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INTERACTIONS IN THE THREE-COMPONENT SYSTEM In_2O_3–SeO_2–H_2O AT 100°C

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ABSTRACT

The solubility isotherm of the system In_2O_3–SeO_2–H_2O at 100°C was studied and drawn. Three indium selenites were found to exist: $In_2(SeO_3)_3 \cdot 6H_2O$; $In_2(SeO_3)_3 \cdot H_2SeO_3$ and $In_2(SeO_3)_3 \cdot 2H_2SeO_3 \cdot H_2O$. X-ray analysis data were adduced and the thermal dissociation of these compounds was studied. The dissociation of the selenites and the formation of $In_2O_3 \cdot 2In_2(SeO_3)_3$ and $2In_2O_3 \cdot In_2(SeO_3)_3$ was confirmed.

INTRODUCTION

In the last century Nilson [1] prepared and described the selenites of In: $In_2(SeO_3)_3 \cdot 6H_2O$; $3In_2(SeO_3)_3 \cdot 2In(OH)_3 \cdot 22H_2O$; $2In_2(SeO_3)_3 \cdot 3H_2SeO_3 \cdot 12H_2O$ and $In_2(SeO_3)_3 \cdot 3H_2SeO_3 \cdot 4H_2O$.

Working almost under the same experimental conditions Tananaev and co-workers [2] found out that the following selenites are possible: $In_2(SeO_3)_3 \cdot 6H_2O$ and $In_2(SeO_3)_3 \cdot 3H_2SeO_3 \cdot 3H_2O$.

Since, according to refs. 2 and 3, gallium hydrogen selenite becomes normal gallium selenite upon remaining in the mother solution, we could come to the conclusion that the question of the possible equilibrium phases of the three-component system In_2O_3–SeO_2–H_2O is still open.

EXPERIMENTAL

The initial $In(OH)_3$ and SeO_2 were obtained by the technique reported in refs. 4 and 5 from high-purity substances. SeO_2 was subjected to threefold sublimation for further purification.

The system was prepared by adding 3 g of $In(OH)_3$ to 100 ml of an aqueous solution of selenious acid at increasing concentrations. The samples were placed into glass ampoules which were sealed and then thermostated

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for 3 months in an air thermostat at 100 ± 1°C. At the end of that period the ampoules were opened, the liquid phase was separated from the solid phase by filtration at the experimental temperatures and was subjected to chemical analysis which was made complexometrically for In^{3+} [6], and iodometrically for SeO_3^{2-} [7].

RESULTS AND DISCUSSION

The solubility isotherm of the system In_2O_3–SeO_2–H_2O at 100°C (Fig. 1) was drawn according to the analysis data in Table 1, and the composition of the solid phases was determined after Schreinemakers. The isotherm of the system In_2O_3–SeO_2–H_2O was drawn at a concentration of SeO_2 in the liquid phase from O to 78.07 wt%. In that concentration range $In_2(SeO_3)_3 \cdot 6H_2O$ and two acidic salts, $In_2(SeO_3)_3 \cdot H_2SeO_3$ and $In_2(SeO_3)_3 \cdot 2H_2SeO_3 \cdot H_2O$, crystallized. $In_2(SeO_3)_3 \cdot H_2SeO_3$ and $In_2(SeO_3)_3 \cdot 2H_2SeO \cdot H_2O$ were obtained here for the first time. In accordance with the number of solid phases obtained, three branches of the solubility isotherm and two eutonic points E_1 and E_2 were established. Eutonic point E_1 corresponds to 12.30 wt% SeO_2, and eutonic point E_2 corresponds to 53.90 wt% SeO_2.

The compounds of the three-component system were determined both by means of the method of Schreinemakers, by chemical analysis of the well-washed and dried solid phases (Tables 1 and 2), and by X-ray analysis (Table 3). The X-ray pattern of $In_2(SeO_3)_3 \cdot 6H_2O$ differs from that in ref. 2,

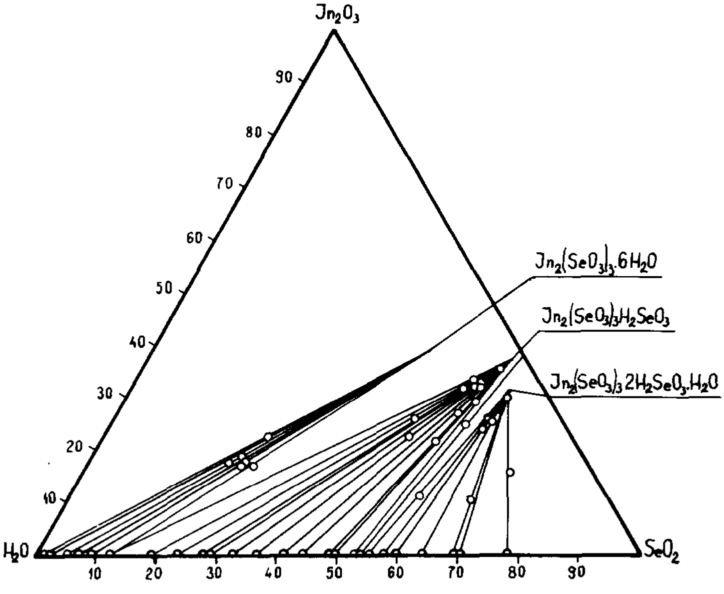

Fig. 1. Solubility isotherm of the system In_2O_3–SeO_2–H_2O at 100°C.

TABLE 1

Solubility isotherm of the system In_2O_3–SeO_2–H_2O at 100°C

No.	Liquid phase		Solid phase		Formula composition of the solid phase
	In_2O_3	SeO_2	In_2O_3	SeO_2	
1	2.07×10^{-3}	1.38	22.29	27.17	$In_2(SeO_3)_3\cdot6H_2O$
2	2.96×10^{-3}	2.38	18.56	24.92	
3	3.49×10^{-3}	5.17	17.19	23.25	
4	4.71×10^{-3}	7.21	17.39	25.94	
5	6.17×10^{-3}	9.22	16.82	25.69	
6	9.79×10^{-3}	12.02	16.51	27.69	
7	2.07×10^{-2}	12.42	33.03	56.13	$In_2(SeO_3)_3\cdot H_2SeO_3$
8	2.05×10^{-2}	19.14	35.13	59.76	
9	1.79×10^{-2}	23.62	31.51	55.01	
10	1.59×10^{-2}	27.60	25.86	49.60	
11	1.36×10^{-2}	29.01	32.37	56.50	
12	5.67×10^{-2}	32.74	32.32	57.50	
13	6.13×10^{-2}	36.53	22.15	51.02	
14	6.46×10^{-2}	41.26	31.56	57.70	
15	1.85×10^{-1}	44.36	26.83	57.20	
16	4.83×10^{-2}	48.77	28.66	58.92	
17	5.29×10^{-2}	49.79	21.17	55.75	
18	6.39×10^{-2}	52.77	35.74	59.50	
19	7.29×10^{-2}	53.90	24.58	58.96	eutonic point
20	2.73×10^{-2}	55.27	11.01	58.02	$In_2(SeO_3)_3\cdot2H_2SeO_3\cdot H_2O$
21	1.97×10^{-2}	57.55	25.58	61.50	
22	1.30×10^{-2}	59.62	23.58	62.12	
23	9.24×10^{-3}	64.01	25.20	62.65	
24	1.03×10^{-4}	69.25	10.25	66.72	
25	2.13×10^{-4}	70.40	30.10	63.10	
26	4.47×10^{-4}	78.07	15.53	70.93	

TABLE 2

Weight loss of $In_2(SeO_3)_3\cdot2H_2SeO_3\cdot H_2O$ and chemical analysis of the heated samples

Temp. (°C)	Weight loss	Chemical analysis		Phases
		In_2O_3	SeO_2	
105	2.04	31.94	63.98	$In_2(SeO_3)_3\cdot2H_2SeO_3$
138	4.08	32.67	65.20	$In_2(SeO_3)_3\cdot H_2SeO_3SeO_2$
213	6.08	33.28	66.73	$In_2(SeO_3)_3\cdot2SeO_2$
268	18.72	38.52	61.40	$In_2(SeO_3)_3\cdot SeO_2$
377	31.14	45.62	54.34	$In_2(SeO_3)_3$
462	43.54	55.50	44.44	$In_2O_3\cdot2In_2(SeO_3)_3$
640	56.14	71.28	28.71	$2In_2O_3\cdot In_2(SeO_3)_3$
675	68.64	99.59	–	In_2O_3

TABLE 3

X-ray patterns of indium selenites

I/I_1	d(Å)	I/I_1	d(Å)	I/I_1	d(Å)
$In_2(SeO_3)_3 \cdot 6H_2O$		$In_2(SeO_3)_3 \cdot H_2SeO_3$		$In_2(SeO_3)_3 \cdot 2H_2SeO_3 \cdot H_2O$	
63	8.536	100	6.249	100	6.602
100	7.246	8	4.207	24	6.021
63	4.643	100	3.184	4	4.979
20	4.267	7	3.046	12	3.948
20	4.019	7	2.928	7	3.477
20	3.616	10	2.829	9	3.324
33	3.151	17	2.696	82	3.229
63	3.035	6	2.138	26	3.081
25	2.635	4	2.106	4	2.938
20	2.441	4	2.065	9	2.864
20	2.415	7	1.612	5	2.763
25	2.331	12	1.589	8	2.736
33	2.091	12	1.585	6	2.479
45	2.000	12	1.567	2	2.313
		5	1.376	4	2.274
		5	1.372	10	2.154
		7	1.275	8	1.984
				6	1.812
				6	1.633

and the X-ray patterns of $In_2(SeO_3)_3 \cdot H_2SeO_3$ and $In_2(SeO_3)_3 \cdot 2H_2SeO_3 \cdot H_2O$ have been described here for the first time.

There are three endothermal and one exothermal peaks in the thermogram of normal indium selenite (Fig. 2). At 205°C $In_2(SeO_3)_3 \cdot 6H_2O$ loses its water of crystallization and turns into amorphous $In_2(SeO_3)_3$ which was established by chemical and X-ray phase analysis. At 430°C amorphous $In_2(SeO_3)_3$ becomes crystalline. The gravimetric analysis shows that no change of weight takes place at 430°C. The chemical analysis of the product which was heated at 205 and 430°C points to the composition: In_2O_3, 45.40 wt%; SeO_2, 54.67 wt%, which exactly corresponds to the stoichiometric composition of $In_2(SeO_3)_3$. The endothermal peak at 575°C corresponds to the transformation $3In_2(SeO_3)_3 \rightarrow 2In_2O_3 \cdot In_2(SeO_3)_3$. The thermal peak at 630°C corresponds to the complete dissociation of $In_2(SeO_3)_3$ and the formation of In_2O_3.

The results of the study of the kinetics of the dissociation of $In_2(SeO_3)_3$ are presented in Fig. 3. They show that $In_2(SeO_3)_3$ is stable up to 400°C. The rate of dissociation at that temperature is still negligible. At 450°C the horizontal section of the isotherm corresponds to 33% weight loss of SeO_2 from the solid phase which exactly corresponds to the transition $In_2(SeO_3)_3 \rightarrow In_2O_3 \cdot 2In_2(SeO_3)_3$. The chemical analysis of the product which was heated at that temperature for 70 min corresponds to the stoichiometric

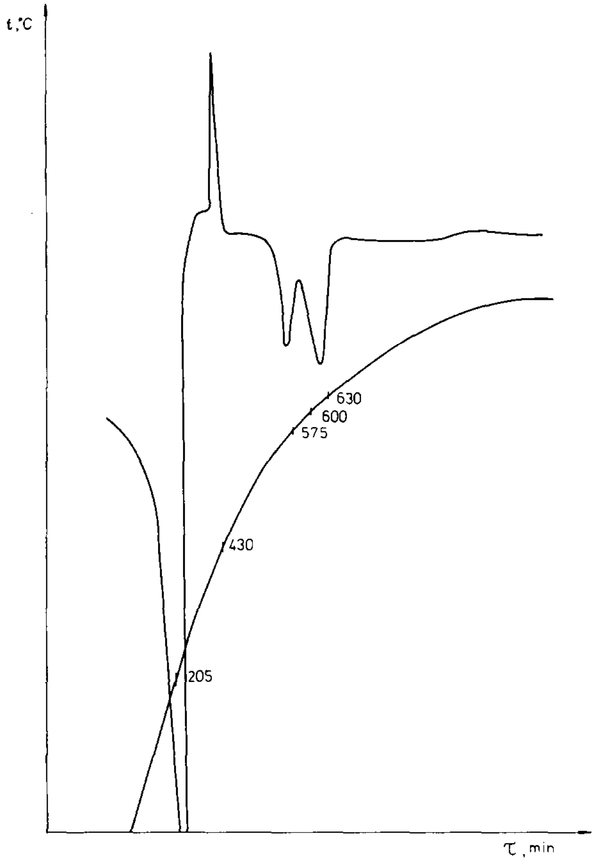

Fig. 2. Thermogram of $In_2(SeO_3)_3 \cdot 6H_2O$.

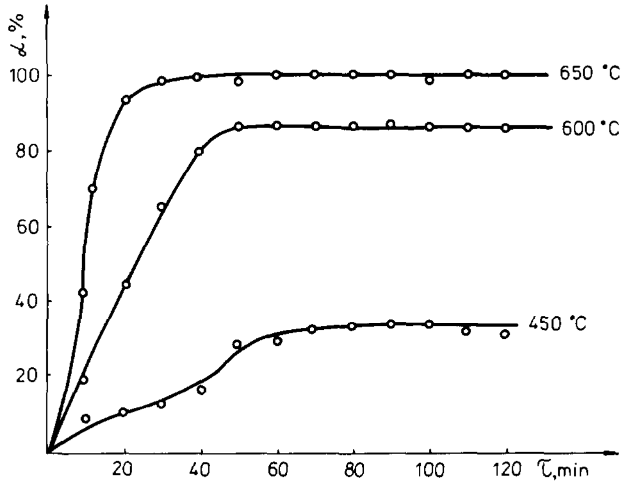

Fig. 3. Kinetic curves of the thermal dissociation of $In_2(SeO_3)_3$. Dependence of the degree of dissociation (α) on time (τ).

composition of $In_2O_3 \cdot 2In_2(SeO_3)_3$ (In_2O_3, 55.50 wt%; SeO_2, 44.44 wt%). The X-ray phase analysis points to the formation of a chemical compound and not a mixture with phase composition In_2O_3 and $In_2(SeO_3)_3$. At 600 and 650°C the rate of dissociation of $In_2(SeO_3)_3$ accompanied by giving off SeO_2 greatly increases, the boundary degree of dissociation at 600°C being 86%, and at 650°C, 100%. At 600°C the composition obtained for 30 min is $2In_2O_3 \cdot In_2(SeO_3)_3$ (In_2O_3, 71.45 wt%; SeO_2, 28.60 wt%). The analysis of the solid residue after dissociation at 600°C (for 30 min) and at 650°C (for 20 min) shows that it contains the phase $2In_2O_3 \cdot In_2(SeO_3)_3$ and not a mixture of oxide and selenite. The products heated at 650°C for more than 30 min are pure In_2O_3 (In, 82.64 wt%).

Our results are in good agreement with ref. 2. In ref. 2, however, the exothermal peak was not discussed.

In the thermogram of $In_2(SeO_3)_3 \cdot H_2SeO_3$ there are five endothermal peaks (Fig. 4) which point to a stage dissociation of the salt. At 135°C the salt loses its constitutional water and changes into pyroselenite $In_2(SeO_3)_3 \cdot SeO_2$ (In_2O_3, 38.52 wt%; SeO_2, 61.73 wt%). At 340°C one mole of SeO_2 is given off and anhydrous $In_2(SeO_3)_3$ (In_2O_3, 45.39 wt%; SeO_2 54.70 wt%) is obtained. Further on, normal indium selenite dissociates according to the scheme suggested above. The peak at temperatures above 600°C is quite interesting in being degenerated into two peaks at 620 and 675°C which makes it possible to suggest that the dissociation of the basic salt is

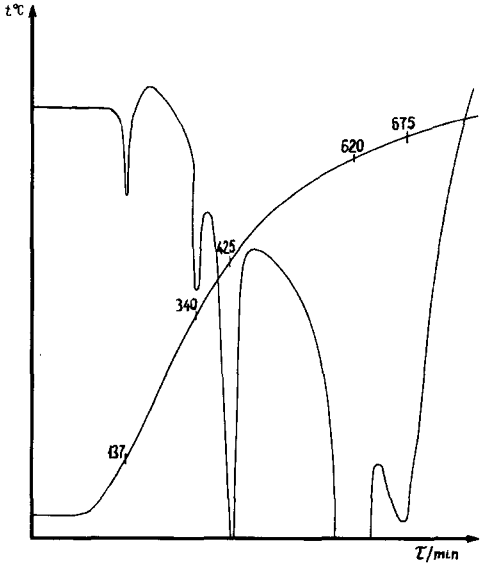

Fig. 4. Thermogram of $In_2(SeO_3)_3 \cdot H_2SeO_3$.

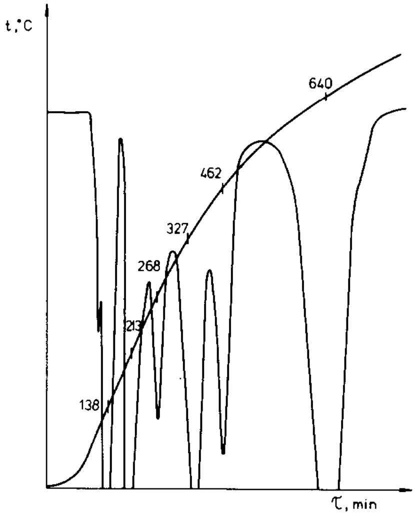

Fig. 5. Thermogram of $In_2(SeO_3)_3 \cdot 2H_2SeO_3 \cdot H_2O$.

complicated. The scheme of thermal dissociation is as follows

$$In_2(SeO_3)_3 \cdot H_2SeO_3 \xrightarrow{137°C} In_2(SeO_3)_3 \cdot SeO_2 \xrightarrow{340°C} In_2(SeO_3)_3$$

$$\xrightarrow{425°C} In_2O_3 \cdot 2In_2(SeO_3)_3 \xrightarrow{620°C} 2In_2O_3 \cdot In_2(SeO_3)_3 \xrightarrow{675°C} In_2O_3$$

There are seven endothermal peaks in the thermogram of $In_2(SeO_3)_3 \cdot 2H_2SeO_3 \cdot H_2O$ (Fig. 5). The chemical and X-ray analyses of the samples which were heated at the temperatures of the corresponding peaks (Table 1) show that the water of crystallization is removed at 105°C and then stage dissociation of the salt takes place according to the scheme

$$In_2(SeO_3)_3 \cdot 2H_2SeO_3 \xrightarrow{138°C} In_2(SeO_3)_3 \cdot H_2SeO_3 \cdot SeO_2$$

$$\xrightarrow{213°C} In_2(SeO_3)_3 \cdot 2SeO_2 \xrightarrow{268°C} In_2(SeO_3)_3 \cdot SeO_2 \xrightarrow{327°C} In_2(SeO_3)_3$$

$$\xrightarrow{462°C} In_2O_3 \cdot 2In_2(SeO_3)_3 \xrightarrow{640°C} 2In_2O_3 \cdot In_2(SeO_3)_3 \xrightarrow{675°C} In_2O_3$$

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