

PHASE STATES OF EUROPIUM SELENITES IN AQUEOUS MEDIUM AND IN THERMAL ANALYSIS

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Abstract

The solubility isotherm of the system $\text{Eu}_2\text{O}_3\text{-SeO}_2\text{-H}_2\text{O}$ was studied at 100°C. Certain amounts of the obtained selenites (normal and acid) were subjected to thermal analysis. The intermediate phases were isolated and chemical and X-ray phase analysis was made. The scheme of thermal decomposition was determined.

Keywords: europium selenites, solubility isotherm, thermal analysis, X-ray pattern

Introduction

Data concerning the selenites of europium are rather scarce. There are no data available for the oxide salts. Hydrogen selenite was studied by Eivor Immonen *et al.* [1]. They obtained $\text{EuH}(\text{SeO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ by mixing $\text{EuCl}_3 \cdot 6\text{H}_2\text{O}$ (made alkaline by addition of ammonia) with a 2 M solution of H_2SeO_3 . After staying in the mother solution for 24 h, small, needle-shaped crystals were formed. A thorough study of their work, however, arouses some doubt about the number of the molecules of crystal water.

The existence of all possible phases in the three-component system $\text{Eu}_2\text{O}_3\text{-SeO}_2\text{-H}_2\text{O}$ may be evidenced by studying and drawing the isotherm of the phase states.

Experimental

Eu_2O_3 with a mole-fraction purity of 0.9999 and high purity hydrochloric acid (commercial products of Merck or Fluka) were used as initial compounds. We obtained SeO_2 by oxidation of selenium in nitric acid. SeO_2 was purified by triple sublimation. Atomic absorption spectroscopic analysis, revealed that the SeO_2 thus prepared contained 99.9999 mass% of the substance. EuCl_3 was obtained by dissolving the oxide in concentrated HCl. The excess of HCl was removed by heating the aqueous solution. The resulting chlorides were dissolved

in water, and an aqueous solution of Na_2SeO_3 was added. Na_2SeO_3 was obtained by mixing equimolar amounts of aqueous solutions of SeO_2 and NaOH (99.99 mass%).

In order to study the system $\text{Eu}_2\text{O}_3\text{--SeO}_2\text{--H}_2\text{O}$ at 100°C , 17 mixtures containing Eu_2O_3 and varying concentrations of SeO_2 (from 0 to 85%) were prepared. The experimental technique was based on the conclusions of Chlopin [2] who proved experimentally the possibility of reaching a stable thermodynamic equilibrium between the solid phase and the solutions. The samples were placed in glass ampoules, which were sealed and thermostatted at $100\pm 0.5^\circ\text{C}$ in an air thermostat. They were periodically shaken. The necessary time for reaching equilibrium was determined experimentally by studying the equilibrium kinetics. Then, the liquid and the solid phases were separated at the experimental temperature and subjected to chemical, crystallo-optical and X-ray phase analyses.

The determination of Europium as Eu_2O_3 was determined by complexometric titration with a 0.05 M solution of EDTA at $\text{pH}=5.5$ and xylenol orange as indication [3]. SeO_3^{2-} ions were determined iodometrically and gravimetrically [4]. The concentration of Eu^{3+} ions in the liquid phase was determined spectrophotometrically at $\text{pH}=4.67$ using Alizarin S as indicator with a Specol-II apparatus (Carl Zeiss, Jena, Germany) [5]. X-ray phase analysis was made with a TURM apparatus (Germany) with Ni-filtered CuK_α -radiation. Thermal analysis was carried out using an OD-102 Derivatograph (MOM, Hungary). A Dokuval optical microscope (Carl Zeiss, Jena, Germany) was used for crystallo-optical analysis.

Results and discussion

The data obtained for the system $\text{Eu}_2\text{O}_3\text{--SeO}_2\text{--H}_2\text{O}$ at 100°C are presented in Table 1 and Fig. 1.

Figure 1 shows that the solubility diagram of the system consists of two fields of crystallization. In the first field of the isotherm, in the low concentration range of H_2SeO_3 , a compound with composition $\text{Eu}_2(\text{SeO}_3)_3\cdot 4\text{H}_2\text{O}$ is obtained. In the second field of the isotherm in the concentration range of SeO_2 from 0.57 to 54.65 mass%, a compound with composition $\text{EuH}(\text{SeO}_3)_2\cdot 2\text{H}_2\text{O}$ crystallizes as the solid phase. The compositions of the compounds obtained were determined by means of Schreinemaker's method and chemical analysis after thorough washing and drying of the solid phases.

Chemical analysis of $\text{Eu}_2(\text{SeO}_3)_3\cdot 4\text{H}_2\text{O}$ gave the concentration of Eu_2O_3 as 47.71%, that of SeO_2 as 45.00%, and that of H_2O as 7.29%. The concentrations calculated theoretically were 47.63, 45.06 and 7.31%, respectively. $\text{EuH}(\text{SeO}_3)_2\cdot 2\text{H}_2\text{O}$ contains 39.70% Eu_2O_3 , 50.54% SeO_2 and 10.05% H_2O (theoretical values were 39.73, 50, and 10.16%, respectively).

X-ray phase analysis of these europium selenites confirmed their phase compositions in an aqueous medium and in thermolysis.

At concentrations of SeO_2 over 54.65 mass%, the solid phase was totally decomposed. The increase in solubility is probably due to the formation of a new acid salt. However, our attempts to isolate and study this phase failed.

Table 1 Solubility isotherm of the system Eu_2O_3 - SeO_2 - H_2O at 100°C

No.	Liquid phase/wt%		Solid phase/wt%		Formula of the solid phase
	Eu_2O_3	SeO_2	Eu_2O_3	SeO_2	
1	—	0.05	34.50	34.50	$\text{Eu}_2(\text{SeO}_3)_3 \cdot 4\text{H}_2\text{O}$
2	—	0.35	33.87	34.06	$\text{Eu}_2(\text{SeO}_3)_3 \cdot 4\text{H}_2\text{O}$
3	0.02	0.57	38.78	39.55	$\text{Eu}_2(\text{SeO}_3)_3 \cdot 4\text{H}_2\text{O}$
4	0.05	0.57	38.34	47.78	$\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$
5	0.10	1.17	37.60	47.45	$\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$
6	0.11	2.48	39.08	48.50	$\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$
7	0.16	5.10	33.28	43.24	$\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$
8	0.25	11.45	35.75	43.42	$\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$
9	0.28	18.85	31.42	43.50	$\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$
10	0.40	30.86	38.55	49.63	$\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$
11	0.51	39.18	37.18	48.73	$\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$
12	0.55	46.12	36.80	48.11	$\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$
13	0.62	51.38	35.10	49.84	$\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$
14	0.80	54.64	33.50	51.26	$\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$

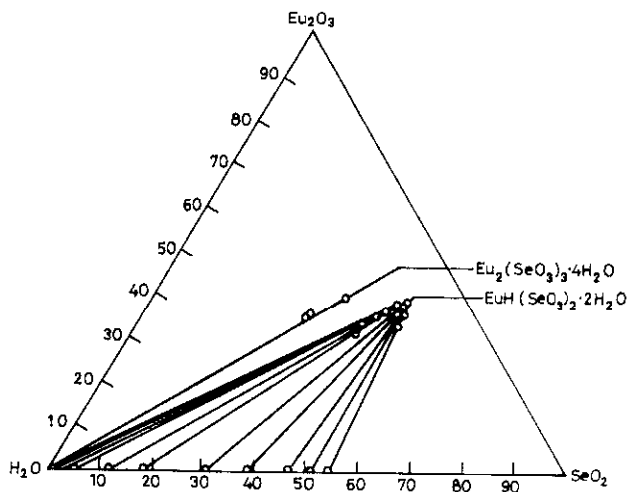


Fig. 1 Solubility isotherm of the system Eu_2O_3 - SeO_2 - H_2O at 100°C

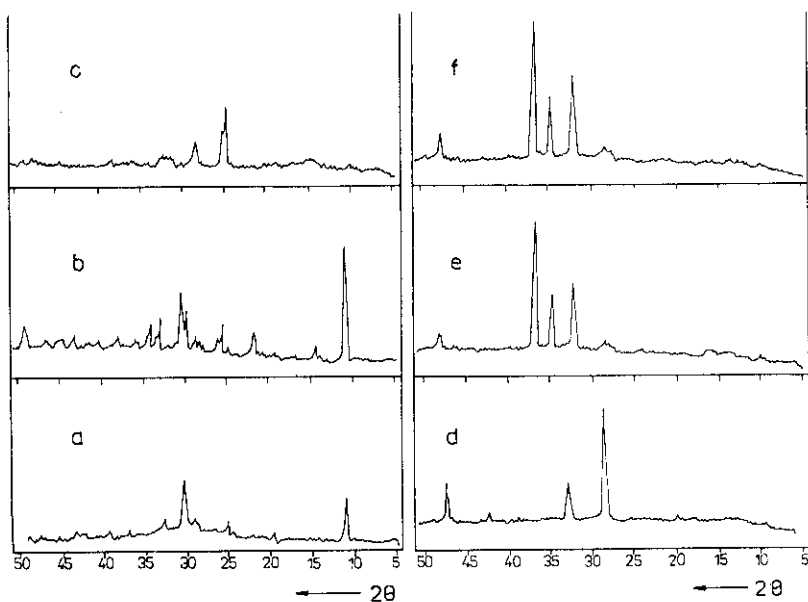


Fig. 2 X-ray patterns of the solid phases of the system; $\text{Eu}_2\text{O}_3\text{-SeO}_2\text{-H}_2\text{O}$ at 100°C , a – $\text{Eu}_2(\text{SeO}_3)_3 \cdot 4\text{H}_2\text{O}$; b – $\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$; c – $\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$, heated at 440°C ; d – $\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$, heated at 720°C ; e – $\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$, heated at $1200\text{--}1300^\circ\text{C}$; f – Eu_2O_3

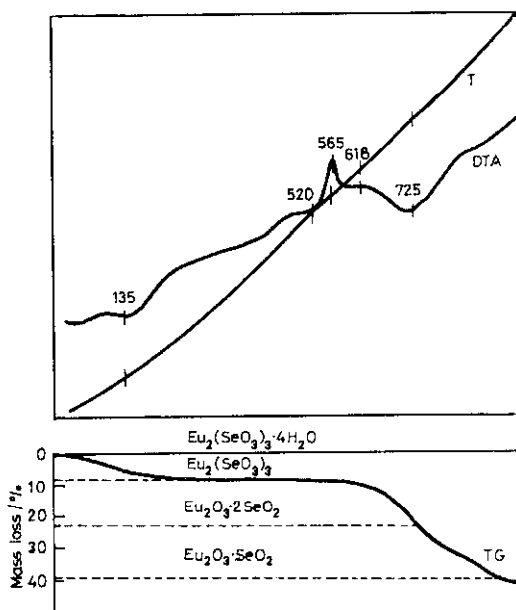


Fig. 3 DTA and TG curves of $\text{Eu}_2(\text{SeO}_3)_3 \cdot 4\text{H}_2\text{O}$

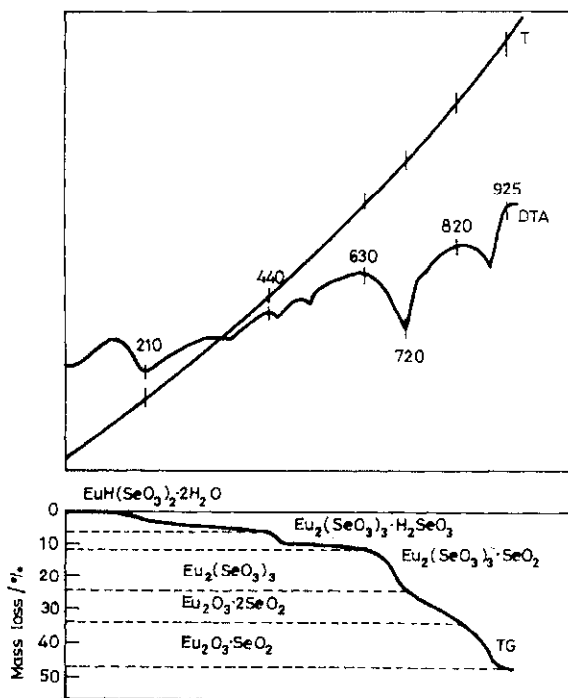


Fig. 4 DTA and TG curves of $\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$

The DTA and TG curves of $\text{Eu}_2(\text{SeO}_3)_3 \cdot 4\text{H}_2\text{O}$ are presented in Fig. 3. They indicate that dehydration starts at 100°C and the anhydrous salt $\text{Eu}_2(\text{SeO}_3)_3$ is obtained. It is stable up to 618°C . The exothermal peak at 565°C is due to crystallization of the amorphous phase $\text{Eu}_2(\text{SeO}_3)_3$ obtained by dehydration. A confirmation of this interpretation is the fact that at temperatures lower than 565°C there are no peaks on the X-ray pattern. $\text{Eu}_2(\text{SeO}_3)_3$ undergoes thermal decomposition between 618 and 700°C yielding $\text{Eu}_2(\text{SeO}_3)_2$. This crystalline phase decomposes in two stages. $\text{Eu}_2\text{O}_3 \cdot \text{SeO}_2$ is formed above 760°C . SeO_2 is completely released between 1200 and 1300°C , which is confirmed by the fact that the X-ray pattern of a sample heated in a furnace at these temperatures completely coincides with the X-ray pattern of commercial Eu_2O_3 .

Figure 4 shows the DTA and TG curves of $\text{EuH}(\text{SeO}_3)_2 \cdot 2\text{H}_2\text{O}$. The salt is thermally stable at 100°C . Above 100°C the compound loses water of crystallization and $\text{Eu}_2(\text{SeO}_3)_3 \cdot \text{H}_2\text{SeO}_3$ is formed. The tetraselenite $\text{Eu}_2(\text{SeO}_3)_3 \cdot \text{SeO}_2$ is formed above 440°C . In the temperature interval 630 – 720°C it decomposes to normal selenite $\text{Eu}_2(\text{SeO}_3)_3$ in stages. In the interval 720 – 820°C the salt releases 1 mole of SeO_2 and is transformed to $\text{Eu}_2\text{O}_3 \cdot 2\text{SeO}_2$ ($\text{Eu}_2\text{O}(\text{SeO}_3)_2$). In the interval 820 – 925°C decomposition results in the formation of a second oxide salt,

$\text{Eu}_2\text{O}_3 \cdot \text{SeO}_2$ ($(\text{EuO})_2\text{SeO}_3$). Complete decomposition takes place between 1200 and 1300°C, when the last residues of SeO_2 disappear.

All transformations were proved by chemical analysis of the phases obtained beforehand by modelling the decomposition conditions and also X-ray phase analysis and comparison of the X-ray patterns of the intermediate phases.

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