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THERMAL DECOMPOSITION PROCESS OF $Bi_2(SO_4)_3$

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$Bi_2(SO_4)_3$ begins to decompose at 465°C, and the decomposition process of $Bi_2(SO_4)_3$ can be represented as follows: $Bi_2(SO_4)_3 \xrightarrow{465°C} Bi_2O_3 \cdot 2Bi_2(SO_4)_3 \xrightarrow{550°C} 2Bi_2O_3 \cdot Bi_2(SO_4)_3 \xrightarrow{580°C} 7Bi_2O_3 \cdot 2Bi_2(SO_4)_3 \xrightarrow{830°C} 12Bi_2O_3 \cdot Bi_2(SO_4)_3 \xrightarrow{880°C} 28Bi_2O_3 \cdot Bi_2(SO_4)_3 \xrightarrow{920°C} Bi_2O_3$.

Little information on the thermal decomposition of $Bi_2(SO_4)_3$ has been available in the early literatures[1]. Later, Arnal et al.[2] have reported that $Bi_2(SO_4)_3$ decomposes above 390°C to form $Bi_2O_3 \cdot SO_3$ via $Bi_2O_3 \cdot 2SO_3$. Panchout and Duval[3] have reported that the decomposition commences at 405°C and ends at 810°C with formation of $(BiO)_2SO_4$ which is stable up to 946°C. Recently, Margulis et al.[4] have reported that the thermal decomposition process of $Bi_2(SO_4)_3$ can be represented as follows: $Bi_2(SO_4)_3 \xrightarrow{425°C} Bi_2O_3 \cdot 2Bi_2(SO_4)_3 \xrightarrow{550°C} 2Bi_2O_3 \cdot Bi_2(SO_4)_3 \xrightarrow{620°C} 3Bi_2O_3 \cdot Bi_2(SO_4)_3 \xrightarrow{860°C} Bi_2O_3$. In this letter, the thermal decomposition process of $Bi_2(SO_4)_3$ was clarified in detail.

$Bi_2(SO_4)_3$ used was prepared according to an well-known procedure[1),4)] by dissolving high-purity commercial bismuth(Bi:99.9999%) in HNO_3 followed by treatment with an excess of H_2SO_4. The resulting solution was evaporated to dense fumes of H_2SO_4, and the residue was heated at 250°C to constant weight. Chemical analysis of the $Bi_2(SO_4)_3$ gave 59.1% Bi, 40.7% SO_4(calcd.: Bi, 59.19%; SO_4, 40.81%).

Decomposition of $Bi_2(SO_4)_3$ on heating was examined by thermogravimetry(TG) and differential thermal analysis(DTA) at an argon flow rate of 50 ml/min. 0.5 g of the sample was heated in a Pt crucible at a rate of 2.5°C/min. Since it was observed that Bi_2O_3 attacked Pt at about 1100°C, the sample was heated up to 1050°C. $Bi_2(SO_4)_3$ began to decompose at 465°C. The TG curve showed three distinct but not well separated weight losses and gave a plateau in the temperature range 770°C to 830°C. Then, an weight loss was again observed above 830°C to 1050°C. It was observed from DTA that the weight losses were accompanied by endotherm. X-ray diffraction data of the sample heated up to 1050°C could not be indexed by those of known Bi_2O_3[5], but showed it to be $28Bi_2O_3 \cdot Bi_2(SO_4)_3$ as will be described later.

Since the thermal decomposition process of $Bi_2(SO_4)_3$ could not be clarified from the results of TG and DTA, $Bi_2(SO_4)_3$ was decomposed under isothermal conditions at temperatures above 470°C in an argon atmosphere until the weight loss reached constant value. The product was examined by X-ray and chemical analyses. X-ray powder diffraction data were taken using Ni filtered Cu radiation. Bi content in the product was determined volumetrically using EDTA and $Th(NO_3)_4$ solutions. SO_4 content was determined gravimetrically as $BaSO_4$.

The results obtained by heating $Bi_2(SO_4)_3$ below 820°C are shown in Tables 1 and 2. Calculated values of weight loss based on the decomposition of $Bi_2(SO_4)_3$ to $Bi_2O_3 \cdot 2Bi_2(SO_4)_3$, $2Bi_2O_3 \cdot Bi_2(SO_4)_3$, and $7Bi_2O_3 \cdot 2Bi_2(SO_4)_3$ with evolution of SO_3 were 11.34, 22.68, and 26.45%, respectively. The compositional formulas given in Table 1 are considered as reasonable from the weight losses observed.

Table 1 EXPERIMENTAL RESULTS ON THERMAL DECOMPOSITION OF $Bi_2(SO_4)_3$ BELOW 820°C

Heating temperature (°C)	Weight loss (%)	Chemical analysis	Compositional formula
470	11.3		
500	11.3	Bi 66.9%	
530	11.4	SO_4 30.5%	$Bi_2O_3 \cdot 2Bi_2(SO_4)_3$
540	11.4		
550	22.7	Bi 76.6%	
570	22.8	SO_4 17.7%	$2Bi_2O_3 \cdot Bi_2(SO_4)_3$
580	26.5		
600	26.5		
650	26.4	Bi 80.6%	
700	26.4	SO_4 12.4%	$7Bi_2O_3 \cdot 2Bi_2(SO_4)_3$
800	26.6		
820	26.6		

Table 2 X-RAY POWDER DIFFRACTION DATA OF DECOMPOSITION PRODUCTS OF $Bi_2(SO_4)_3$ BELOW 820°C (CuKα:λ=1.5418Å)

Product at 470-540°C		Product at 550-570°C				Product at 580-820°C			
d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
5.72	25	6.76	15	1.961	5	10.4	20	2.55	20
5.47	50	4.04	20	1.863	5	9.4	5	2.50	5
4.25	15	3.92	20	1.828	5	6.33	5	2.032	15
3.66	20	3.08	100	1.791	30	5.22	10	1.989	5
3.49	100	3.04	85	1.737	30	4.77	10	1.933	5
3.40	70	2.94	85	1.707	25	3.43	5	1.895	10
3.36	70	2.70	15	1.544	10	3.25	100	1.859	15
3.15	100	2.281	10			3.19	20	1.698	10
3.06	30	2.254	25			3.11	100	1.687	10
3.00	15	2.222	15			2.94	15	1.634	5
2.77	15	2.113	15			2.92	30	1.595	15
2.58	15	2.049	15			2.83	40	1.556	5
2.39	25	2.023	10			2.57	5		

Next, the decomposition of $Bi_2(SO_4)_3$ on heating above 830°C was examined in the same way as described above. The weight of the sample gradually decreased over a period of 17-102 hr before it reached constant value. The results are shown in Tables 3 and 4. X-ray diffraction data of the products obtained at 920-950°C showed them to be α-Bi_2O_3[6]. The weight losses at 920-950°C did not reached constant value, showing continuous decrease of 0.02-0.04%/hr, because of the evaporation of Bi_2O_3[4), 7)] formed by the decomposition.

Table 3 EXPERIMENTAL RESULTS ON THERMAL DECOMPOSITION OF $Bi_2(SO_4)_3$ ABOVE 830°C

Heating temperature (°C)	Weight loss (%)	Chemical analysis	Compositional formula
830	31.6	Bi 86.1%	$12Bi_2O_3 \cdot Bi_2(SO_4)_3$
850	31.6	SO_4 4.6%	
870	31.6		
880	33.1	Bi 88.1%	$28Bi_2O_3 \cdot Bi_2(SO_4)_3$
900	33.1	SO_4 2.0%	
920	34.3	Bi 89.6%	Bi_2O_3
950	34.3	SO_4 trace	

Table 4 X-RAY POWDER DIFFRACTION DATA OF DECOMPOSITION PRODUCTS OF $Bi_2(SO_4)_3$ ABOVE 830°C

(CuKα:λ=1.5418Å)

Product at 830-870°C		Product at 880-900°C		Product at 920-950°C					
d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)	I/I_1
3.21	100	3.21	100	4.51	5	2.557	15	1.877	5
2.28	10	2.88	10	4.08	5	2.536	10	1.873	5
2.76	25	2.73	25	3.62	5	2.501	5	1.759	10
1.973	15	2.49	5	3.45	15	2.430	5	1.746	10
1.953	10	1.981	25	3.31	30	2.392	10	1.728	10
1.698	10	1.933	10	3.25	100	2.243	5	1.675	10
1.667	15	1.722	20	3.19	20	2.176	5	1.656	5
1.605	10	1.658	20	2.755	5	2.132	5	1.645	5
		1.605	10	2.706	35	2.006	5	1.595	5
				2.691	35	1.957	25	1.583	5
				2.637	5	1.910	5	1.563	5

From the experimental results mentioned above, $Bi_2(SO_4)_3$ begins to decompose at 465°C, and the decomposition process of $Bi_2(SO_4)_3$ can be represented as follows:

$$Bi_2(SO_4)_3 \xrightarrow{465°C} Bi_2O_3 \cdot 2Bi_2(SO_4)_3 \xrightarrow{550°C} 2Bi_2O_3 \cdot Bi_2(SO_4)_3 \xrightarrow{580°C} 7Bi_2O_3 \cdot 2Bi_2(SO_4)_3 \xrightarrow{830°C} 12Bi_2O_3 \cdot Bi_2(SO_4)_3 \xrightarrow{880°C} 28Bi_2O_3 \cdot Bi_2(SO_4)_3 \xrightarrow{920°C} Bi_2O_3.$$

The literature data on the initiation temperature of thermal decomposition of $Bi_2(SO_4)_3$ ranged from 390°C to 570°C[1)-4)]. From the result of this work, the temperature was found to be 465°C. The decomposition process of $Bi_2(SO_4)_3$ to $2Bi_2O_3 \cdot Bi_2(SO_4)_3$ agrees with those reported by Arnal et al.[2)] and Margulis et al.[4)]. But, the thermal decomposition process of the $2Bi_2O_3 \cdot Bi_2(SO_4)_3$ to Bi_2O_3 which is revealed in this work is quite different from that reported by Margulis et al.[4)].

From the results mentioned above, bismuth compounds represented as $7Bi_2O_3 \cdot 2Bi_2(SO_4)_3$, $12Bi_2O_3 \cdot Bi_2(SO_4)_3$, and $28Bi_2O_3 \cdot Bi_2(SO_4)_3$ were newly found to exist. The analyses of the X-ray powder diffraction data of these compounds were carried out to determine the crystal structures. As the results, all of these compounds could be indexed on tetragonal lattice. Unit cell dimensions were a= 14.75Å, c=12.47Å for $7Bi_2O_3 \cdot 2Bi_2(SO_4)_3$, a=11.04Å, c=5.64Å for $12Bi_2O_3 \cdot Bi_2(SO_4)_3$, and a=10.93Å, c=5.76Å for $28Bi_2O_3 \cdot Bi_2(SO_4)_3$.

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