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Short Communication

FORMATION AND THERMAL STABILITY OF SELENITES AND HYDROGEN SELENITES OF SAMARIUM

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Abstract

The solubility isotherm of the Sm_2O_3–SeO_2–H_2O system was studied at 100°C. The two compounds obtained in the three-component system were identified by the Schreinemakers' method as well as by chemical, thermoanalytical and X-ray diffraction analyses after their isolation in pure state.

Keywords: phase state, samarium selenites, solubility isotherm, thermal degradation, X-ray

Introduction

The first data concerning the selenites of samarium can be found in the works of Espil and Cleve [1, 2], who obtained normal and hydrogen compounds with different composition.

For some time past, a number of samarium salts have been obtained. $Sm_2(SeO_3)_3 \cdot 5H_2O$ was synthesized by different authors [3, 4]. Other authors [5] obtained $Sm_2(SeO_3)_3 \cdot H_2SeO_3$ by a reaction between solutions of selenious acid and samarium nitrate. Synthesis of $SmH(SeO_3)_2 \cdot 2H_2O$ was described in [6]. Another reference [7] concerns the synthesis of $SmH(SeO_3)_2 \cdot 2.5H_2O$ whose parameters of the crystal lattice were determined. Later, Koskenlinna *et al*. [8] obtained $SmH(SeO_3)_2 \cdot 2H_2O$ from aqueous solutions of SeO_2 and $SmCl_3$ with a wide range of

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concentrations. The crystal system and the parameters of this product were determined. Savchenko *et al*. [9] obtained normal and hydrogen salts with different composition and studied their thermal properties. A larger review on inorganic complex compounds of the rare earths and structures of the rare earths selenites is given in [10, 11].

The above review leads to the conclusion that the preparative methods used by the authors do not settle the question about the synthesis of all possible selenites of samarium.

The data concerning all possible phases in the three-component system Sm_2O_3–SeO_2–H_2O can be obtained by studying and drawing the solubility isotherm, and this is the aim of the present study.

Experimental

Sm_2O_3 with the purity of 99.99 mass% (Aldrich, Germany) and SeO_2, obtained by the authors by oxidation of high-purity Se with nitric acid, were used to prepare the system. SeO_2 was subjected to additional triple sublimation to achieve better purification.

In order to study the Sm_2O_3–SeO_2–H_2O at 100°C, 20 samples were prepared each containing 2 g Sm_2O_3 and varying concentrations of selenious acid (from 0 to 85 mass%). The samples were sealed in glass ampoules (‘Rasotherm’) and placed in an air thermostat at 100±0.5°C for two months. To determine the necessary time for reaching chemical equilibrium, kinetic curves were obtained. For that purpose, more ampoules with the same composition were prepared and opened periodically. Equilibrium was reached when chemical analysis showed that the liquid and the solid phases did not change their composition. It was considered that crystallographic equilibrium was established when the peak intensities and the interplanar distances in the X-ray patterns no longer changed. After chemical and X-ray equilibrium was reached, the liquid and the solid phases were separated at the experimental temperature and subjected to chemical, thermal and X-ray phase analyses.

Chemical analysis for samarium ions was made by reverse complexometric titration using xylenol orange as an indicator [12], and SeO_3^{2-} ions were analyzed iodometrically and gravimetrically [13]. The concentration of Sm^{3+} in the liquid phase was determined spectrophotometrically on a Spekol-11 apparatus (Carl Zeiss Jena, Germany) using pyrocatecholviolet as an indicator.

X-ray phase analysis was made with a URD-6 apparatus (Carl Zeiss Jena, Germany) at Cu anode and K_α-emission and a nickel filter for β-emission. Thermal analysis was carried out using an OD-102 derivatograph (MOM, Hungary). The operating conditions of the thermal analysis are the temperature range from 20 to 1000°C, heating rate 5°C min^{-1}, sample mass 250 mg, thermocouple Pt/PtRh, standard substance α-Al_2O_3, in a medium of chemically pure nitrogen using metalloceramic crucibles.

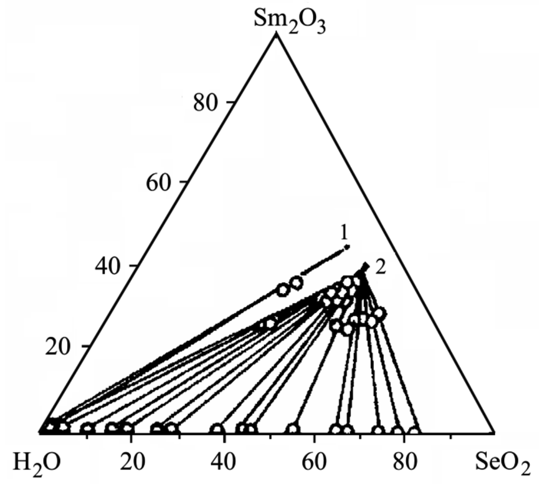

Fig. 1 Solubility isotherm of the system Sm_2O_3–SeO_3–H_2O at 100°C; 1 – $Sm_2(SeO_3)_3 \cdot 4H_2O$ and 2 – $SmH(SeO_3)_2 \cdot 2H_2O$

Table 1 Solubility isotherm of the system Sm_2O_3–SeO_2–H_2O at 100°C

No.	Liquid phase/mass%		Solid phase/mass%		Formula composition
	Sm_2O_3	SeO_2	Sm_2O_3	SeO_2	
1	$2.0 \cdot 10^{-3}$	0.19	36.80	37.91	$Sm_2(SeO_3)_3 \cdot 4H_2O$
2	$3.2 \cdot 10^{-3}$	0.62	37.28	47.04	$Sm_2(SeO_3)_3 \cdot 4H_2O$
3	$4.8 \cdot 10^{-3}$	0.62	38.10	45.80	$SmH(SeO_3)_2 \cdot 2H_2O$
4	$5.0 \cdot 10^{-3}$	4.76	27.16	36.94	$SmH(SeO_3)_2 \cdot 2H_2O$
5	$7.2 \cdot 10^{-3}$	10.27	39.26	49.51	$SmH(SeO_3)_2 \cdot 2H_2O$
6	$7.3 \cdot 10^{-3}$	15.88	34.56	46.47	$SmH(SeO_3)_2 \cdot 2H_2O$
7	$1.0 \cdot 10^{-2}$	18.97	34.50	46.89	$SmH(SeO_3)_2 \cdot 2H_2O$
8	$1.5 \cdot 10^{-2}$	25.22	46.89	49.27	$SmH(SeO_3)_2 \cdot 2H_2O$
9	$2.7 \cdot 10^{-2}$	29.13	34.87	47.25	$SmH(SeO_3)_2 \cdot 2H_2O$
10	$2.7 \cdot 10^{-2}$	38.92	34.18	49.32	$SmH(SeO_3)_2 \cdot 2H_2O$
11	$3.2 \cdot 10^{-2}$	44.27	36.40	49.95	$SmH(SeO_3)_2 \cdot 2H_2O$
12	$3.9 \cdot 10^{-2}$	46.04	33.10	49.53	$SmH(SeO_3)_2 \cdot 2H_2O$
13	$4.2 \cdot 10^{-2}$	55.96	26.49	52.56	$SmH(SeO_3)_2 \cdot 2H_2O$
14	$6.2 \cdot 10^{-2}$	65.50	25.92	54.70	$SmH(SeO_3)_2 \cdot 2H_2O$
15	$7.4 \cdot 10^{-2}$	68.85	28.82	54.90	$SmH(SeO_3)_2 \cdot 2H_2O$
16	$8.2 \cdot 10^{-2}$	74.45	29.21	56.62	$SmH(SeO_3)_2 \cdot 2H_2O$
17	$9.2 \cdot 10^{-2}$	78.62	28.47	57.11	$SmH(SeO_3)_2 \cdot 2H_2O$
18	$9.6 \cdot 10^{-2}$	82.54	30.42	57.05	$SmH(SeO_3)_3 \cdot 2H_2O$

Results and discussion

The results from studying the Sm_2O_3–SeO_2–H_2O are given in Table 1 and Fig. 1.

As figure shows, at 82.54 mass% of liquid SeO_2 two compounds are obtained in the system: $Sm_2(SeO_3)_3\cdot 4H_2O$ (congruently soluble) and $SmH(SeO_3)_2\cdot 2H_2O$ (incongruently soluble). A great part of the diagram consists of the field of crystallization of $SmH(SeO_3)_2\cdot 2H_2O$. The composition of the eutonic point between $Sm_2(SeO_3)_3\cdot 4H_2O$ and $SmH(SeO_3)_2\cdot 2H_2O$ is: 0.62 mass% of liquid SeO_2 and $4.8\cdot 10^{-3}$ mass% of Sm_2O_3.

The presence of two compounds in the three-component system was confirmed by X-ray data.

Figure 2 shows the derivatogram of $Sm_2(SeO_3)_3\cdot 4H_2O$. Heating the compound, dehydration takes place by stages in the temperature interval 100–310°C, 4 mole of H_2O are liberated, and anhydrous $Sm_2(SeO_3)_3$ is obtained. This salt is thermally stable, and crystallization processes start at 360–450°C. This fact can be explained by a considerable amorphisation of the product due to dehydration and its crystallization in the above temperature interval. An X-ray diagram of a sample of $Sm_2(SeO_3)_3$, heated at 340°C, shows that the compound is amorphous, while at 450°C it is already crystal-

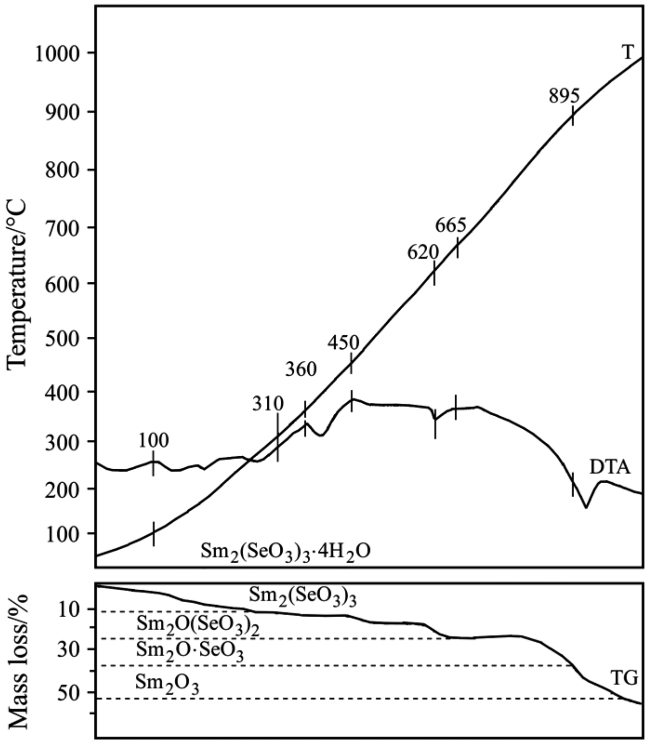

Fig. 2 Thermoanalytical curves of $Sm_2(SeO_3)_3\cdot 4H_2O$

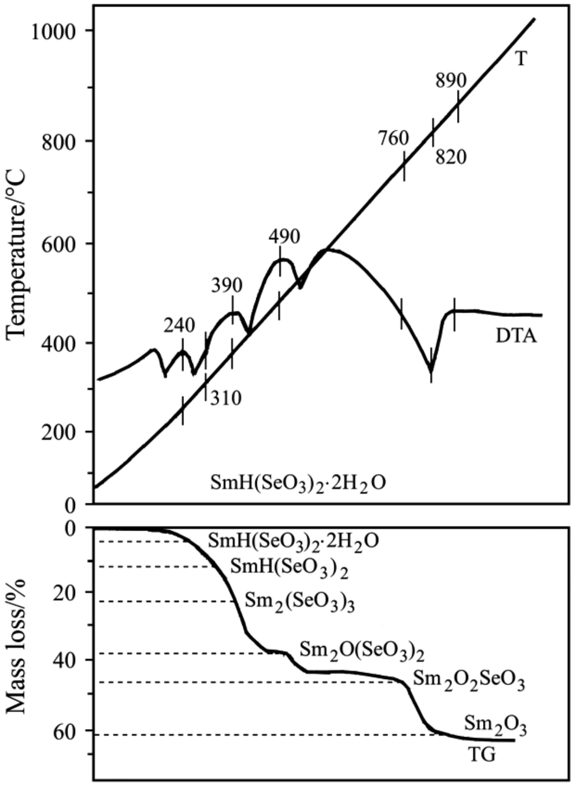

Fig. 3 Thermoanalytical curves of $SmH(SeO_3)_2{\cdot}2H_2O$

line. Normal selenite is thermally stable at 450°C. At a higher temperature, decomposition takes place accompanied by liberation of 1 mole of SeO_2 and $Sm_2O_3{\cdot}2SeO_2$ is obtained. The mass loss is 23.58 mass% (theoretical calculation is 24.28 mass%).

In the temperature interval 665–895°C, $Sm_2O_3{\cdot}2SeO_2$ loses one additional mole of SeO_2 and turns into another basic salt – $Sm_2O_2{\cdot}SeO_3$. The last stage of decomposition takes place at 1000°C, and a molecule of SeO_2 is liberated. The mass loss is 50.01 *vs*. 53.72 mass% calculated theoretically.

Figure 3 presents the thermoanalytical curves of $SmH(SeO_3)_2{\cdot}2H_2O$.

The salt is thermally stable at 160°C. In the temperature interval 160–270°C it loses 8.36 mass% due to the loss of 4 moles of crystallization water *vs*. 8.18 mass% calculated theoretically. In the temperature interval 270–310°C the hydrogenselenite loses its constitutional water and turns into $Sm_2(SeO_3)_3{\cdot}SeO_2$. The mass loss compared to the initial mass is 10.43 mass% (theoretical calculation is 10.20 mass%). Liberation of 1 mole of SeO_2 from tetraselenite takes place at 390°C. At 390–490°C the salt loses 36.95 mass% from its mass (theoretical calculation is 35.34 mass%) and turns into a basic salt $Sm_2O(SeO_3)_2$. In the temperature interval 580–760°C the salt loses yet

Table 2 Crystallographic data of samarium selenites

Compound	Crystal system	Space group	Lattice parameters			V_{cell}/Å^3	Z	ρ_x/g cm^{-3}
			a/Å	b/Å	c/Å			
$SmH(SeO_3)_2 \cdot 2H_2O$	orthorhombic	$P2_12_12_1$	6.6701	7.0312	16.4230	770.470	4	3.803
$Sm_2Se_4O_{11}$	monoclinic	$P2_1/m$	16.2442	7.5509	7.3922 β=94.759	903.580	4	5.827
$Sm_2(SeO_3)_3$	monoclinic	$P2_1/c$	17.2914	9.9508	12.1298 β=106.16	2004.628	4	3.519
Sm_2SeO_5	orthorhombic	Imma	18.8034	13.0723	5.5561	1365.710	8	4.472

another mole of SeO_2 and a basic salt with composition $Sm_2O_2 \cdot SeO_3$ is formed. Complete decomposition to Sm_2O_3 takes place at a temperature higher than 1000°C. The mass loss at 1050°C is 59.57 *vs*. 60.48 mass% calculated theoretically.

The decomposition stages for both salts were confirmed by identifying the intermediate decomposition products obtained and also by chemical and X-ray phase analysis of these products.

The lattice parameters of the unit cells of the selenites obtained from the three-component system and those obtained by their thermal decomposition were determined (Table 2) with an exception of $Sm_2(SeO_3)_3 \cdot 4H_2O$. Our calculation for the parameters of the unit cells of $SmH(SeO_3)_2 \cdot 2H_2O$ are in good agreement with those reported in [8].

This paper represents continuation of our investigation on the three-component systems of the type Ln_2O_3–SeO_2–H_2O [14–22].

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