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Short Communication

PHYSICOCHEMICAL STUDY ON GADOLINIUM SELENITES

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Abstract

The solubility isotherm of the system Gd_2O_3–SeO_2–H_2O at 100°C was studied. The compounds of the three-component system were identified by the Schreinemakers' method as well as by chemical and X-ray phase analyses. Simultaneous TG and DTA analyses of all compounds of the system were made. The mechanism of thermal decomposition was described.

Keywords: gadolinium selenites, phase state, solubility isotherm, thermal dissociation, X-ray

Introduction

The information on gadolinium selenites is very scarce. Giesbrecht *et al*. [1] obtained amorphous hydrates $Gd_2(SeO_3)_3 \cdot 4$ to $5H_2O$ by adding 0.05 M Na_2SeO_3 to 0.05 $GdCl_3$. The authors [2] have reported that they obtained anhydrous gadolinium hydrogen selenite. By interaction between aqueous solutions of $GdCl_3$ (containing NH_3) and H_2SeO_3, a crystalline $GdH(SeO_3)_2 \cdot 2.5H_2O$ was obtained [3]. Compounds' elementary cell parameters were determined. A larger review on inorganic complex compounds of the rare earth is given in [4].

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Experimental

Methods of investigation

Gd_2O_3 (purity not less than 99.99 mass%) and high purity hydrochloric acid (Aldrich, Germany) were used as initial materials. SeO_2 was prepared by us through Se oxidation in a nitric acid. For further purification, SeO_2 was subjected to a threefold sublimation. According to AAS data, the obtained SeO_2 has purity not less than 99.99 mass%. Gadolinium selenite was obtained by dissolving the initial oxide in a concentrated hydrochloric acid, the excess of which was eliminated by fuming the aqueous solution. The so obtained anhydrous chloride was dissolved in water and an aqueous Na_2SeO_3 solution was adding to them, also obtained by ourselves through mixing equimolar amounts of aqueous solution of SeO_2 and NaOH (99.99 mass%).

In order to study the Gd_2O_3–SeO_2–H_2O system at 100°C, 14 samples of Gd_2O_3 of varying concentrations of SeO_2 (from 0 to 75 mass%) were charged. The samples were placed into glass ampoules which were welded and put into an air thermostat at 100±0.5°C. Periodically they were shaken. By observing the kinetics of reaching the chemical and crystallographic equilibrium, the time necessary for thermostating was settled. The liquid and solid phases were then separated at the test temperature and put to chemical, X-ray-phase and gravimetric analysis.

Gadolinium determination as Gd_2O_3 was made by direct complexometric titration with 0.05 M solution of complexon III, xylenoleorange as indicator and pH=5.5 [5]. The selenite ions were analyzed iodometrically and gravimetrically [6]. The concentration of Gd^{3+} ions in the liquid phase was determined spectrophotometrically on a 'Specol-11' apparatus (Carl Zeiss Jena, Germany) [7]. The X-ray-phase analysis was carried out by URD-6 (Carl Zeiss Jena, Germany) at a Cu-anode and $K\alpha$-emission and a nickel filter of β-emission. Thermoanalytical investigations were performed on OD-102 derivatograph (MOM, Hungary). The tests were made in ceramic crucibles. The heating interval was from 25 to 1000°C; rate of heating was $5°C\ min^{-1}$; α-Al_2O_3 was used as a standard. The atmosphere was inert.

Results and discussions

The data obtained from the Gd_2O_3–SeO_2–H_2O system at 100°C are represented in Table 1 and Fig. 1.

The system has been investigated up to 73.68 mass% SeO_2 in a liquid phase.

The Schreinemackers' beams show that the two solid phases: $Gd_2(SeO_3)_3{\cdot}4H_2O$ and $GdH(SeO_3)_2{\cdot}2H_2O$ crystallize in the system. The most of the diagram covers the field of crystallization of $GdH(SeO_3)_2{\cdot}2H_2O$ (from 0.52 to 73.68 mass%). $Gd_2(SeO_3)_3{\cdot}4H_2O$ crystallizes in the interval of 0 to 0.52 mass% SeO_2 in a liquid phase. The solutions content at the eutonic point between the two salts is 0.52 mass% SeO_2 in a liquid phase and Gd_2O_3–$6.0{\cdot}10^{-3}$ mass%.

Table 1 Solubility isotherm of the system Gd_2O_3–SeO_2–H_20 at 100°C

No.	Liquid phase/mass%		Solid phase/mass%		Formula composition
	Gd_2O_3	SeO_2	Gd_2O_3	SeO_2	
1	$4.2\cdot10^{-3}$	0.14	36.12	33.71	$Gd_2(SeO_3)_3\cdot4H_2O$
2	$5.0\cdot10^{-3}$	0.32	39.42	37.05	$Gd_2(SeO_3)_3\cdot4H_2O$
3	$6.0\cdot10^{-3}$	0.52	32.59	28.05	$GdH(SeO_3)_2\cdot2H_2O$
4	$7.0\cdot10^{-3}$	0.52	25.65	32.15	$GdH(SeO_3)_2\cdot2H_2O$
5	$8.9\cdot10^{-3}$	4.99	36.90	46.51	$GdH(SeO_3)_2\cdot2H_2O$
6	$9.3\cdot10^{-3}$	16.64	30.52	40.27	$GdH(SeO_3)_2\cdot2H_2O$
7	$9.8\cdot10^{-3}$	27.75	27.88	41.58	$GdH(SeO_3)_2\cdot2H_2O$
8	$1.5\cdot10^{-2}$	36.53	33.23	47.53	$GdH(SeO_3)_2\cdot2H_2O$
9	$1.7\cdot10^{-2}$	43.84	29.20	48.51	$GdH(SeO_3)_2\cdot2H_2O$
10	$2.2\cdot10^{-2}$	52.88	30.89	50.40	$GdH(SeO_3)_2\cdot2H_2O$
11	$2.9\cdot10^{-2}$	60.40	28.05	52.62	$GdH(SeO_3)_2\cdot2H_2O$
12	$3.4\cdot10^{-2}$	63.92	28.85	53.17	$GdH(SeO_3)_2\cdot2H_2O$
13	$4.0\cdot10^{-2}$	67.52	34.82	51.90	$GdH(SeO_3)_2\cdot2H_2O$
14	$6.2\cdot10^{-2}$	73.68	33.18	53.85	$GdH(SeO_3)_2\cdot2H_2O$

The comparison of the solid phases X-ray analysis confirm the results derived from the investigation of the state diagram for availability of two compounds in the triplicate system.

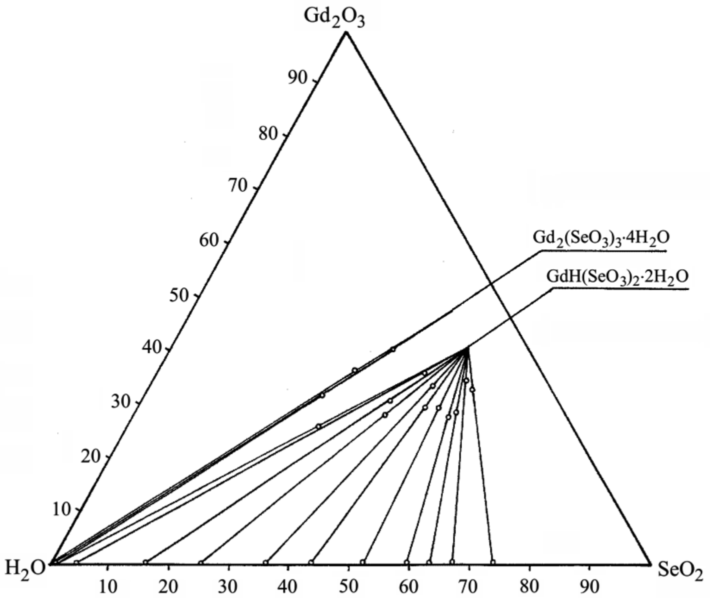

Fig. 1 Solubility isotherm of the system Gd_2O_3–SeO_2–H_2O at 100°C

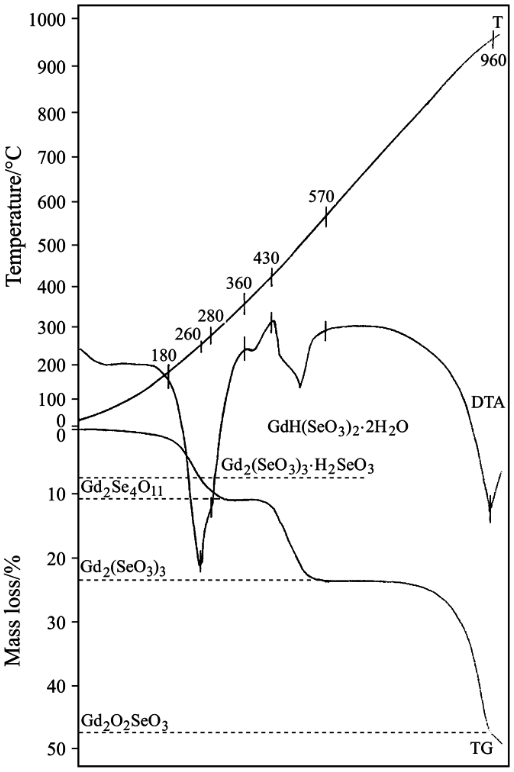

Fig. 2 Thermoanalytical curves of $GdH(SeO_3)_2 \cdot 2H_2O$

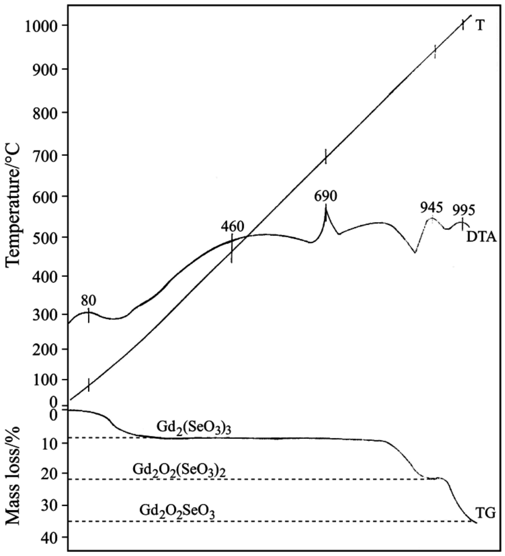

Fig. 3 Thermoanalytical curves of $Gd_2(SeO_3)_3 \cdot 4H_2O$

Table 2 Crystallographic data of gadolinium selenites

Compound	Crystal system	Space group	Lattice parametes				V_{cell}/ Å^3	Z	ρ_x/ g cm^{-3}
			a/Å	b/Å	c/Å	β			
$GdH(SeO_3)_2 \cdot 2H_2O$	orthorhombic	$P2_12_12_1$	6.6251	6.9931	16.3842	–	758.758	4	3.922
$Gd_2Se_4O_{11}$	monoclinic	$P2_1/m$	14.6551	11.9333	5.2628	95.84	914.989	4	5.852
$Gd_2(SeO_3)_3$	monoclinic	$P2_1/c$	17.1246	9.8666	12.0185	106.12	1950.824	4	2.368
Gd_2SeO_5	orthorhombic	Imma	18.6963	12.8892	5.4161	–	1305.174	8	4.817

Figure 2 shows the thermoanalytical curves of $GdH(SeO_3)_2\cdot 2H_2O$.

Until 180°C the salt is thermally stable, and above this temperature the compound loses 4 moles of H_2O and turns in anhydrous hydrogen selenite with a composition: $Gd_2(SeO_3)_3\cdot H_2SeO_3$. Within the temperature interval 280–360°C one more mole of H_2O is further separated and gadolinium tetraselenite, $Gd_2(SeO_3)_3\cdot SeO_2$ is obtained. The mass loss amounts to 10.36 mass% *vs*. 10.04 mass% which is theoretically calculated. Within the temperature interval 430–570°C tetraselenite decomposes to $Gd_2(SeO_3)_3$. The mass loss makes up 23.30 mass% *vs*. 22.42 mass% which is theoretically calculated. Within the temperature interval 570–960°C two SeO_2 moles consequently set off and the salt transforms into the basic salt $Gd_2O_3\cdot SeO_2$. Full decomposition as well as separation of SeO_2 traces can be observed at a temperature of 1100–1200°C.

When heating $Gd_2(SeO_3)_3\cdot 4H_2O$ (Fig. 3), a thermal dissociation originally runs with consecutively elimination of crystallization water within a temperature range of 80–460°C. Destruction leads to obtaining $Gd_2(SeO_3)_3$ which is X-ray amorphous.

The 690°C exothermal effect corresponds to the crystallization of the amorphous product. The proofs for this are the results of the X-ray phase analysis. On X-ray diagram of a product heated up to a temperature preceding the exothermal effect no reflexes are observed, and on samples heated at temperatures over the exothermal effect such reflexes are recorded. The anhydrous gadolinium selenite is then decomposed according to a scheme described on the acid salt.

All the conversions were proved by a chemical analysis on the obtained phases when modeling the conditions of thermal decomposition as well as by X-ray phase analysis and the comparison of the intermediate X-ray pattern.

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 $Gd_2(SeO_3)_3\cdot 4H_2O$.

This paper represents continuation of our investigation on the three-component systems of the type Ln_2O_3–SeO_2–H_2O [8–15].

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