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A STUDY OF THE SELENITES OF CERIUM
Phase states in aqueous medium and thermal properties

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Abstract

The solubilities of the systems CeO_2–SeO_2–H_2O and Ce_2O_3–SeO_2–H_2O were studied at 100°C. The field of crystallization of $Ce(SeO_3)_2$ was established in the system CeO_2–SeO_2–H_2O, and fields of crystallization of $Ce_2(SeO_3)_3$ and $Ce_2(SeO_3)_3 \cdot H_2SeO_3$ were established in the system Ce_2O_3–SeO_2–H_2O. The compound obtained were identified by means of chemical, X–ray and derivatograph analysis. The mechanism of thermal dissociation of $Ce(SeO_3)_2$, $Ce_2(SeO_3)_3$ and $Ce_2(SeO_3)_3 \cdot H_2SeO_3$ was studied.

Keywords: cerium selenites, equilibrium, phase diagrams, solubility, X–ray

Introduction

Bercelius [1] and Nilson [2] were the first to publish data about the selenites of cerium. Jolin [3] obtained amorphous cerium selenite, and Espil [4] obtained yellow powder of anhydrous cerium selenite. Nilson [2] and Jolin [3] obtained cerium hydrogenselenites having a different number of moles of crystallization water by treating a normal salt with selenious acid. Barbieri and Calzolari [5] obtained orange-yellow powder of cerium selenite by heating a mixture of cerium nitrate, selenious acid and nitric acid.

Markovski and Safina [6] described syntheses of the selenites of tri- and four-valent cerium at different ratios of cerium and selenious acid in the temperature range from 25 to 40°C. Depending on the conditions of precipitation, several salts were obtained: $Ce(SeO_3)_2$, $Ce(HSeO_3)_3 \cdot H_2O$, $Ce_2(SeO_3)_3 \cdot H_2SeO_3$, $Ce_2(SeO_3)_3 \cdot H_2O$, $Ce_2(SeO_3)_3 \cdot 3H_2O$ and $Ce_2O_3 \cdot 2SeO_2 \cdot 15H_2O$. The authors were not able to obtain acid selenite of Ce(IV).

In [6], standard heats of formation of cerium selenites were calculated by determining the heats of dissolution of the selenites of cerium in nitric acid.

The structure of Ce(IV) was determined and reported in [7]. $Ce(SeO_3)_2$ crystallizes in an orthorhombic system. The authors [8] determined the parameters of the crystal lattice of Ce_2SeO_5.

The aim of the present work is to study the solubility of the systems CeO_2–SeO_2–H_2O and Ce_2O_3–SeO_2–H_2O at 100°C and to determine the thermal dissociation of the compound obtained.

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Experimental

25 samples were prepared to study each of the systems. For that purpose, $Ce(SeO_3)_2$ was obtained from high-purity cerium(IV) chloride and sodium selenite, and $Ce_2(SeO_3)_3$ – from high-purity cerium(III) chloride and sodium selenite. Razotherm glass ampoules were used and each was filled with 2 g of $Ce(SeO_3)_2$, respectively $Ce_2(SeO_3)_3$ and with H_2SeO_3 in various concentrations (from 0.1 to 80 mass%). The ampoules were sealed and placed in an air thermostat at 100±0.5°C. They were periodically shaken. After chemical and X–ray phase equilibrium was reached, the system was studied. For that purpose, the ampoules were opened, the liquid and solid phases were separated at the experimental temperature and were subjected to chemical analysis.

The procedure of preparing the systems and studying the kinetics of reaching an equilibrium were described in [9].

Chemical analysis for Ce^{3+} ions was made by direct complexometric titration using xylenol orange as an indicator [10]. Analysis for Ce^{4+} ions was made by reverse complexometric titration with eriochrome black T as an indicator [10], and that for selenite ions was made iodometrically and gravimetrically [11].

X–ray analyses were made on a URD–6 apparatus (Germany) at Cu anode and $K\alpha$ emission, and a Ni filter for β emission.

An OD–102 derivatograph (MOM, Hungary) was used for derivatograph analysis. The experimental temperature interval was 25–1000°C. The experiments were made in inert medium using ceramic crucibles at a heating rate of 5°C min^{-1} and sample mass 250 mg. $\alpha–Al_2O_3$ was used as a standard substance.

Results and discussion

Figure 1 and Table 1 show the results from studying the system $CeO_2–SeO_2–H_2O$ at 100°C. The only compound obtained in the whole concentration range of the experiments was anhydrous cerium(IV) selenite $Ce(SeO_3)_2$. The composition of the compound was determined by the Schreinemakers' method after analyzing the washed

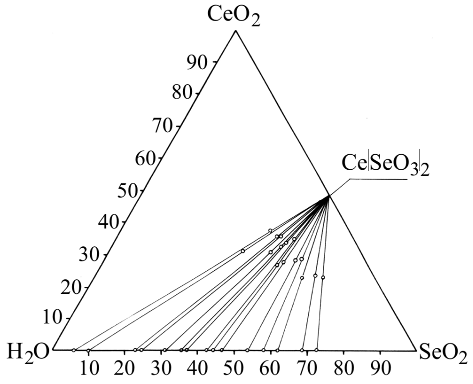

Fig. 1 Solubility isotherm of the system $CeO_2–SeO_2–H_2O$ at 100°C

and dried solid phases. Chemical analysis gave the composition of the solid phase as 43.62 mass% CeO_2 and 56.33 mass% SeO_2. This composition was also confirmed by decomposition of the salt and gravimetric analysis of the residue of CeO_2 and volumetric determination of the sublimate of SeO_2.

Table 1 Solubility isotherm of the system CeO_3–SeO_2–H_2O at 100°C

No.	Liquid phase/mass%		Solid phase/mass%		Formula composition
	CeO_2	SeO_2	CeO_2	SeO_2	
1	$5.20\cdot10^{-3}$	1.52	37.00	47.00	$Ce(SeO_3)_2$
2	$5.00\cdot10^{-3}$	6.13	38.11	49.62	$Ce(SeO_3)_2$
3	$4.80\cdot10^{-3}$	10.10	30.36	41.50	$Ce(SeO_3)_2$
4	$5.50\cdot10^{-3}$	22.80	32.00	47.01	$Ce(SeO_3)_2$
5	$4.60\cdot10^{-3}$	25.48	32.01	48.23	$Ce(SeO_3)_2$
6	$4.20\cdot10^{-3}$	31.37	31.37	48.50	$Ce(SeO_3)_2$
7	$4.20\cdot10^{-3}$	35.65	32.84	51.02	$Ce(SeO_3)_2$
8	$4.10\cdot10^{-3}$	37.37	33.09	51.60	$Ce(SeO_3)_2$
9	$3.90\cdot10^{-3}$	42.78	35.25	53.07	$Ce(SeO_3)_2$
10	$3.70\cdot10^{-3}$	44.08	27.40	51.63	$Ce(SeO_3)_2$
11	$3.70\cdot10^{-3}$	46.94	28.34	52.75	$Ce(SeO_3)_2$
12	$3.80\cdot10^{-3}$	54.45	28.78	55.51	$Ce(SeO_3)_2$
13	$3.70\cdot10^{-3}$	58.18	29.37	56.30	$Ce(SeO_3)_2$
14	$3.40\cdot10^{-3}$	62.20	23.60	59.03	$Ce(SeO_3)_2$
15	$3.10\cdot10^{-3}$	69.03	24.01	63.93	$Ce(SeO_3)_2$
16	$3.00\cdot10^{-3}$	72.84	23.87	63.75	$Ce(SeO_3)_2$

The presence of only one compound in the system CeO_2–SeO_2–H_2O at 100°C was confirmed by the results from X–ray phase analysis. It should be noted that acid salts were not obtained at 250°C by the authors [6] in 1910 and by Markovski and Safina [7] in 1968. In this respect, Ce(IV) is similar to Sn(IV), for which no hydrogen selenites were obtained at 100 and 250°C, either [12].

Figure 2 gives the simultaneous T, TG and DTA curves of $Ce(SO_3)_2$. There are a number of endothermal peaks on it due to liberation of adsorption water and decomposition of the selenite. The slight endothermal peaks at 120, 180, 260 and 360°C are associated with liberation of adsorption water. As we have observed it many times, liberation of this water is accompanied by partial high-temperature hydrolysis and liberation of CeO_2 in a gaseous form. This can explain the loss of 7.24 mass% of the initial sample. Further on, thermal decomposition takes place in two phases: at 550, 640 and 700°C, passing through a stage at which oxoselenite $CeO_2\cdot SeO_2$ is formed. The highest temperature at which the sample was heated was 900°C but complete decomposition did not take place,

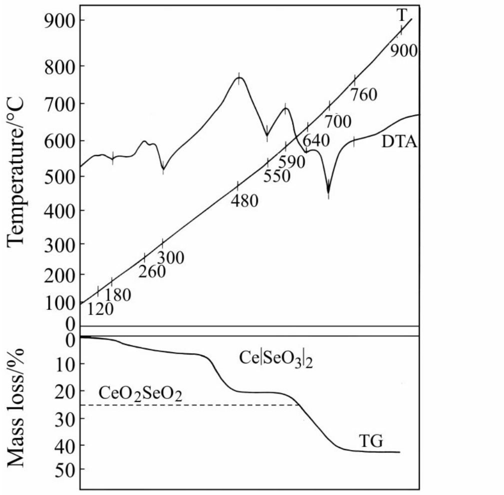

Fig. 2 Simultaneous T, TG and DTA curves of $Ce(SeO_3)_2$

and CeO_2 was not formed. This is characteristic of other selenites and hydrogen selenites of the rare earth's and it was described by other authors, too [13]. Complete liberation of SeO_2 is achieved after continued heating of the sample at 1100–1200°C. These conclusions were made both on the basis of thermogravimetric analysis data and by chemical and X-ray phase analyses.

Table 2 Solubility isotherm of the system Ce_2O_3–SeO_2–H_2O at 100°C

No.	Liquid phase/mass%		Solid phase/mass%		Formula composition
	Ce_2O_3	SeO_2	Ce_2O_3	SeO_2	
1	$1.10\cdot10^{-2}$	1.52	45.60	48.80	$Ce_2(SeO_3)_3$
2	$1.20\cdot10^{-2}$	6.42	44.58	46.90	$Ce_2(SeO_3)_3$
3	$2.10\cdot10^{-2}$	9.24	43.08	46.12	$Ce_2(SeO_3)_3$
4	$2.10\cdot10^{-2}$	15.25	40.21	44.87	$Ce_2(SeO_3)_3$
5	$3.10\cdot10^{-2}$	15.25	40.20	54.50	$CeH(SeO_3)_2$
6	$3.50\cdot10^{-2}$	16.17	40.23	55.13	$CeH(SeO_3)_2$
7	$3.60\cdot10^{-2}$	21.13	37.93	53.08	$CeH(SeO_3)_2$
8	$4.00\cdot10^{-2}$	29.39	38.23	53.20	$CeH(SeO_3)_2$
9	$4.10\cdot10^{-2}$	33.05	41.00	55.25	$CeH(SeO_3)_2$
10	$4.40\cdot10^{-2}$	44.91	30.82	52.50	$CeH(SeO_3)_2$
11	$4.70\cdot10^{-2}$	50.30	31.30	54.60	$CeH(SeO_3)_2$
12	$4.85\cdot10^{-2}$	57.45	30.17	56.08	$CeH(SeO_3)_2$
13	$4.90\cdot10^{-2}$	59.95	29.19	57.14	$CeH(SeO_3)_2$
14	$5.30\cdot10^{-2}$	61.35	32.04	56.95	$CeH(SeO_3)_2$

Figure 3 and Table 2 show the results from studying the system Ce_2O_3–SeO_2–H_2O at 100°C. Two salts were formed in the system. In the concentration range 1.52–15.25 mass% of SeO_2 in the liquid phase, $Ce_2(SeO_3)_3$ was formed. Hydrogen salt $CeH(SeO_3)_2$ was formed in the interval 15.25–61.35 mass% of SeO_2 in the liquid phase. The phase obtained were identified by the Schreinemakers' method and also by other methods of physicochemical analysis.

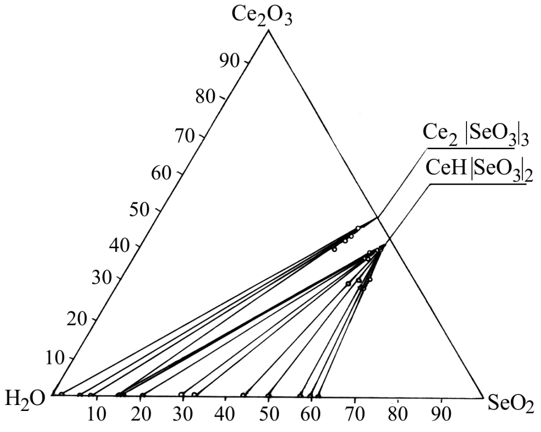

Fig. 3 Solubility isotherm of the system Ce_2O_3–SeO_2–H_2O at 100°C

Figure 4 presents the simultaneous T, TG and DTA curves of $Ce_2(SeO_3)_3$. The compound starts liberating adsorption water at 230°C, but visible decomposition begins at 605°C. The endothermal peak in the temperature interval 605–810°C consists of three superposed endothermal peaks, which form the total endothermal peak. In

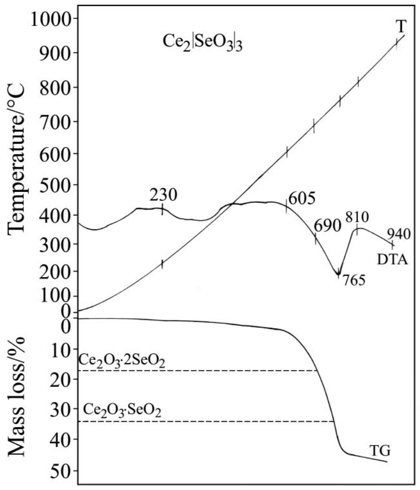

Fig. 4 Simultaneous T, TG and DTA curves of $Ce_2(SeO_3)_3$

the temperature range 605–690°C, the selenite loses 1 mol of SeO_2 and turns into $Ce_2O_3 \cdot 2SeO_2$. This transformation is confirmed by the mass change of the selenite from 16.90 mass% against 16.78 mass% calculated from the TG curve. $Ce_2O_3 \cdot 2SeO_2$ loses one mole of SeO_2 in the temperature range 690–765°C and turns into $(CeO)_2SeO_3$ or $Ce_2O_3 \cdot SeO_2$. The mass loss due to that transformation is 33.85 mass% (theoretical calculation is 33.56 mass%). The selenite was heated at 940°C but complete decomposition transforming it into Ce_2O_3 did not take place.

Figure 5 shows the simultaneous T, TG and DTA curves of $CeH(SeO_3)_2$ ($Ce_2(SeO_3)_3 \cdot H_2SeO_3$). The compound is thermally stable at 400°C. In the temperature range 400–740°C, the selenite loses 1 mole of constitutional water and turns into cerium tetraselenite $Ce_2Se_4O_{11}$ or $Ce_2(SeO_3)_3 \cdot SeO_2$. The mass loss is 3.6 mass% (theoretical calculation is 2.8 mass%). At 740–820°C, tetraselenite loses 1 mol of SeO_2, and $Ce_2(SeO_3)_3$ is obtained. The mass loss is 19.40 mass% against 18.32 mass% calculated theoretically. In the temperature interval 820–860°C, another mole of SeO_2 is liberated, and a base salt with composition $Ce_2O_3 \cdot 2SeO_2$ is formed. The mass loss is 30.40 mass% (theoretical calculation for the corresponding transition is 30.36 mass%). In the temperature range 860–920°C, decomposition takes place accompanied by liberation of another mole of SeO_2 and the selenite turns into $Ce_2O_3 \cdot SeO_2$. The mass loss is 43.21 mass% (theoretical calculation is 44.40 mass%). Decomposition of $Ce_2O_3 \cdot SeO_2$ to Ce_2O_3 is not complete at 1000°C, which is the highest temperature at which the selenite was heated. The mass loss at 1000°C is 54.8 mass% (theoretical calculation for complete decomposition and transition of the selenite into an oxide is 58.45 mass%). The results from chemical analysis of samples heated at the corresponding temperature and losing equivalent mass during heating are a confirmation of the above schemes of thermal decomposition. This paper represents continuation of our investigation on the three-component systems of the type Ln_2O_3–SeO_2–H_2O [14–16]

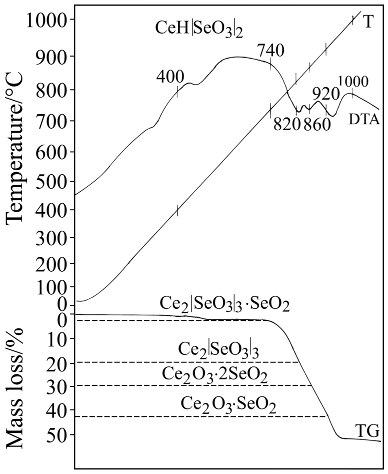

Fig. 5 Simultaneous T, TG and DTA curves of $CeH(SeO_3)_2$

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