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A STUDY OF THE SYSTEM $CdO–SeO_2–H_2O$ AT 25 AND 100°C

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Abstract

The solubility of the system $CdO–SeO_2–H_2O$ was studied at 25 and 100°C. The fields of crystallization of α-$CdSeO_3$, $3CdSeO_3{\cdot}H_2SeO_3$ and $CdSeO_3{\cdot}SeO_2$ were established at 25°C. At 100°C crystallize α-$CdSeO_3$, $3CdSeO_3{\cdot}SeO_2$, $2CdSeO_3{\cdot}SeO_2$ and $CdSeO_3{\cdot}SeO_2$. The compounds obtained were identified by means of chemical, X-ray and crystal-optical analysis. The mechanism of thermal dissociation of α-$CdSeO_3$, $3CdSeO_3{\cdot}H_2SeO_3$ and $CdSeO_3{\cdot}SeO_2$ was studied.

Keywords: cadmium selenites, phase transformations, solubility isotherm, thermal dissociation

Introduction

Literature data concerning the synthesis, composition and properties of cadmium selenites are rather scarce. Markovskiy and Sapozhnikov [1] described the synthesis of $CdSeO_3$ by an interaction between solutions of cadmium sulfate or chloride and sodium, potassium or ammonium selenite in stoichiometric ratios. Varma and Kruschu [2] reported that they have synthesized $CdSeO_3{\cdot}2.5H_2O$. There are also considerable discrepancies in the composition of acid salts. Nilson gave their composition as $3CdSeO_3{\cdot}H_2SeO_3$, $2CdSeO_3{\cdot}H_2SeO_3$ and $CdSeO_3{\cdot}3H_2O$ [3], Boutzoreano suggested $2CdSeO_3{\cdot}H_2SeO_3$ [4], and according to Wohler the composition was $2CdSeO_3{\cdot}H_2SeO_3{\cdot}H_2O$ [5]. The cadmium selenites mentioned were synthesized at fixed concentrations of the initial compounds without determining the concentration interval of crystallization and their behaviour at heating. The existence of other cadmium selenites has not been discussed so far, either. Therefore, a study of the phase equilibrium in the system $CdO–SeO_2–H_2O$ at 25 and 100°C and the thermolysis mechanism of the compounds obtained was carried out.

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Experimental

Sample preparation

The experimental technique and procedure were described by Ojkova and Gospodinov [6]. The initial reagents were pure-for-analysis CdO and SeO$_2$. Studying the system at 25°C, the samples were thermostated in thermostatic glasses with continuously circulating water through them coming from an ultrathermostat. At 100°C, the samples were placed in glass ampules and were thermostated in an air thermostat. In both cases the accuracy of the temperature was ±0.1°C.

Methods

After equilibrium was reached, the liquid and solid phases were separated at the experimental temperature and were analysed chemically. Some solid phases were also subjected to X-ray phase, crystal-optical and thermal analyses. The concentration of Cd^{2+} was determined by inversely complexometrical titration using an eriochrom black T indicator [7]. The selenite ions were determined iodometrically and gravimetrically as elementary selenium [8]. X-ray phase analysis was carried out on a ‘Dron-2’ apparatus with Cu anode and K_α-emission and Ni filter for β-emission. Thermal analyses were made with a MOM OD-102 derivatograph. The operating conditions were: temperature range up to 1000°C; heating rate 10°C min^{-1}; sample mass 200–300 mg; thermocouple Pt/PtRh; standard substance α-Al$_2$O$_3$; in a medium of chemically pure nitrogen, using metalloceramic crucibles. A ‘Dokuval’ optical microscope was used for crystal-optical analyses.

Results and discussion

The experimental data of the phase equilibrium in the system CdO–SeO$_2$–H$_2$O at 25°C are given in Table 1 and Fig. 1.

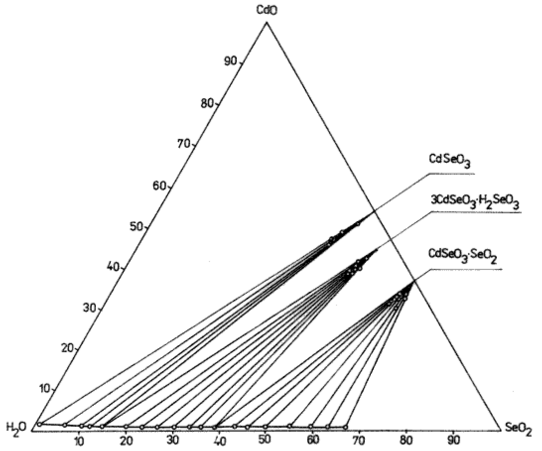

Fig. 1 Solubility isotherm of the system CdO–SeO$_2$–H$_2$O at 25°C

Table 1 Solubility of the system CdO–SeO_2–H_2O at 25°C

No.	Liquid phase/mass%		Solid phase/mass%		Formula composition of solid phase
	CdO	SeO_2	CdO	SeO_2	
1	1.65	0.73	49.50	41.51	α-$CdSeO_3$
2	1.60	6.15	47.60	40.77	α-$CdSeO_3$
3	1.37	10.02	51.15	44.45	α-$CdSeO_3$
4	1.30	11.87	46.10	40.62	α-$CdSeO_3$
5	1.12	14.35	47.04	41.60	α-$CdSeO_3$
6	1.12	14.35	41.95	49.07	$3CdSeO_3 \cdot H_2SeO_3$
7	1.49	19.48	40.02	48.43	$3CdSeO_3 \cdot H_2SeO_3$
8	1.13	23.20	41.25	49.41	$3CdSeO_3 \cdot H_2SeO_3$
9	1.12	26.51	39.03	48.85	$3CdSeO_3 \cdot H_2SeO_3$
10	1.10	29.93	40.01	49.48	$3CdSeO_3 \cdot H_2SeO_3$
11	1.08	33.26	39.10	49.57	$3CdSeO_3 \cdot H_2SeO_3$
12	0.99	35.97	42.24	51.05	$3CdSeO_3 \cdot H_2SeO_3$
13	0.95	39.03	40.04	50.98	$3CdSeO_3 \cdot H_2SeO_3$
14	0.95	39.03	34.63	61.24	$CdSeO_3 \cdot SeO_2$
15	1.10	43.02	33.75	61.50	$CdSeO_3 \cdot SeO_2$
16	0.90	46.10	31.45	61.02	$CdSeO_3 \cdot SeO_2$
17	0.89	49.75	32.70	61.48	$CdSeO_3 \cdot SeO_2$
18	0.80	55.01	32.65	62.41	$CdSeO_3 \cdot SeO_2$
19	0.61	59.96	30.87	62.60	$CdSeO_3 \cdot SeO_2$
20	0.52	63.45	34.01	62.95	$CdSeO_3 \cdot SeO_2$
21	0.48	67.36	32.60	63.60	$CdSeO_3 \cdot SeO_2$

The solubility diagram of the system CdO–SeO_2–H_2O at 25°C shows three equilibrium crystallization fields divided by two eutonic points. At a concentration of SeO_2 in the liquid phase up to 14.33 mass%, the resulting solid phase is α-$CdSeO_3$. In the concentration interval 14.33–39.14 mass% SeO_2 in the liquid phase, the composition of the equilibrium solid phase is $3CdSeO_3 \cdot H_2SeO_3$, and in the concentration interval 39.14–67.02 mass% SeO_2 in the liquid phase, the solid phase crystallizes as $CdSeO_3 \cdot SeO_2$.

The experimental data of the solubility and the phase equilibrium of the system CdO–SeO_2–H_2O at 100°C are given in Table 2 and Fig. 2.

The solubility diagram of the system CdO–SeO_2–H_2O at 100°C shows that four crystallization fields are formed: α-$CdSeO_3$ and the polyselenites $3CdSeO_3 \cdot SeO_2$, $2CdSeO_3 \cdot SeO_2$ and $CdSeO_3 \cdot SeO_2$. It should be noted that the crystallization field of α-$CdSeO_3$ increases at 100°C, the acid salt $3CdSeO_3 \cdot H_2SeO_3$ does not crystallize, and two new polyselenites, tetraselenite $3CdSeO_3{\cdot}SeO_2$ and triselenite $2CdSeO_3{\cdot}SeO_2$, are formed.

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

No.	Liquid phase/mass%		Solid phase/mass%		Formula composition of solid phase
	CdO	SeO_2	CdO	SeO_2	
1	0.25	1.55	48.39	41.75	α-$CdSeO_3$
2	0.38	3.28	44.64	39.62	α-$CdSeO_3$
3	0.50	5.64	51.90	44.92	α-$CdSeO_3$
4	0.16	10.20	45.58	40.51	α-$CdSeO_3$
5	0.10	23.16	45.52	43.10	α-$CdSeO_3$
6	0.57	30.25	45.63	52.74	$3CdSeO_3{\cdot}SeO_2$
7	0.75	35.75	45.27	53.83	$3CdSeO_3{\cdot}SeO_2$
8	0.76	39.82	38.71	54.86	$3CdSeO_3{\cdot}SeO_2$
9	0.78	45.44	36.91	54.38	$3CdSeO_3{\cdot}SeO_2$
10	0.76	51.78	28.38	54.99	$3CdSeO_3{\cdot}SeO_2$
11	0.78	53.62	38.44	56.13	$3CdSeO_3{\cdot}SeO_2$
12	0.82	60.86	32.88	63.01	$3CdSeO_3{\cdot}SeO_2$
13	0.53	65.08	33.41	63.66	$3CdSeO_3{\cdot}SeO_2$
14	0.65	71.35	32.93	64.22	$3CdSeO_3{\cdot}SeO_2$
15	0.48	83.62	17.31	73.85	$3CdSeO_3{\cdot}SeO_2$

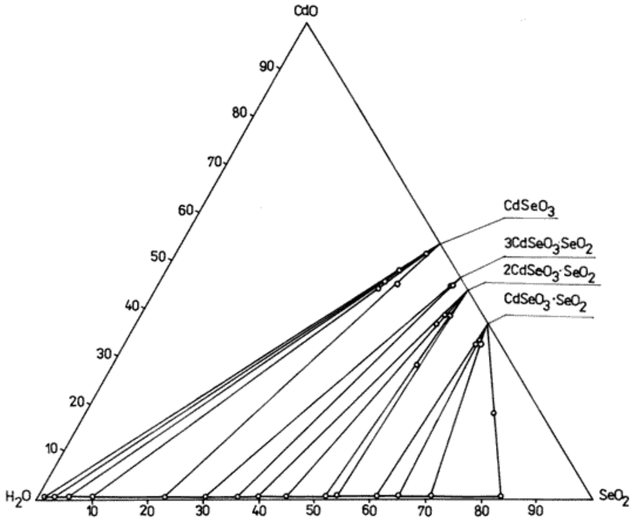

Fig. 2 Solubility isotherm of the system CdO–SeO_2–H_2O at 100°C

The identity of the solid phases obtained was also confirmed by crystal-optical and X-ray phase analyses.

The data of the existence of $2CdSeO_3 \cdot H_2SeO_3$ and $2CdSeO_3 \cdot 3H_2O$ reported by Nilson were confirmed at neither experimental temperatures. The densities of three selenites were determined picnometrically in ethylalcohol as d_4^{20}=5.15±0.01 g cm^{-3} for α-$CdSeO_3$; d_4^{20}=4.80±0.01 g cm^{-3} for $3CdSeO_3 \cdot H_2SeO_3$ and d_4^{20}=5.12±0.01 g cm^{-3} for $3CdSeO_3 \cdot SeO_2$.

Figure 3 shows the DTG and TG curves of acid cadmium selenite, $CdSeO_3 \cdot H_2SeO_3$. The endothermal peak in the temperature interval 230–320°C corresponds to the loss of 1 mol constitutional water and the transformation of selenite into tetraselenite with composition $3CdSeO_3 \cdot SeO_2$. The next endothermal peak in the temperature interval 320–435°C is assigned to the liberation of one mol SeO_2 and the transformation of tetraselenite into normal selenite, $CdSeO_3$. The endothermal peak at 650°C corresponds to polymorphous transition of $CdSeO_3$ which is confirmed by the lack of any change in the sample mass at the temperature of the endothermal peak and also by the difference in the X-ray patterns of $CdSeO_3$ heated at 600 and 660°C. Besides, melting of the sample is not established at 650°C. In the temperature interval 660–1000°C $CdSeO_3$ decomposes with liberation of one mol SeO_2 and cadmium selenite transforms into cadmium oxide. The identity of the solid phases was confirmed by X-ray analysis.

Figure 4 shows the TG and DTA curves of diselenite $CdSe_2O_5$. It can be seen that its thermal decomposition takes place in two stages. The endothermal peak in the tempera-

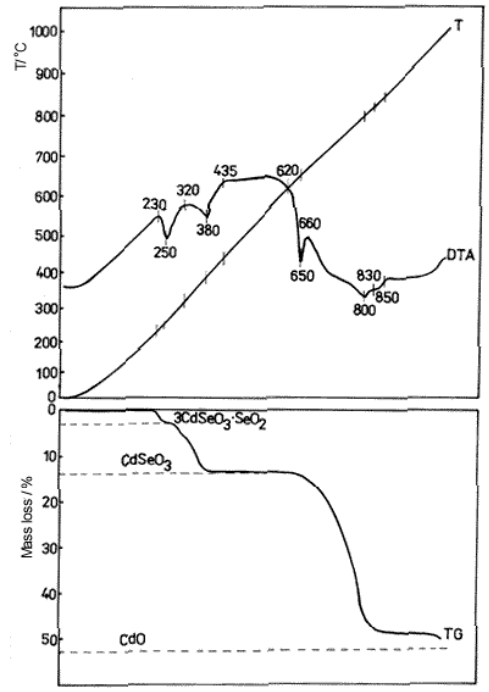

Fig. 3 TG and DTA curves of $3CdSeO_3 \cdot H_2SeO_3$

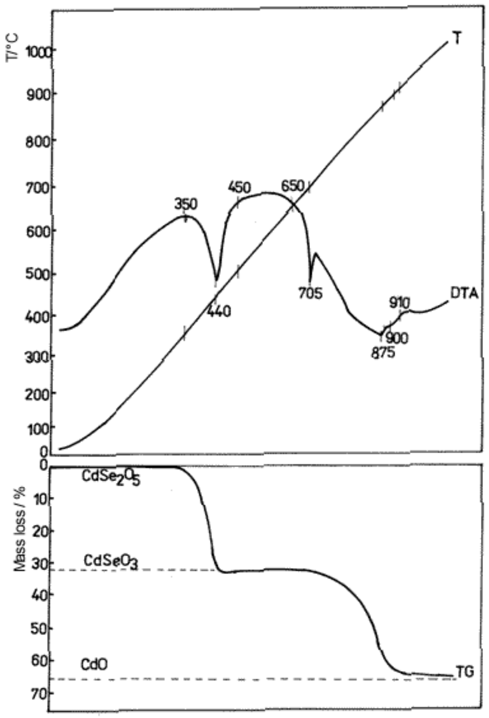

Fig. 4 Thermoanalytical curves of $CdSeO_3 \cdot SeO_2$

ture interval 350–435°C corresponds to the loss of one mol SeO_2 and the transformation of diselenite into normal selenite. In the temperature interval 660–1000°C $CdSeO_3$ decomposes with liberation of one mol SeO_2 and cadmium selenite transforms into CdO. The endothermal peak at 705°C is assigned to the melting of normal cadmium selenite.

Because of the fast heating up to 1000°C, $CdSeO_3 \cdot H_2SeO_3$ and $CdSe_2O_5$ did not decompose to an oxide completely. The presence of a small amount of $CdSeO_3$ together with the main decomposition product, CdO, was proved by X-ray analysis.

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