from Basic Bismuth Nitrate

Heating temperature (°C)	Heating time (hr)
400	24–48
425	19–24
450	4–6

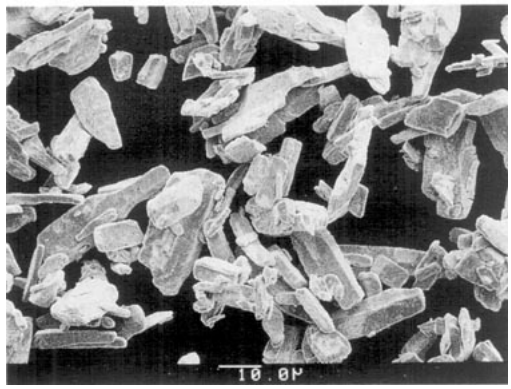

FIG. 4. A scanning electron micrograph of $Bi_5O_7NO_3$.

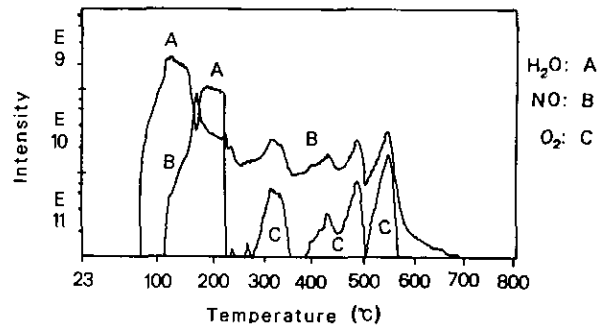

FIG. 6. The profile of ion intensity (logarithmic display) against temperature for thermal decomposition of bismuth nitrate pentahydrate.

described in the last section. As one example, experimental results at 450°C are shown in Fig. 3, where a horizontal axis represents heating time of basic bismuth nitrate and a vertical axis represents mass loss of the product when the product is heated again and decomposed perfectly into Bi_2O_3. (This mass loss is not of basic bismuth nitrate.) The symbol (●) and the symbol (○) correspond to a single phase (pure $Bi_5O_7NO_3$) and mixed phases (impure phase), respectively. Line (A) in Fig. 3 shows the mass loss of 4.4 wt% and the symbol of the single phase takes a position near it. This supports the theory that the constitution of the single phase is $Bi_5O_7NO_3$, because the decomposition of $Bi_5O_7NO_3$ into Bi_2O_3 is accompanied with the mass loss of about 4.4 wt%. Figure 3 shows that the formation of pure $Bi_5O_7NO_3$ is possible by heating at 450°C for 4–6 hr.

Similar results were obtained by thermal decomposition at the other temperatures and all the experimental results are summarized in Table 1. Pure $Bi_5O_7NO_3$ was obtained under the experimental conditions of the heating temperature and the time shown in Table 1, but the heating time changes with the other experimental conditions such as the mass of starting material, the form of crucible, flow of air, etc. Heating above 450°C causes rapid decomposition and makes it difficult to get pure $Bi_5O_7NO_3$. On the other hand, heating below 400°C causes too slow of a decomposition rate.

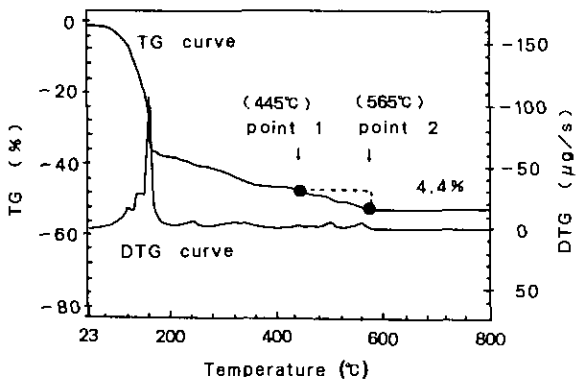

FIG. 5. TG and DTG curves of bismuth nitrate pentahydrate.

The $Bi_5O_7NO_3$ product was a glossy yellow powder and was well crystallized. A scanning electron micrograph of the material is shown in Fig. 4. This sample was synthesized at 450°C and confirmed to be pure $Bi_5O_7NO_3$ by its X-ray powder diffraction pattern.

2. *Synthesis from Bismuth Nitrate Pentahydrate*

Thermal decomposition of bismuth nitrate pentahydrate was also observed by a thermobalance and a mass spectrometer and the experimental results are given in Figs. 5 and 6, respectively.

Figure 5 shows that the decomposition began near 60°C and proceeded rapidly to near 150°C, and then proceeded gradually and came to completion at 565°C.

Figure 6 shows that the first and the third peaks observed below 230°C correspond to the release of H_2O, and the second peak and all of the other peaks observed above 230°C correspond to the decomposition of NO_3. It is therefore concluded that the thermal decomposition above 230°C is suitable for the synthesis of $Bi_5O_7NO_3$ because the decomposed products do not contain H_2O or OH.

In Fig. 5, the thermal decomposition from point 1 (445°C) to point 2 (565°C) was accompanied by the mass loss of 4.4 wt%. Thus, the compound produced near 445°C must have the average composition represented by $Bi_5O_7NO_3$.

It was concluded from these experimental results that the temperature range 230–445°C is the most suitable for

TABLE 2

The Successful Experimental Conditions of the Synthesis of $Bi_5O_7NO_3$ from Bismuth Nitrate Pentahydrate

Heating temperature (°C)	Heating time (hr)
400	27.5–40
425	5–10
450	2–3.5

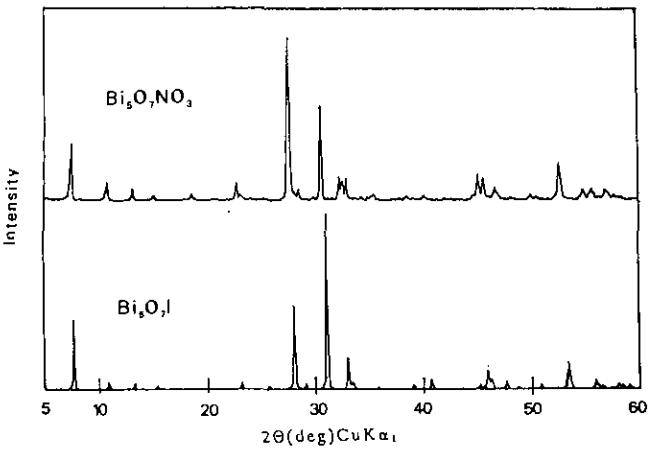

FIG. 7. The X-ray powder diffraction patterns of $Bi_5O_7NO_3$ and Bi_5O_7I.

the synthesis of $Bi_5O_7NO_3$ by the thermal decomposition of bismuth nitrate pentahydrate. Therefore, the thermal decomposition of bismuth nitrate pentahydrate was studied in detail over the temperature range 230–450°C. All the experimental procedures were the same as those for the decomposition of basic bismuth nitrate. The successful experimental results are summarized in Table 2. Pure $Bi_5O_7NO_3$ was obtained by heating bismuth nitrate pentahydrate at the temperature and for the time shown in Table 2.

When bismuth nitrate pentahydrate is heated, its decomposition begins with melting and, therefore, the $Bi_5O_7NO_3$ produced is a sintered yellow solid.

3. The Structure of $Bi_5O_7NO_3$

An X-ray powder diffraction pattern of $Bi_5O_7NO_3$ was obtained from a specimen synthesized from basic bismuth nitrate. This pattern is shown in Fig. 7 with the pattern of Bi_5O_7I and the two patterns are quite similar. That is, $Bi_5O_7NO_3$ is expected to be isostructural with Bi_5O_7I, which belongs to the space group *Cmca* with an orthorhombic cell of the lattice parameters $a = 16.224$, $b = 5.342$, and $c = 23.006$ Å (9). Therefore, with the reference of the X-ray diffraction data for Bi_5O_7I, the diffraction peaks of $Bi_5O_7NO_3$ were indexed on the basis of an orthorhombic cell of $a = 16.280$, $b = 5.548$, and $c = 23.301$ Å. The X-ray powder diffraction data are listed in Table 3 and all the observed peaks are well indexed on the above cell. The produced compound is very pure.

TABLE 3
X-Ray Powder Diffraction Data for $Bi_5O_7NO_3$

h k l	d_{obs} (Å)	d_{cal} (Å)	I_{obs} (%)
0 0 2	11.684	11.650	34
2 0 0	8.140	8.140	11
2 0 2	6.681	6.672	7
0 0 4	5.831	5.825	3
1 1 2	4.771	4.787	4
1 1 4	3.897	3.900	10
0 0 6		3.883	
3 1 4	3.229	3.228	100
1 1 6	3.116	3.122	7
0 0 8	2.913	2.912	57
0 2 0	2.764	2.774	13
3 1 6	2.741	2.744	11
2 0 8		2.742	
6 0 0	2.713	2.713	13
5 1 4	2.525	2.529	4
0 0 10	2.327	2.331	3
3 1 8		2.329	
2 0 10	2.239	2.240	3
6 0 6		2.224	
0 2 8	2.005	2.008	16
8 0 2		2.004	
6 0 8	1.986	1.985	14
0 0 12	1.941	1.941	8
6 2 0		1.939	
1 1 12	1.817	1.821	3
1 3 2		1.815	
3 1 12	1.736	1.736	23
3 3 4	1.674	1.676	5
8 0 8	1.671	1.668	6
9 1 4	1.647	1.649	6
6 2 8	1.614	1.614	6
10 0 2	1.611	1.612	5

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