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THERMAL ANALYSIS OF THE EQUILIBRIUM PHASES IN THE SYSTEM Ho_2O_3–SeO_2–H_2O

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Abstract

The selenites of holmium have been used as initial substances to obtain the respective selenides which have valuable semiconductive properties. Similarly to tellurites of rare-earth elements they can find an application as materials for making lasers as well. Concerning the various usages of the selenites of lanthanides lately (holmium in particular), obtaining and study of the selenites of holmium prove to be a question of present interest.

Keywords: holmium, phase diagrams, rare-earths, reaction mechanisms, solubility, X-ray structure determination

Introduction

Studies of the selenites of holmium are rather scarce. There are only two publications available concerning their synthesis and thermal stability [1, 2].

The interaction between solutions of $HoCl_3$ and Na_2SeO_3 was studied by potentiometric and conductometric titration [1]. A selenite with composition $Ho_2(SeO_3)_3 \cdot 4H_2O$ was identified. X-ray analysis showed that the selenite obtained was amorphous. The interaction of aqueous solutions of $HoCl_3$ (containing ammonia) with H_2SeO_3 resulted in an acid salt with composition $HoH(SeO_3)_2 \cdot 2.5H_2O$ [2]. It was claimed that double selenites of holmium with ammonia are not formed.

Thermal analysis [1] proved that the selenite completely loses its crystallization water at 200 and begins to decompose at a temperature over 400°C. Thermal treatment of $HoH(SeO_3)_2 \cdot 2.5H_2O$ at 800°C in a hydrogen medium showed that $Ho_2Se_3O_4$ was formed.

Nowadays de Pedro [3] synthesized anhydrous selenites of holmium by the method of solid phase synthesis and determined the parameters of the crystal lattice of $Ho_2Se_3O_9$ and of $Ho_2Se_3O_5$ [4].

The aim of the present work is to study the possible compounds in the system Ho_2O_3–SeO_2–H_2O at 100°C and to determine their thermoanalytical characteristics.

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Experimental

Ho_2O_3 with the purity of 99.999% (main substance), hydrochloric acid (Aldrich) and SeO_2 obtained by the authors from selenium with purity 99.999% in high purity nitric acid were used to study the system. According to spectral analysis data the product obtained has the purity of 99.999% (The calculation was made on the basis of the sum of the concentrations of 10 impurities).

In order to obtain holmium selenite, holmium oxide was dissolved in hydrochloric acid, the solution was diluted and a diluted solution of sodium selenite (obtained by the authors) was added to it. The selenite obtained was $Ho_2(SeO_3)_3 \cdot 4H_2O$. It was filtered, dried and samples were prepared.

An earlier publication [5] contains a detailed description of the way the samples were prepared and how the kinetics of reaching equilibrium was studied and the solubility isotherm was drawn.

Chemical analysis of the equilibrium liquid and solid phases for holmium ions was made complexometrically [6] and the selenite ions were gravimetrically or iodometrically analysed [7]. The compounds of the system were identified by the solubility isotherm and by chemical and X-ray phase analysis after separation in the pure state. X-ray phase analysis was made with a URD-6 apparatus (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.

Results and discussion

The results of studying the solubility and the nature of the solid phases in the system Ho_2O_3–SeO_2–H_2O at 100°C are presented in Table 1. The experimental data obtained were used to draw the solubility isotherm of the system (Fig. 1). It consists of two fields of crystallization of the solid phases, which correspond to the formation of saturated equilibrium solutions of $Ho_2(SeO_3)_3 \cdot 4H_2O$ and $Ho_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O$. The coordinates of the eutonic point are 0.0024 mass% for Ho_2O_3 and 0.42 mass% for SeO_2.

The composition of the compounds obtained was proved by chemical, gravimetrical and X-ray phase analysis of the washed and dried solid phases. $Ho_2(SeO_3)_3 \cdot 4H_2O$ was found to be X-ray amorphous. Well-formed crystals of $HoH(SeO_3)_3 \cdot 4H_2O$ were identified by determining their crystallographic parameters: a=6.553, b=6.921, c=16.319 Å, V=740.0 Å^3, D_x=4.091 g cm^{-3}. The compound crystallises in an orthorhombic system with a space group $P2_12_12_1$. The compound is isostructural with $SmH(SeO_3)_2 \cdot 2H_2O$, described by Koskenlinna [8].

Table 1 Solubility isotherm of the system Ho_2O_3–SeO_2–H_2O at 100°C

No.	Liquid phase/mass%		Solid phase/mass%		Formula composition
	Ho_2O_3	SeO_2	Ho_2O_3	SeO_2	
1	$3.3 \cdot 10^{-3}$	0.14	39.44	36.44	$Ho_2(SeO_3)_3 \cdot 4H_2O$
2	$5.0 \cdot 10^{-3}$	0.43	44.16	40.52	$Ho_2(SeO_3)_3 \cdot 4H_2O$
3	$6.2 \cdot 10^{-3}$	0.43	38.34	45.49	$HoH(SeO_3)_2 \cdot 2H_2O$
4	$6.8 \cdot 10^{-3}$	6.52	35.25	42.60	$HoH(SeO_3)_2 \cdot 2H_2O$
5	$7.5 \cdot 10^{-3}$	10.26	29.05	38.12	$HoH(SeO_3)_2 \cdot 2H_2O$
6	$7.8 \cdot 10^{-3}$	25.30	38.50	47.95	$HoH(SeO_3)_2 \cdot 2H_2O$
7	$8.1 \cdot 10^{-3}$	30.12	35.47	46.50	$HoH(SeO_3)_2 \cdot 2H_2O$
8	$8.2 \cdot 10^{-2}$	42.10	38.16	48.16	$HoH(SeO_3)_2 \cdot 2H_2O$
9	$8.5 \cdot 10^{-2}$	51.48	35.67	49.20	$HoH(SeO_3)_2 \cdot 2H_2O$
10	$8.8 \cdot 10^{-2}$	57.25	32.50	50.74	$HoH(SeO_3)_2 \cdot 2H_2O$
11	$9.0 \cdot 10^{-2}$	64.63	28.78	56.11	$HoH(SeO_3)_2 \cdot 2H_2O$
12	$9.5 \cdot 10^{-2}$	72.12	32.60	53.48	$HoH(SeO_3)_2 \cdot 2H_2O$
13	$9.6 \cdot 10^{-2}$	79.52	36.51	52.55	$HoH(SeO_3)_2 \cdot 2H_2O$

The TG curve of $Ho_2(SeO_3)_3 \cdot 4H_2O$ is presented in Fig. 2. It shows that selenite is thermally stable at 100°C. At 120°C two moles of crystallization water are liberated and $Ho_2(SeO_3)_3 \cdot 2H_2O$ is obtained. At 260°C the mass loss is 6.80 mass% (theoretical calculation is 6.88 mass%), corresponding to the total liberation of three moles of crystallization water. Crystallization water is completely liberated at 460°C. Here we observe the well-known fact that immediately after crystallization water is liberated and amorphous

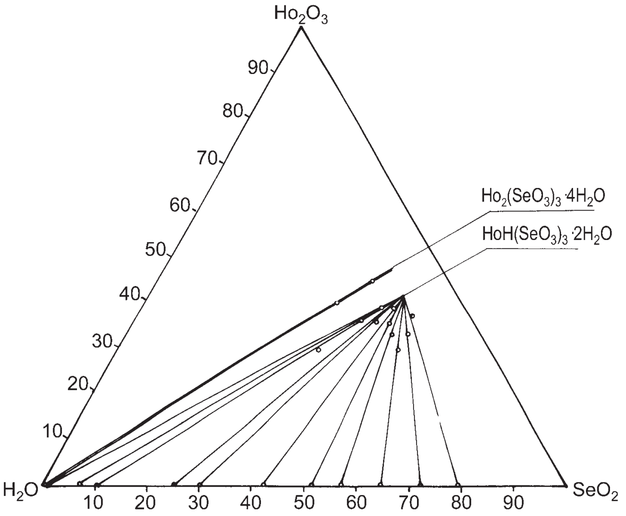

Fig. 1 Solubility isotherm of the system Ho_2O_3–SeO_2–H_2O at 100°C

anhydrous selenite is obtained, an exopeak follows at 460°C corresponding to the crystallization of the anhydrous salt. The liberation of one mole of SeO_2 and the formation of oxoselenite starts at 520°C. Complete liberation of one mole of SeO_2 does not take place until 940°C. In this case, the oxoselenite obtained is amorphous, too. The exopeak at 700°C corresponds exactly to the crystallization of the new salt. The liberation of the second mole of SeO_2 immediately after the complete liberation of the first mole. It should be noted that the derivatograph analysis was made up to 980°C, and at 980°C the mass loss is only 25.60 mass% (theoretical calculation is 37.55 mass%). The difference between the experimental and theoretically calculated mass loss is due to the fact that at 980°C the decomposition of $Ho_2(SeO_3)_3·4H_2O$ is incomplete. Complete liberation of the final traces of SeO_2 and the formation of the pure phase Ho_2O_3 cannot take place until 1200–1300°C for 3 or 4 h.

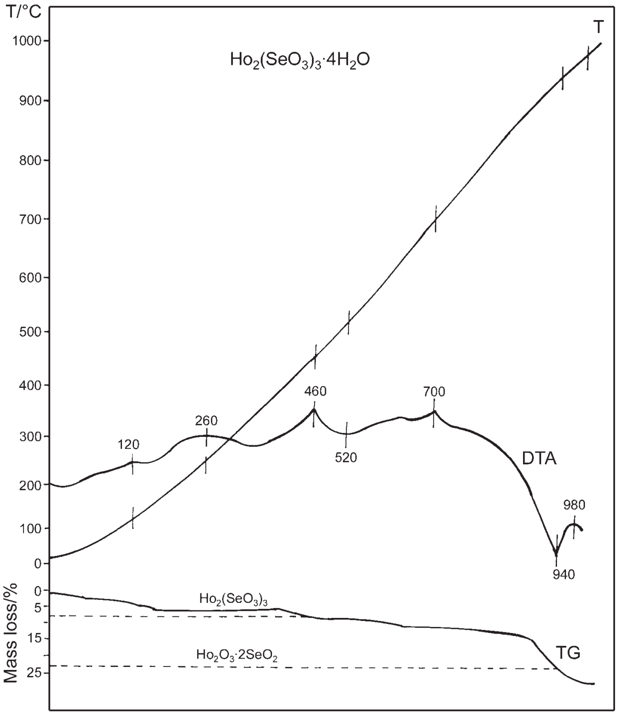

Fig. 2 TG, DTG and DTA curves of $Ho_2(SeO_3)_3·4H_2O$

Figure 3 shows the curve of $Ho_2(SeO_3)_3·H_2SeO_3·4H_2O$. The compound liberates adsorption water at 100°C. A well-formed endothermal peak at 180–200°C corresponds to the liberation of crystallization water by stages and the formation of anhydrous hydrogen selenite $Ho_2(SeO_3)_3·H_2SeO_3$. The endothermal peak at 280°C corresponds to the liberation of one mole of constitutional water and the formation of tetraselenite $Ho_2(SeO_3)_3{\cdot}SeO_2{:}(Ho_2Se_4O_{11})$. The total mass loss corresponding to that transformation according to the curve is 9.0 mass% (theoretical calculation is 9.83 mass%). The endothermal peak at 340°C which is not connected with mass loss probably corresponds to a polymorphous transformation. The complex endothermal peak at 460–490–540–600°C points to the liberation of one mole of SeO_2 by stages and the formation of complex phases. Normal $Ho_2(SeO_3)_3$ is obtained at 640°C and the total mass loss according to the TG curve corresponds to 22.60 mass% (theoretical calculation is 22.04 mass%). The complex endothermal peak at 640–1000°C with a minimum at 950°C corresponds to the complete liberation of one mole of SeO_2 and the transformation of normal selenite into oxoselenite $Ho_2O_3{\cdot}2SeO_2$. The last but one mole of SeO_2 is liberated partially at 1000°C. The mass loss at 1000°C is 39.70 mass% (theoretical calculation is 46.38 mass%). The difference between experimental and theoretically calculated mass loss is due to the fact that at 1000°C the decomposition of $Ho_2(SeO_3)_3{\cdot}H_2SeO_3{\cdot}4H_2O$ is incomplete. Complete liberation of SeO_2 and formation of a pure phase Ho_2O_3 was achieved by heating hydrogen selenite at 1200–1300°C for 3 or 4 h.

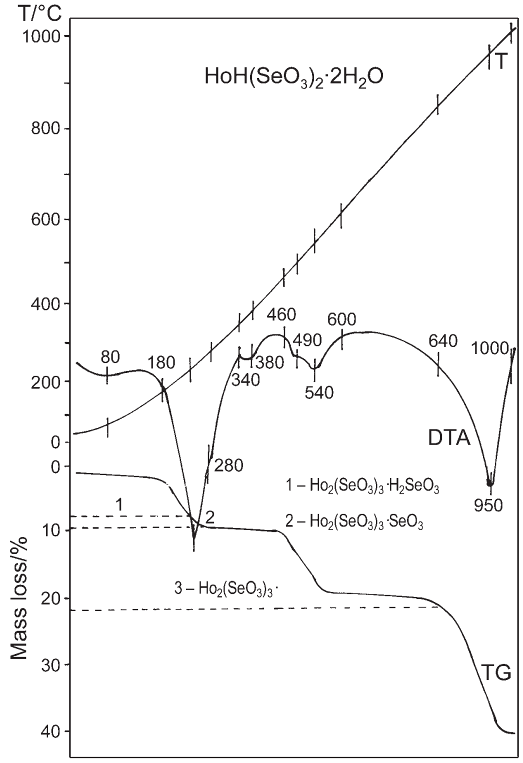

Fig. 3 TG, DTG and DTA curves of $Ho_2(SeO_3)_3{\cdot}H_2SeO_3{\cdot}4H_2O$

Conclusions

The solubility isotherm of the system Ho_2O_3–SeO_2–H_2O at 100°C was studied and drawn. The equilibrium phases of the system were identified by the Schreinemakers method and by chemical and X-ray phase analysis after they were isolated in the pure state.

All compounds of this system were subjected to derivatograph analysis and the mechanism of their thermal decomposition was described.

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