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SOLUBILITY ISOTHERM AND SOME PROPERTIES OF THE PHASES OF THE Ga_2O_3–SeO_2–H_2O SYSTEM

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ABSTRACT

The solubility isotherm of the three-component system Ga_2O_3–SeO_2–H_2O at 100°C was studied within a wide concentration range of selenious acid.

INTRODUCTION

Data about the possible selenites in the three-component system Ga_2O_3–SeO_2–H_2O, their thermal stability and identification properties (X-ray data, IR spectra, colour and solubility in water), are dependent on clarifying the chemistry of oxidation of gallium selenides upon the oxidating activation of semiconducting materials based on them.

Attempts at obtaining gallium selenites have been reported in refs. 1 and 2. Normal gallium selenite is obtained in the form of $Ga_2(SeO_3)_3 \cdot 6H_2O$. The composition of gallium hydrogen selenite in refs. 1 and 2 is $Ga_2(SeO_3)_3 \cdot H_2SeO_3$. According to ref. 2 the phase obtained is non-equilibrium and turns into $Ga_2(SeO_3)_3 \cdot 6H_2O$ on remaining in its mother solution.

The problem of the possible gallium selenites may be most thoroughly solved by studying the solubility isotherm of the system Ga_2O_3–SeO_2–H_2O. In this case, as in all other cases, the system consisting of metal oxide–selenious oxide–water was studied at 100°C. This temperature was chosen because of several considerations, namely:

(1) the solubility of SeO_2 in water at 100°C is highest which makes it possible to study the three-component system at a greater concentration of selenious acid;

(2) re-crystallization processes of the solid phases formed take place for a shorter period of time, and purer solid products of better crystallinity can be obtained;

(3) less time is required to reach both chemical and X-ray equilibrium;

(4) this temperature does not allow radioamorphous products to be obtained and if they do, they soon crystallize;

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(5) high temperature is favourable for the processes of dehydration in systems forming crystal hydrates which enables the formation of crystal hydrates containing less water or anhydrous salts.

In order to study the phase equilibria in this three-component system, $Ga(OH)_3$ was used as obtained by a technique described in ref. 3, and SeO_2 obtained from selenium (class B-5) and HNO_3 (Merck), and then purified several times by sublimation. Besides that, parallel samples of basic gallium selenite and selenious acid were prepared.

The system was prepared and the kinetics of chemical and crystallographic equilibrium were studied as in ref. 4.

Three months after preparing the system the liquid phase was separated from the solid phase by means of a shot-filter G-4 at the experimental temperature and then subjected to chemical analysis which was made complexometrically [5] for Ga and iodometrically [6] for SeO_2.

The data from the analysis of the equilibrium liquid and solid phases of the system Ga_2O_3–SeO_2–H_2O at 100°C are given in Table 1 and are presented in Fig. 1 by the method of Gibbs–Roozeboom. The results from two experimental series are analogical.

TABLE 1

Equilibrium study of the system Ga_2O_3–SeO_2–H_2O at 100°C

No.	Liquid phase (wt%)		Solid phase (wt%)		Formula composition of the solid phase
	Ga_2O_3	SeO_2	Ga_2O_3	SeO_2	
1	8.13×10^{-3}	1.01	13.61	28.82	$Ga_2(SeO_3)_3\cdot 6H_2O$
2	6.87×10^{-3}	1.45	12.54	23.66	
3	5.92×10^{-3}	4.00	13.70	26.10	
4	5.17×10^{-3}	4.65	15.03	28.50	
5	4.62×10^{-3}	5.99	12.84	26.68	
6	6.13×10^{-3}	14.77	12.89	31.00	
7	1.45×10^{-2}	27.84	10.77	37.25	
8	1.57×10^{-2}	30.04	6.94	35.96	
9	1.88×10^{-2}	33.19	16.81	43.50	
10	1.84×10^{-2}	34.44	11.35	41.21	
11	2.32×10^{-2}	34.88	19.55	70.74	$Ga_2(SeO_3)_3\cdot 3H_2SeO_3$
12	1.98×10^{-2}	35.27	14.84	62.06	
13	1.19×10^{-2}	40.60	19.06	69.05	
14	1.12×10^{-2}	41.21	13.63	61.01	
15	1.08×10^{-2}	43.86	18.66	70.09	
16	1.06×10^{-2}	44.55	16.30	67.37	
17	1.02×10^{-2}	49.18	20.41	71.95	
18	1.00×10^{-2}	50.07	20.58	71.98	
19	9.98×10^{-3}	50.75	20.04	72.02	
20	9.88×10^{-3}	53.63	20.41	72.28	
21	8.93×10^{-3}	60.12	13.95	68.24	
22	8.76×10^{-3}	71.99	19.02	72.60	
23	8.41×10^{-3}	74.40	17.13	73.53	

The isothermal diagram shows that, depending on the concentration of SeO_2 in the system, two compounds are obtained: $Ga_2(SeO_3)_3 \cdot 6H_2O$ and $Ga_2(SeO_3)_3 \cdot H_2SeO_3$. At a concentration of SeO_2 from 0 to 34.44 wt% the conodes meet at a point corresponding to the theoretical composition of $Ga_2(SeO_3)_3 \cdot 6H_2O$. In the concentration range from 34.88 to 74.40 wt% an acid salt with composition $Ge_2(SeO_3)_3 \cdot 3H_2SeO_3$ was formed. The eutonic point is within the narrow concentration range 34.44–34.88 wt% SeO_2. The compounds obtained dissolve incongruently in water. The acid salt $Ga_2(SeO_3)_3 \cdot 3H_2SeO_3$ was first obtained here.

Gallium selenites are very slightly soluble in their mother solution. The solubility of normal gallium selenite decreases at first and then begins to increase, while that of $Ga_2(SeO_3)_3 \cdot 3H_2SeO_3$ continuously decreases when the concentration of the solution of selenious acid increases (i.e., depending on the wt% SeO_2 in the liquid phase).

The compounds obtained are white substances of well-expressed crystallinity. The X-ray pattern of $Ga_2(SeO_3)_3 \cdot 6H_2O$ (Table 2) differs from that in ref. 7, while the X-ray pattern of $Ga_2(SeO_3)_3 \cdot 3H_2SeO_3$ was first obtained here (Table 2).

The thermograms of gallium selenites were drawn with an apparatus for differential thermal analysis described in ref. 8. Al_2O_3 was used as the reference material.

In order to explain the nature of the peaks in the thermograms the weight loss of each compound during heating as well as the change in its chemical composition were determined by chemical and X-ray analysis.

The thermogram of $Ga_2(SeO_3)_3 \cdot 6H_2O$ (Fig. 2) contains three endother-

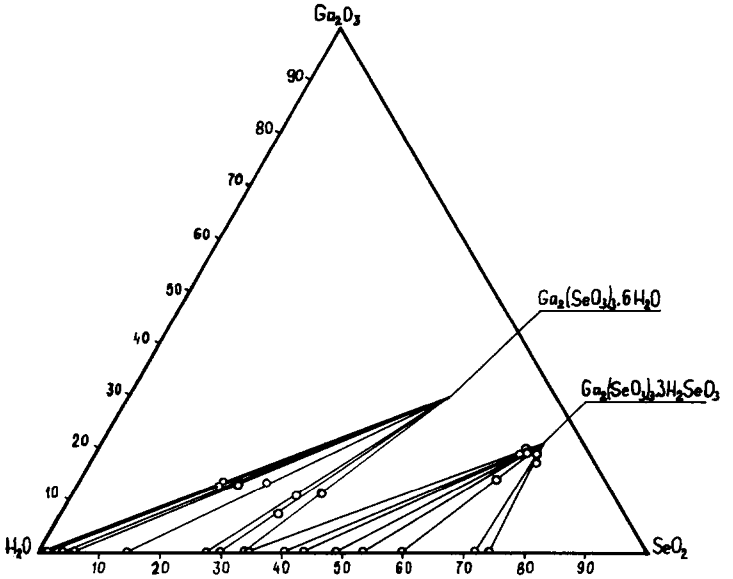


Fig. 1. Solubility isotherm of the system Ga_2O_3–SeO_2–H_2O at 100°C.

TABLE 2

X-ray data of gallium selenites

No.	I/I_1	d(Å)	I/I_1	d(Å)
	$Ga_2(SeO_3)_3 \cdot 6H_2O$		$Ga_2(SeO_3)_3 \cdot 3H_2SeO_3$	
1	53	8.215	100	6.799
2	100	6.910	30	5.149
3	11	6.070	52	4.529
4	5	5.535	74	4.470
5	3	5.092	6	4.076
6	18	4.458	5	3.844
7	9	4.111	53	3.714
8	6	3.880	60	3.391
9	53	3.509	26	3.302
10	37	3.386	26	3.160
11	20	3.005	17	3.138
12	55	2.938	17	3.056
13	29	2.761	21	3.014
14	17	2.557	18	2.907
15	11	2.415	26	2.718
16	20	2.239	12	2.625
17	11	2.160	14	2.588
18	15	2.013	10	2.504
19	11	1.941	18	2.340
20	61	1.905	15	2.239
21	5	1.817	16	2.089
22	5	1.786	7	1.966
23	5	1.740	11	1.958
24	9	1.703	15	1.862
25	16	1.500	12	1.368
26	11	1.462	13	1.361

mal peaks corresponding to the three phases of dissociation it undergoes. Gravimetric and chemical analyses show that the peak at 350°C corresponds to the dehydration of the crystal hydrate and the formation of anhydrous salt. According to chemical analysis data the content of Ga_2O_3 in $Ga_2(SeO_3)_3 \cdot 6H_2O$ heated for 2 h at 350°C is 35.97% and that of SeO_2 is 63.39% which corresponds to the compound $Ga_2(SeO_3)_3$. X-ray analysis showed that the selenite obtained is radioamorphous.

An analogical phenomenon in the dehydration of metal sulphate crystal hydrates has been described in the literature. It is noted in refs. 9 and 10 that the beginning of crystallization of similar formations coincides in temperature with the liberation of the last quantities of water from the compound. The surplus energy of the radioamorphous product is quite great and amounts to 1–7 kcal [11].

The second endothermal peak at 428°C corresponds to the transformation of $Ga_2(SeO_3)_3$ into basic gallium selenite, $Ga_2O_3 \cdot 2Ga_2(SeO_3)_3$, and the endothermal peak at 595°C corresponds to the dissociation of this salt to $Ga_2O_3 \cdot Ga_2(SeO_3)_3$. At 620°C Ga_2O_3 is obtained.

The kinetic curves (Fig. 3) show that anhydrous gallium selenite begins to dissociate visibly to gallium selenite at 400°C. At 450°C dissociation is more intensive. For 60 min $Ga_2(SeO_3)_3$ turns into $Ga_2O_3 \cdot 2Ga_2(SeO_3)_3$ (Ga_2O_3, 45.83%; SeO_2, 54.19%). At 570°C the sample dissociates to $Ga_2O_3 \cdot Ga_2(SeO_3)_3$. At 620°C the product loses all SeO_2 and turns into Ga_2O_3 (Ga, 74.39 wt%).

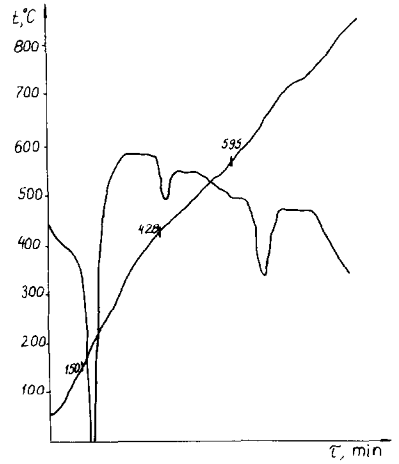
In the thermogram of $Ga_2(SeO_3)_3 \cdot 3H_2SeO_3$ the endothermal peaks are at 250, 278, 325, 390, 445, 575 and 620°C (Fig. 4).

On the basis of the results from heating the samples at these temperatures and gravimetric, chemical and X-ray analyses of the products obtained the following scheme of thermal dissociation is suggested

$$Ga_2(SeO_3)_3 \cdot 3H_2SeO_3 \xrightarrow{250°C} Ga_2(SeO_3)_3 \cdot 3SeO_2 \xrightarrow{278°C} Ga_2(SeO_3)_3 \cdot 2SeO_2$$

$$\xrightarrow{325°C} Ga_2(SeO_3)_3 \cdot SeO_2 \xrightarrow{390°C} Ga_2(SeO_3)_3 \xrightarrow{445°C} Ga_2O_3 \cdot 2Ga_2(SeO_3)_3$$

$$\xrightarrow{575°C} Ga_2O_3 \cdot Ga_2(SeO_3)_3 \xrightarrow{620°C} Ga_2O_3$$



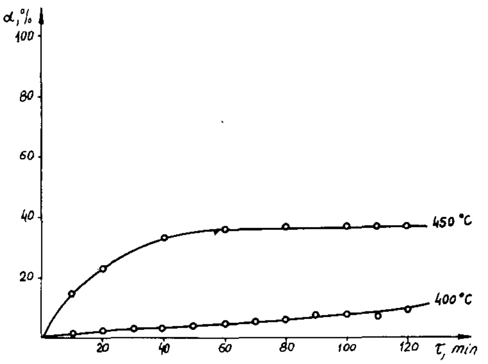


Fig. 2. Thermogram of $Ga_2(SeO_3)_3 \cdot 6H_2O$.

Fig. 3. Dependence of the degree of dissociation of $Ga_2(SeO_3)_3$ (α) on time (τ).

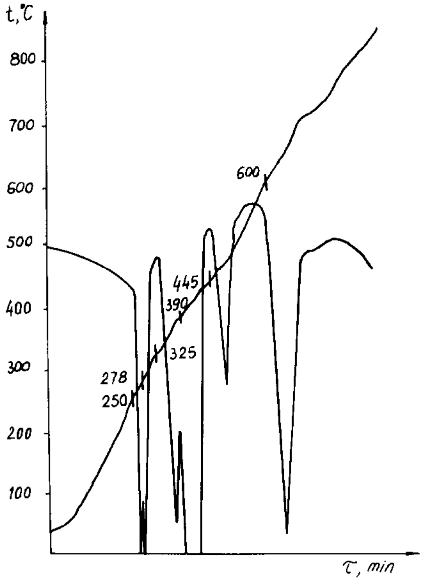


Fig. 4. Thermogram of $Ga_2(SeO_3)_3 \cdot 3H_2SeO_3$.

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