CHEMISTRY LETTERS, pp. 1311-1314, 1973. Published by the Chemical Society of Japan

POLYMORPHOUS FORMS OF Sb_2O_3 FORMED BY THERMAL DECOMPOSITION OF $Sb_8O_{11}Cl_2$

Ryoko MATSUZAKI, Atsuko SOFUE, and Yuzo SAEKI
Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Ookayama, Meguro-ku, Tokyo 152

The modification of Sb_2O_3 formed by the thermal decomposition of $Sb_8O_{11}Cl_2$ varied with the method of preparing $Sb_8O_{11}Cl_2$. Cubic Sb_2O_3 was obtained by the thermal decomposition of $Sb_8O_{11}Cl_2$, which was prepared by decomposing $Sb_4O_5Cl_2$, below 560°C.

Sb_2O_3 is known in two crystalline modifications, a cubic form, senarmontite, and an orthorhombic form, valentinite, the latter being the commoner form. The temperature at which cubic and orthorhombic forms of Sb_2O_3 are in equilibrium has been reported as 570±10°C[1], or 557°C[2], the cubic form being stable below this temperature.

Recently, Belluomini et al.[3] have found the existence of $Sb_8O_{11}Cl_2$, and have reported that the $Sb_8O_{11}Cl_2$ decomposes above 470°C according to the reaction, $Sb_8O_{11}Cl_2(s) \rightarrow Sb_2O_3(s) + SbCl_3(g)$. But, they did not mention the modification of Sb_2O_3 formed. In this letter, the variations of the modification of Sb_2O_3 formed by the thermal decomposition of $Sb_8O_{11}Cl_2$ with the method of preparing $Sb_8O_{11}Cl_2$, and with its decomposition condition were reported.

Samples of $Sb_8O_{11}Cl_2$ were prepared by the following methods based on the report of Belluomini et al.[3].

Sample A : 10 g of special grade $SbCl_3$ was hydrolyzed with 100 ml of H_2O at 35°C. The precipitated $Sb_4O_5Cl_2$ was washed with ethyl ether. The $Sb_4O_5Cl_2$ was decomposed in an argon atmosphere at 460°C to $Sb_8O_{11}Cl_2$.

Sample B : 10 g of $SbCl_3$ was hydrolyzed with 1500 ml of H_2O at boiling temperature. The precipitated $Sb_8O_{11}Cl_2$ was washed with ethyl ether, and dried at 120°C.

The chemical analyses of the both samples gave identical results: 79.8% Sb; 5.8% Cl (calcd.: Sb, 79.78%; Cl, 5.81%). The samples were also confirmed as $Sb_8O_{11}Cl_2$[3] by X-ray analysis. X-ray diffraction lines of Sample B were diffuse, and the intensities of the lines were lower than those of Sample A.

2.0 g of the sample placed in a platinum boat was heated under an argon atmosphere at a specified temperature above 500°C for a specified period. The product obtained in the boat was examined by chemical and X-ray[4] analyses. Antimony was determined by titration with 0.1 N $KBrO_3$. The sample was dissolved in 6 N HCl, and titrated at about 65°C using methyl orange as indicator. Chlorine was determined gravimetrically as AgCl. The sample was boiled with Na_2CO_3 solution in a platinum dish. The filtrate was acidified with HNO_3, and AgCl was precipitated from the filtrate by $AgNO_3$ solution. X-ray diffraction data were taken with Ni filtered Cu radiation.

The modifications of Sb_2O_3 formed by heating Samples A and B under various

conditions are shown in Tables 1 and 2, respectively.

In order to discuss the above-mentioned experimental results, the transformations of cubic and orthorhombic Sb_2O_3 under the experimental condition in this work were examined, respectively. A sample of cubic Sb_2O_3 used was prepared by the thermal decomposition of Sample A at 560°C for 2 hr. A sample of orthorhombic Sb_2O_3 was prepared by the thermal decomposition of Sample B at 560°C for 2 hr. By heating cubic Sb_2O_3 at 500-590°C for 0.5-3 hr, its transformation to orthorhombic form was not observed. The result with orthorhombic Sb_2O_3 is shown in Table 3.

Considering the fact that the transformation of cubic Sb_2O_3 to orthorhombic form was not observed, the orthorhombic Sb_2O_3 formed by the thermal decomposition of Sample A above 570°C(Table 1) is not considered to be due to the transformation of cubic Sb_2O_3 formed. From the result shown in Table 3, the cubic Sb_2O_3 formed by the thermal decomposition of Sample B at 500°C for 2-3 hr and at 560°C for 3 hr(Table 2) is considered to be due to the transformation of orthorhombic Sb_2O_3 formed.

Table 1 MODIFICATION OF Sb_2O_3 FORMED BY THE THERMAL DECOMPOSITION OF SAMPLE A UNDER VARIOUS CONDITIONS

Temperature (°C)	Heating time (hr)	Form of Sb_2O_3*	Notes
500	0.5	Cubic	Undecomposed $Sb_8O_{11}Cl_2$ 78%**
	1.0	Cubic	Undecomposed $Sb_8O_{11}Cl_2$ 38%
	2.0	Cubic	Undecomposed $Sb_8O_{11}Cl_2$ 21%
	3.0	Cubic	
560	0.5	Cubic	Undecomposed $Sb_8O_{11}Cl_2$ 13%
	1.0	Cubic	
	2.0	Cubic	
	3.0	Cubic	
570	0.5	Cubic(l)+Orthorhombic(tr)	Undecomposed $Sb_8O_{11}Cl_2$ 10%
	1.0	Cubic(l)+Orthorhombic(tr)	
	2.0	Cubic(l)+Orthorhombic(tr)	
	3.0	Cubic(l)+Orthorhombic(tr)	
580	0.5	Cubic(m)+Orthorhombic(m)	Undecomposed $Sb_8O_{11}Cl_2$ 6%
	1.0	Cubic(m)+Orthorhombic(m)	
	2.0	Cubic(m)+Orthorhombic(m)	
	3.0	Cubic(m)+Orthorhombic(m)	
590	0.5	Orthorhombic	Undecomposed $Sb_8O_{11}Cl_2$ 2%
	1.0	Orthorhombic	
	2.0	Orthorhombic	
	3.0	Orthorhombic	

* Percentages : l-large, m-moderate, tr-trace

** The percentage of undecomposed $Sb_8O_{11}Cl_2$ was calculated from the chemical analysis

Table 2 MODIFICATION OF Sb_2O_3 FORMED BY THE THERMAL DECOMPOSITION OF SAMPLE B UNDER VARIOUS CONDITIONS

Temperature (°C)	Heating time (hr)	Form of Sb_2O_3*	Notes
500	0.5	Orthorhombic	Undecomposed $Sb_8O_{11}Cl_2$ 77%**
	1.0	Orthorhombic	Undecomposed $Sb_8O_{11}Cl_2$ 39%
	2.0	Orthorhombic(l)+Cubic(tr)	Undecomposed $Sb_8O_{11}Cl_2$ 20%
	3.0	Orthorhombic(l)+Cubic(tr)	
560	0.5	Orthorhombic	Undecomposed $Sb_8O_{11}Cl_2$ 11%
	1.0	Orthorhombic	
	2.0	Orthorhombic	
	3.0	Orthorhombic(l)+Cubic(tr)	
570	0.5	Orthorhombic	Undecomposed $Sb_8O_{11}Cl_2$ 7%
	1.0	Orthorhombic	
	3.0	Orthorhombic	
580	0.5	Orthorhombic	Undecomposed $Sb_8O_{11}Cl_2$ 2%
	1.0	Orthorhombic	
	3.0	Orthorhombic	

* Percentages : l-large, tr-trace

** The percentage of undecomposed $Sb_8O_{11}Cl_2$ was calculated from the chemical analysis

Table 3 RESULTS OF HEATING EXPERIMENTS ON ORTHORHOMBIC Sb_2O_3

Temperature (°C)	Heating time (hr)	Form of Sb_2O_3*
500	1	Orthorhombic(l)+Cubic(tr)
	2	Orthorhombic(l)+Cubic(tr)
	3	Orthorhombic(l)+Cubic(s)
560	1	Orthorhombic
	2	Orthorhombic
	3	Orthorhombic(l)+Cubic(tr)
570	2	Orthorhombic
	3	Orthorhombic
580	3	Orthorhombic

* Percentages : l-large, s-small, tr-trace

From the above-mentioned results, it may be concluded that the modification of Sb_2O_3 formed by the thermal decomposition of $Sb_8O_{11}Cl_2$ varies with the method of preparing $Sb_8O_{11}Cl_2$. According to the reported papers, cubic Sb_2O_3 has been formed by

sublimation of orthorhombic Sb_2O_3 at 400-500°C in vacuo[2,5], or by heating orthorhombic Sb_2O_3 placed in a platinum boat in a sealed, evacuated Pyrex tube at 470-550°C for 12-24 hr[1]. It has also been reported that cubic Sb_2O_3 is formed together with orthorhombic form in the smoke from d. c. arcs, in air at atmospheric pressure, between two electrodes of Sb metal[6]. It seems to be of interest that cubic Sb_2O_3 was obtained by the thermal decomposition of $Sb_8O_{11}Cl_2$, which was prepared by decomposing $Sb_4O_5Cl_2$, below 560°C.

REFERENCES

1) E. J. Roberts and F. Fenwick, J. Amer. Chem. Soc., 50, 2125 (1928).
2) W. B. Hincke, J. Amer. Chem. Soc., 52, 3869 (1930).
3) G. Belluomini, M. Fornaseri, and M. Nicoletti, Period. Mineral., 36, 147 (1967)., Mineral. Magaz., 36, 1037 (1968).
4) ASTM card 5-0534, 11-0689.
5) M. C. Bloom and M. J. Buerger, Z. Kristallographie, 96, 365 (1937)., G. Cohn and C. F. Goodeve, Trans. Farady Soc., 36, 433 (1940).
6) J. Harvey, H. I. Matthews, and H. Wilman, Disc. Farady Soc., No. 30, 113 (1960).

(Received October 23, 1973)