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PHASES IN THE SYSTEM Tb_2O_3-SeO_2-H_2O AT 100°C AND THEIR PHYSICOCHEMICAL STUDY

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The solubility isotherm of the system Tb_2O_3–SeO_2–H_2O at 100ºC 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: *phase state, solubility isotherm, terbium selenites, thermal dissociation, X-ray*

Introductions

From literature data two terbium selenites are known: $Tb_2(SeO_3)_3{\cdot}4H_2O$ [1] and $TbH(SeO_3)_2{\cdot}2.5H_2O$ [2]. The first one was obtained by systematic studying the interaction of $TbCl_3$ and Na_2SeO_3 by the methods of potentiometric and conductometric titration. The data from X-ray phase analysis show that the compound is amorphous.

The second compound was obtained by the interaction of aqueous solutions of $TbCl_3$ in ammonia with H_2SeO_3. It is crystalline. According to X-ray analysis data, the compound crystallises in a monoclinic system, space group $P2_1$ or $P2_{1m}$.

Other authors [3] obtained $Tb_2(SeO_3)_3$ and Tb_2SeO_5 and determined the parameters of their crystal lattice.

Experimental

High-purity (99.99 mass%) metal oxides and SeO_2 obtained by the authors were used to prepare the system. Spectroscopic analysis data show that selenium dioxide has purity rate of B–4 (99.9999%).

In order to study the diagram of the phase states of the system Tb_2O_3–SeO_2–H_2O, 25 samples were prepared by adding 2 g of Tb_2O_3 to 50 mL of an aqueous solution of H_2SeO_3 with increasing concentration from 0 to 80 mass%. The samples were sealed in glass ampules.

To determine the time needed to reach equilibrium in the system, 10 more samples with the same chemical composition were prepared. Periodically, every 10 days, one ampule was opened each time and the sample was subjected to chemical and X-ray phase analysis. When the composition of the liquid and solid phases no longer changed, it was considered that chemical equilibrium was reached. X-ray data concerning the solid phases were used to study crystallographic equilibrium. When the intensities and the interplanar distances of the peaks no longer changed, equilibrium was reached. Then, the ampules were opened, and the liquid and solid phases were separated by filtering through a G4 filter.

Chemical analysis for metal ions was made complexometrically [4]. Selenite ions were analysed iodometrically and gravimetrically as elementary selenite [5]. The concentration of Tb^{3+} ions in the liquid phase was determined photometrically on a Spekol-11 apparatus (Germany) [6].

X-ray phase analysis was carried out on a URD-6 apparatus (Germany) at Cu anode for K_α emission and a nickel filter for β emission. X-ray analysis was made on a CAD-4 automatic diffractometer (ENPAF-NONIUS, Holland). An OD-102 derivatograph (MOM, Hungary) was used for thermal analysis. The heating interval was from 25 to 1000°C at a heating rate 5°C min^{-1} in an inert atmosphere. Ceramic crucibles and α-Al_2O_3 as a reference standard were used.

Results and discussion

Table 1 and Fig. 1 show that two, compounds, $Tb_2(SeO_3)_3{\cdot}4H_2O$ and $TbH(SeO_3)_2{\cdot}2H_2O$, are formed in the system Tb_2O_3–SeO_2–H_2O at 100°C. At low concentrations of SeO_2 in the liquid phase (0.06–1.02 mass%), the compound $Tb_2(SeO_3)_3{\cdot}4H_2O$ is formed with solubility $1.2{\cdot}10^{-3}$ mass% Tb_2O_3 in the liquid phase. Increasing the concentration of selenious acid in the liquid phase, the solubility of the

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Table1 Solubility isotherm of the system Tb_2O_3–SeO_2–H_2O at 100°C

No	Liquid phase/mass%		Solid phase/mass%		Formula composition
	Tb_2O_3	SeO_2	Tb_2O_3	SeO_2	
1	$0.5\cdot10^{-3}$	0.17	34.31	31.02	$Tb_2(SeO_3)_3\cdot4H_2O$
2	$0.5\cdot10^{-3}$	0.60	37.52	33.67	$Tb_2(SeO_3)_3\cdot4H_2O$
3	$0.8\cdot10^{-3}$	1.02	39.04	37.05	$Tb_2(SeO_3)_3\cdot4H_2O$
4	$0.9\cdot10^{-3}$	1.02	34.85	42.51	$TbH(SeO_3)_2\cdot2H_2O$
5	$1.2\cdot10^{-3}$	6.11	36.22	45.47	$TbH(SeO_3)_2\cdot2H_2O$
6	$1.5\cdot10^{-3}$	10.20	38.21	47.25	$TbH(SeO_3)_2\cdot2H_2O$
7	$2.2\cdot10^{-3}$	20.97	33.29	44.50	$TbH(SeO_3)_2\cdot2H_2O$
8	$2.5\cdot10^{-3}$	31.50	37.40	48.21	$TbH(SeO_3)_2\cdot2H_2O$
9	$3.0\cdot10^{-3}$	42.90	28.65	47.12	$TbH(SeO_3)_2\cdot2H_2O$
10	$3.3\cdot10^{-3}$	49.67	35.12	49.75	$TbH(SeO_3)_2\cdot2H_2O$
11	$3.8\cdot10^{-3}$	53.29	31.17	50.20	$TbH(SeO_3)_2\cdot2H_2O$
12	$4.8\cdot10^{-3}$	60.63	30.96	52.44	$TbH(SeO_3)_2\cdot2H_2O$
13	$5.2\cdot10^{-3}$	65.34	33.08	52.30	$TbH(SeO_3)_2\cdot2H_2O$
14	$6.0\cdot10^{-3}$	70.15	30.09	55.12	$TbH(SeO_3)_2\cdot2H_2O$

compound increases insignificantly. At a concentration interval 1.02–73.85 mass% SeO_2, the Schreinemakers intersection point corresponds to a concentration of Tb_2O_3 40.66 mass%, SeO_2– 49.33 mass%, and H_2O–10.00 mass%. Therefore, at this concentration field the solid phase is the compound $TbH(SeO_3)_2\cdot2H_2O$. Its solubility in the mother solution is $5.0.10^{-3}$ mass%.

Figure 2 gives the derivatogram of $Tb_2(SeO_3)_3\cdot4H_2O$. The compound is thermally stable at 80°C. At a higher temperature, dehydration starts accompanied by liberation of crystallisation water. The highly amorphous product easily liberates two more moles of SeO_2 and at 320°C the compound is completely transformed into $Tb_2O_3\cdot SeO_2$/$(TbO)_2SeO_3$/. Gravimetric analysis data obtained at 670°C show that the mass loss is 37.97 mass% (theoretical calculation is 38, 14 mass%). The exothermal peaks at 400 and 690°C correspond to partial and complete

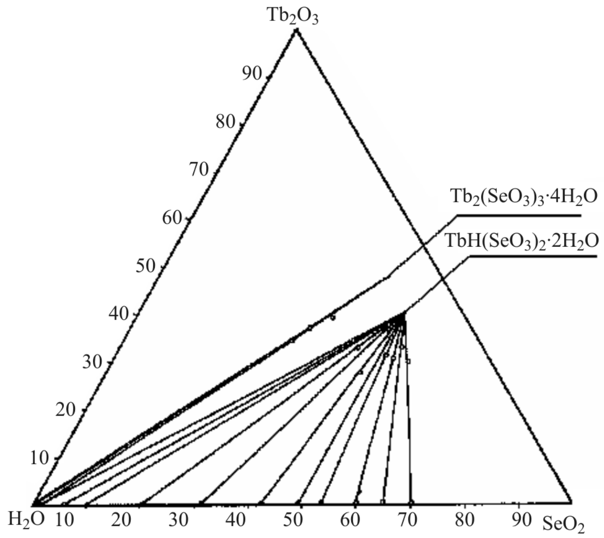

Fig. 1 Solubility isotherm of the system Tb_2O_3–SeO_2–H_2O at 100°C

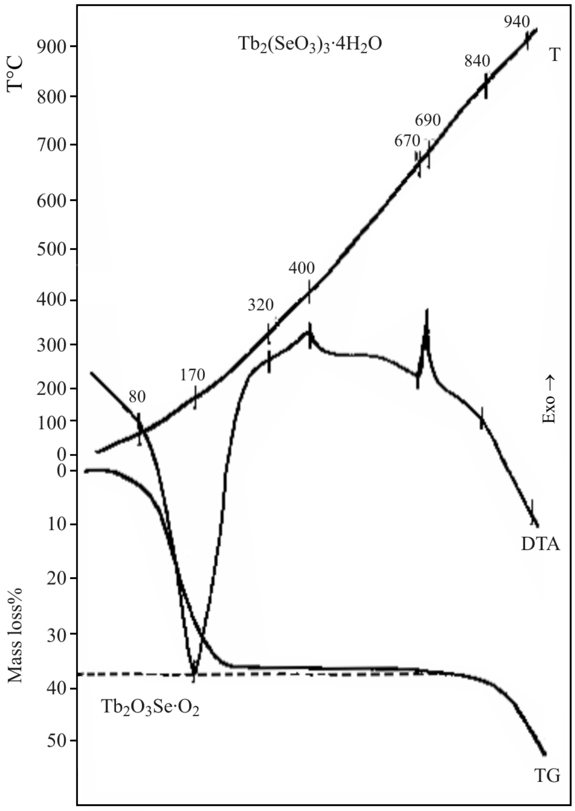

Fig. 2 Derivatogram of $Tb_2(SeO_3)_3\cdot4H_2O$

crystallisation of the amorphous phase at 400 and 690°C, respectively. A confirmation of this interpretation may be the fact that there are no peaks on the X-ray diagram at 400°C. In the temperature interval 400–690°C, partial crystallisation takes place, and X-ray diagram containing well-formed peaks is obtained only at a temperature higher than 690°C. At 840°C the liberation of the last mole of SeO_2 begins, but at 940°C the mass loss is 50.00 mass% against 52.53 mass% calculated theoretically for the complete liberation of SeO_2 and the formation of pure Tb_2O_3.

Figure 3 shows the derivatogram of $TbH(SeO_3)_2{\cdot}2H_2O$. The compound undergoes thermal decomposition by several stages. Dehydration of the crystalhydrate begins at a temperature higher than 80°C, while intensive thermal decomposition takes place in the temperature interval 180–240°C. The salt loses its crystallisation water and turns into $Tb_2(SeO_3)_3{\cdot}H_2SeO_3$. In the temperature interval 240–260°C 1 mole of H_2O is liberated and the compound is transformed into $Tb_2(SeO_3)_3{\cdot}SeO_2$. In the temperature interval 260–380°C it loses 1 mole of SeO_2 and turns into normal terbium selenite $Tb_2(SeO_3)_3$. X-ray phase analysis data show that the resulting compound is amorphous. The exothermal peak at 440°C corresponds to the crystallisation of the amorphous $Tb_2(SeO_3)_3$. In the temperature interval 520–660°C, $Tb_2(SeO_3)_3$ liberates 1 mole of SeO_2 and turns into $Tb_2O_3{\cdot}2SeO_2$. The mass loss is 35.01 mass% (theoretical calculation is 34.67%). In the temperature interval 660–920°C, another mole of SeO_2 is liberated and $Tb_2O_3{\cdot}SeO_2$ is formed. Complete liberation of the last mole of SeO_2 and the formation of Tb_2O_3 did not take place at 960°C, which is the highest temperature at which the selenite was heated.

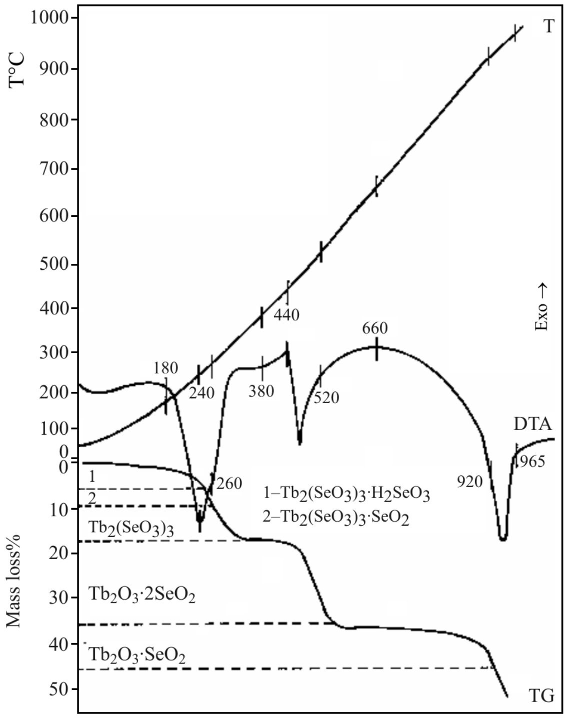

Fig. 3 Derivatogram of $TbH(SeO_3)_2{\cdot}2H_2O$

The presence of different phases of the thermal decomposition of $Tb_2(SeO_3)_3{\cdot}4H_2O$ and $TbH(SeO_3)_2{\cdot}2H_2O$ is proved by X-ray phase analysis of the phases obtained by modelling the conditions of thermal analysis.

The parameters of the crystal lattice of the compounds obtained from aqueous solutions were determined. The parameters of the crystal lattice of the intermediate phases obtained by thermal decomposition of these products were also determined.

The compound $TbH(SeO_3)_2{\cdot}2H_2O$ crystallises into an orthorhombic system, space group $P2_12_12_1$ and parameters: a=6.600 Å; b=6.962 Å; c=16.351 Å; z=4; d_{calc}.=3.977 g cm^{-3}.

$Tb_2(SeO_3)_3$ crystallises into a monoclinic system, space group $P2_1/c$ and parameters: a=17.1318 Å; b=9.8524 Å; c=11.9913 Å; β=106.00; z=4; d_{calc}.=4.771 g cm^{-3}.

$Tb_2Se_4O_{11}$ crystallises into a monoclynic system, space group $P2_1/m$ and parameters: of the elementary cell: a=16.6775 Å; b=11.8607 Å; c=5.2548 Å; β=84.14; z=4; d_{calc}.=5.201 g cm^{-3}.

Tb_2SeO_5 crystallises into an orthorhombic system, space group Imma and parameters: a=18.7484 Å; b=12.9812 Å; c=5.4418 Å; z=8; d_{calc}. = 4.7830 g cm^{-3}.

This paper represents continuation of our investigation on the three-component systems of the type Ln_2O_3–SeO_2–H_2O [7–14].

Conclusions

- The solubility isotherm of the system Tb_2O_3–SeO_2–H_2O at 100°C was studied and drawn.
- The possible compounds obtained in the system under the experimental conditions were separated and identified.
- The thermal decomposition of the compounds was studied and its chemistry was determined.

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