PHYSICOCHEMICAL STUDY ON SELENITES OF THE THREE-COMPONENT SYSTEM Yb_2O_3–SeO_2–H_2O

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Abstract

The solubility isotherm of the three-component system Yb_2O_3–SeO_2–H_2O at 100°C was studied. There are two fields of crystallization in the solubility diagram at this temperature – a small one of $Yb_2(SeO_3)_3 \cdot 4H_2O$ and a large one of $YbH(SeO_3)_2 \cdot 2H_2O$. These compounds were identified by the Schreinemakers' method, and by chemical and X-ray analyses as well. Simultaneous TG and DTA curves of the two compounds obtained were made and the mechanism of the thermal decomposition was described.

Introduction

The ytterbium selenites can serve as initial substances for obtaining selenides and oxyselenides having valuable photoconductive and superconductive properties [1].

The data of ytterbium selenites dated back to 1970s and 1980s. In work [2], on the change of pH of the settling system (use of $YbCl_3$ and Na_2SeO_3) the formation of normal ytterbium selenite of $Yb_2(SeO_3)_3 \cdot 4H_2O$ composition is ascertained. By X-ray phase analysis it is proved that it is X-ray amorphous. In [3] is described the obtaining of a selenite by interaction between ammoniac solution of $YbCl_3$ and selenium acid to which $YbH(SeO_3)_2 \cdot 2.5H_2O$ of crystal state is attributed. The crystal system and crystal lattice parameters of this compound are determined.

Systematic study of the triple system has not been carried out; that is why the mode and the field of compounds' existence are not known.

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Experimental

Preparation

Twenty one samples of ytterbium oxides and selenium acid, having purity not less than max. 99.99% were charged. Charging became as in glass ampoules ('Rasotherm') 2 g Yb_2O_3 were added to 50 mL solution of selenium acid of rising concentration from 0 to 85%. The ampoules were closed and placed for conditioning in an air thermostat at a temperature of 100±0.5°C. To determine the time for reaching equilibrium, except for them, ampoules of the same selenium acid compositions were charged. These were periodically opened in order to observe the composition of the solid and liquid phases. As an indication for reaching the equilibrium serves the criterion that their composition does not change any more. As a criterion for ascertaining the gain of crystallographic equilibrium serves the termination of the change on the reflex of the solid phases in X-ray patterns in relation to intensity and interflat distances. After reaching the equilibrium, the liquid and solid phases were separated by filtration through filter G-4 at the test conditions and were subjected to analysis.

Methods

The concentration of the metal ions in the solid phase was determined by complexometric titration using xylenol orange as an indicator [4]. Selenium was determined iodometrically and gravimetrically [5]. The concentration of Yb^{3+} in the liquid phase was determined spectrophotometrically on a Specol-11 apparatus (Karl Zeiss, Germany) [6]. The X-ray phase analysis was carried out on an URD–6 apparatus (Germany), at anode Cu and K_α-emission and a Ni-filter for β-emission. The thermal analysis was effected by OD-102, MOM, Hungary. The operating conditions of the thermal analysis were: 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 discussions

On the basis of the results obtained, the solubility isotherm is plotted, according to the method of Schreinemakers'. From Fig. 1 and Table 1, it is seen that the diagram of solubility of the system Yb_2O_3–SeO_2–H_2O is presented by two fields of crystallization. The first crystallization field (content of SeO_2 in the liquid phase from 0 to 0.87 mass%) is the field of $Yb_2(SeO_3)_3·4H_2O$. In the concentration range from 0.87 to 80.10 mass% SeO_2 in the liquid phase, $YbH(SeO_3)_2·2H_2O$ solid phase is realized. The point of 0.87 mass% SeO_2 and $4.0·10^{-4}$ mass% Yb_2O_3 appears to be eutonic.

The compounds obtained are identified through chemical, X-ray phase and derivatographic analyses also.

On Fig. 2, simultaneous DTA and TG curves of $Yb_2(SeO_3)_3·4H_2O$ are presented. The compound is stable up to 80°C. Within the range 100–215°C a process of crys-
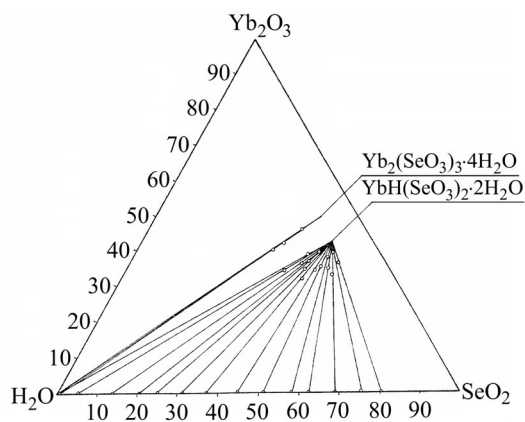
Fig. 1 Solubility isotherm of the system Yb_2O_3–SeO_2–H_2O at 100°C

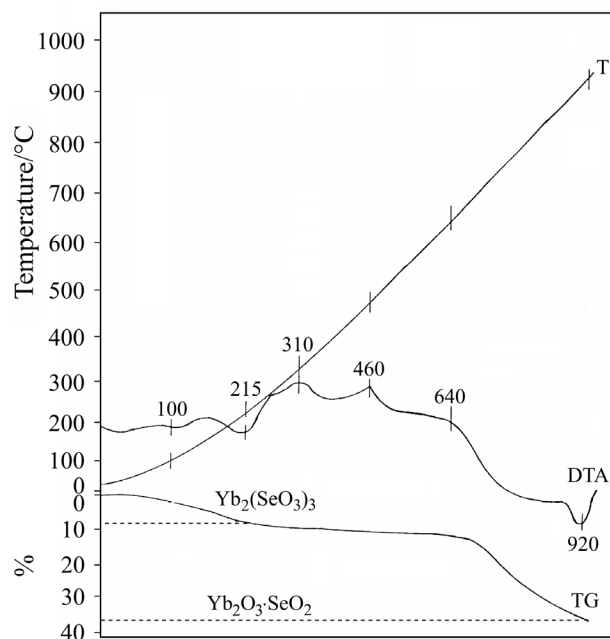**Fig. 2** DTA and TG curves of $Yb_2(SeO_3)_3 \cdot 4H_2O$

tallization water liberation takes place and a normal anhydrous selenite is produced. The mass loss represents 8.98 mass%, at theoretically calculated 9.00 mass%. According to the data of the chemical analysis, samples obtained at these temperature conditions contain: Yb_2O_3 – 54.27 and SeO_2 – 45.84 mass%, at theoretically calculated Yb_2O_3 – 54.21 mass% and SeO_2 – 45.79 mass%. The liberation of the crystallization water leads to obtaining of amorphous anhydrous selenite. X-ray phase analysis appears in confirmation of this. The exothermic effects at 310 and 460°C corre-

spond to partial (at 310°C) and full (at 460°C) crystallization of the amorphous product. $Yb_2(SeO_3)_3$ is stable up to 640°C. After this temperature, by stages, one molecule of SeO_2 liberates and after that two more molecules of SeO_2 and the selenite converts into basic salt with a composition of $Yb_2O_3 \cdot SeO_2$ or $(YbO)_2SeO_3$. The mass loss makes up 35.90 at 36.79 mass% – theoretically calculated. This salt is stable up to 920°C, the temperature, to which the selenite has been heated. The complete selenite decomposition (with liberation of the last SeO_2 molecule) and obtaining of Yb_2O_3 occurs only at temperatures of 1200–1300°C.

Table 1 Solubility isotherm of the system Yb_2O_3 –SeO_2 –H_2O at 100°C

No.	Liquid phase/ mass%		Solid phase/ mass%		Formula composition
	Yb_2O_3	SeO_2	Yb_2O_3	SeO_2	
1	$3.3 \cdot 10^{-4}$	0.17	46.02	35.89	$Yb_2(SeO_3)_3 \cdot 4H_2O$
2	$3.6 \cdot 10^{-4}$	0.40	39.90	33.27	$Yb_2(SeO_3)_3 \cdot 4H_2O$
3	$4.0 \cdot 10^{-4}$	0.87	42.12	35.46	$Yb_2(SeO_3)_3 \cdot 4H_2O$
4	$5.2 \cdot 10^{-4}$	0.87	38.49	42.52	$YbH(SeO_3)_2 \cdot 2H_2O$
5	$7.0 \cdot 10^{-4}$	5.61	34.50	39.08	$YbH(SeO_3)_2 \cdot 2H_2O$
6	$7.6 \cdot 10^{-4}$	13.84	36.15	42.40	$YbH(SeO_3)_2 \cdot 2H_2O$
7	$8.5 \cdot 10^{-4}$	20.48	38.76	45.57	$YbH(SeO_3)_2 \cdot 2H_2O$
8	$8.8 \cdot 10^{-4}$	25.63	37.12	43.38	$YbH(SeO_3)_2 \cdot 2H_2O$
9	$9.2 \cdot 10^{-4}$	31.27	34.87	44.10	$YbH(SeO_3)_2 \cdot 2H_2O$
10	$9.6 \cdot 10^{-4}$	37.20	32.08	44.90	$YbH(SeO_3)_2 \cdot 2H_2O$
11	$1.0 \cdot 10^{-3}$	45.12	34.70	47.05	$YbH(SeO_3)_2 \cdot 2H_2O$
12	$1.1 \cdot 10^{-3}$	51.30	35.69	48.12	$YbH(SeO_3)_2 \cdot 2H_2O$
13	$1.2 \cdot 10^{-3}$	58.16	37.90	48.56	$YbH(SeO_3)_2 \cdot 2H_2O$
14	$1.3 \cdot 10^{-3}$	63.15	35.22	50.05	$YbH(SeO_3)_2 \cdot 2H_2O$
15	$1.3 \cdot 10^{-3}$	69.22	32.53	52.48	$YbH(SeO_3)_2 \cdot 2H_2O$
16	$1.4 \cdot 10^{-3}$	75.34	38.27	49.28	$YbH(SeO_3)_2 \cdot 2H_2O$
17	$1.5 \cdot 10^{-3}$	80.10	36.50	52.60	$YbH(SeO_3)_2 \cdot 2H_2O$

The thermal decomposition of $YbH(SeO_3)_2 \cdot 2H_2O$ is shown in Fig. 3 and also runs by stages. The well manifested endothermic effect at 200°C corresponds to an intensive dehydration of the hydrogen selenite within the temperature range 120–200°C as crystallization water is liberated and anhydrous salt of $Yb_2(SeO_3)_3 \cdot H_2SeO_3$ is obtained. The mass loss during this conversion is 7.84 mass% in comparison with the theoretically calculated – 7.76%. In the narrow temperature range of 200–240°C the anhydrous hydrogen selenite liberates 1 mol constitutional water and converts itself into tetraselenite with a composition of $Yb_2(SeO_3)_3 \cdot SeO_2$ or $Yb_2Se_4O_{11}$. The mass loss represents 10.00 mass%

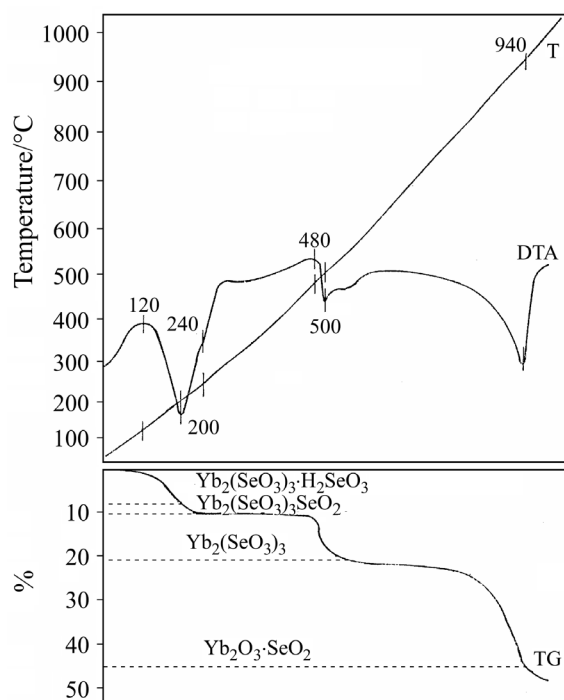**Fig. 3** DTA and TG curves of $YbH(SeO_3)_2 \cdot 2H_2O$

in comparison with 7.70 mass% theoretically calculated. Tetraselenite is thermostable up to 480°C. In the temperature range of 480–500°C a SeO_2 molecule is separated and $Yb_2(SeO_3)_3$ is obtained. The mass loss, in relation to TG curve, corresponds to 21.70 mass%, in comparison with 21.66% theoretically calculated. The chemical analysis of the sample obtained at these conditions shows content of Y_2O_3–54.34 mass% and SeO_2–45.68 mass%, in comparison with Y_2O_3–54.21 mass% and SeO_2–45.79 mass% theoretically calculated. It is seen from the TG curve that the formation of SeO_2 runs fluently. One more molecule of SeO_2 is separated and the anhydrous selenite transforms into a basic salt with a composition of $Yb_2O_3 \cdot 2SeO_2$, from which the next SeO_2 molecule separates and $Yb_2O_3 \cdot SeO_2$ is obtained. The process ends at 940°C. The mass loss is 45.00 mass%, in comparison with the theoretically calculated 45.57%. The liberation of the last SeO_2 molecule runs at a higher temperature and lower speed. At a temperature of 960°C, by which the sample was heated in accordance with the TG curve, the mass loss is only 50.00 mass% *vs.* 57.53 mass% theoretically calculated. The full thermal dissociation is practically carried out at temperatures of 1200–1300°C.

The phases obtained during the thermal analysis were proved not only thermogravimetrically but through chemical and X-ray phase analyses also on samples after their formation in pure mode at modeling DTA conditions.

Conclusions

The solubility isotherm of the system $Yb_2O_3 - SeO_2 - H_2O$ at 100°C was studied. The equilibrium phases of the system were identified by the Schreinemakers' method and by chemical and X-ray phase analyses after they were isolated in the pure state.

Derivatograph analysis of the compounds obtained was made. The mechanism of thermal analysis was determined.

This paper represents continuation of our investigation on the three-component systems of the type Ln_2O_3–SeO_2–H_2O [7–10].

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