A STUDY OF THE COMPOUNDS PRESENT IN THE THREE-COMPONENT SYSTEM Dy_2O_3–SeO_2–H_2O AT 100°C

G. G. Gospodinov[1] *and M. G. Stancheva*[2]

[1]Assen Zlatarov University, Department of Inorganic Chemistry, Bourgas University of Technology, 8010 Bourgas
[2]Institute of Chemical Technologies and Biotechnologies, 7200 Razgrad, Bulgaria

Abstract

The solubility isotherm of the system Dy_2O_3–SeO_2–H_2O at 100°C was studied and drawn. The selenites present in the system were identified and isolated. A thorough TG, DTG and DTA analysis was made. By modelling the conditions of TG, DTG and DTA analysis, the phases of the thermal decomposition were isolated and identified. The chemistry of the reaction was described.

Keywords: system Dy_2O_3–SeO_2–H_2O, TG- DTG- DTA analysis,

Introduction

Two publications concerned with obtaining and identifying dysprosium selenites appeared in 1967 and 1976. Dysprosium selenite of the composition $Dy_2(SeO_3)_3 \cdot 4H_2O$ was claimed to have been obtained [1]. It was proved by X-ray analysis that the compound is amorphous. According to other authors [2], mixing of an aqueous solution of $DyCl_3$, containing NH_3, with H_2SeO_3 results in $DyH(SeO_3)_2 \cdot 2.5H_2O$. These publications do not provide any data concerning the properties and the region of existence of the compounds obtained.

Experimental

In order to study the system Dy_2O_3–SeO_2–H_2O at 100°C, 25 samples containing Dy_2O_3 and varying concentrations of SeO_2 (0–95 mass%) were prepared. The samples were sealed in glass ampoules and placed in an air thermostat at 100±0.5°C. They were periodically shaken. After equilibrium was attained, the ampoules were opened, the liquid and the solid phases were separated at 100°C and subjected to chemical, X-ray phase and crystallooptical analyses. Chemical analysis was made complexometrically for Dy_2O_3 using xylenol orange as an indicator [3], and iodometrically and gravimetrically for SeO_2 [4]. X-ray phase analysis was carried out on a TURM apparatus (Germany) at Cu anode and K_α emission and a nickel filter

for β emission. TG, DTG and DTA analysis was made on an OD-102 derivatograph (MOM, Hungary). A 'Dokuval' optical microscope (Carl Zeiss, Jena) was used for crystallooptical analysis.

Results and discussion

The experimental results concerning phase equilibria in the system Dy_2O_3–SeO_2–H_2O at 100°C are given in Fig. 1 and Table 1.
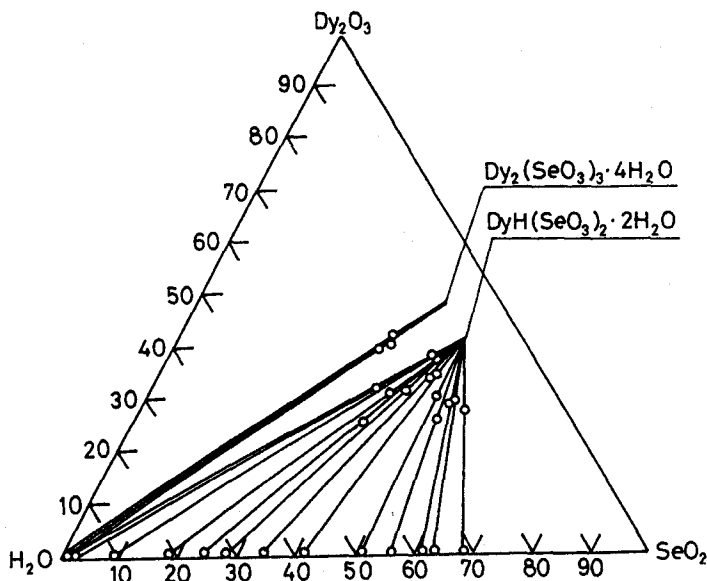
Fig. 1 Solubility isotherm of the system Dy_2O_3–SeO_2–H_2O at 100°C

The solubility isotherm shows that the connodes connecting the figurative points of the equilibrium liquid and solid phases form two crystallization fields, i.e. two compounds are obtained in the concentration interval under study. In the first crystallization field the connodes converge into a point with coordinates 47.95 mass% Dy_2O_3, 42.73 mass% SeO_2 and 9.26 mass% H_2O, which corresponds to crystallization of $Dy_2(SeO_3)_3 \cdot 4H_2O$. This compound is formed in the concentration interval 0–0.92 mass% SeO_2 in the liquid phase. At a concentration of SeO_2 in the liquid phase from 0.92 to 68.35 mass%, a field of equilibrium of dysprosium hydrogen selenite $DyH(SeO_3)_2 \cdot 2H_2O$ ($Dy_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O$) is established. The identity of the solid phases in the two crystallization fields was confirmed by X-ray phase (Fig. 2) and crystallooptical analyses.

At a concentration of SeO_2 in the liquid phase higher than 68.35 mass%, the solid phase dissolves completely. This increase in solubility may be due to the formation of a new acid salt. Our attempt to isolate and study this phase failed.
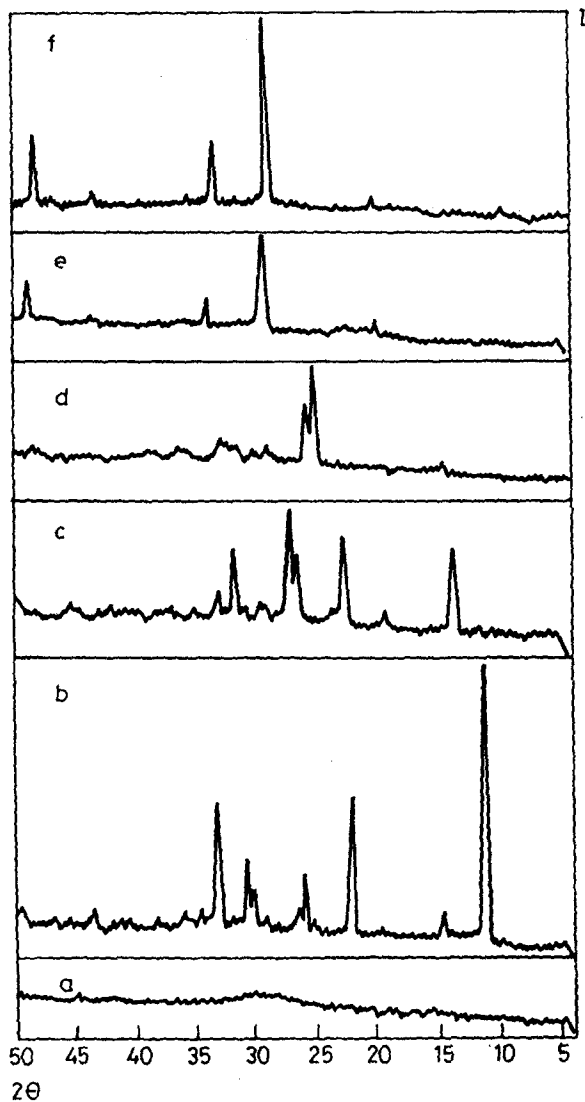
Fig. 2 X-ray patterns of the solid phases of the system $Dy_2O_3-SeO_2-H_2O$ at 100°C:
a – $Dy_2(SeO_3)_3 \cdot 4H_2O$; b – $Dy_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O$;
c – $Dy_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O$ heated at 230°C;
d – $Dy_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O$ heated at 450°C;
e – $Dy_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O$ heated at 1000–1100°C; f – pure Dy_2O_3

The derivatogram of $Dy_2(SeO_3)_3 \cdot 4H_2O$ (Fig. 3) shows that in the temperature interval 250–410°C, 4 moles of H_2O are gradually liberated and anhydrous dysprosium selenite is formed.

Table 1 Solubility isotherm of the system $Dy_2O_3-SeO_2-H_2O$ at 100°C

No.	Liquid phase comp./wt%		Solid phase comp./wt%		Formula of the solid phase
	Dy_2O_3	SeO_2	Dy_2O_3	SeO_2	
1	–	0.056	41.08	37.50	$Dy_2(SeO_3)_3 \cdot 4H_2O$
2	–	0.126	39.35	36.42	$Dy_2(SeO_3)_3 \cdot 4H_2O$
3	–	0.920	40.58	38.06	$Dy_2(SeO_3)_3 \cdot 4H_2O$
4	$1.2 \cdot 10^{-3}$	0.920	37.68	45.25	$DyH(SeO_3)_2 \cdot 2H_2O$
5	$2.2 \cdot 10^{-3}$	2.12	31.68	38.56	$DyH(SeO_3)_2 \cdot 2H_2O$
6	$5.6 \cdot 10^{-3}$	9.28	37.22	46.15	$DyH(SeO_3)_2 \cdot 2H_2O$
7	$7.1 \cdot 10^{-3}$	18.47	30.49	41.08	$DyH(SeO_3)_2 \cdot 2H_2O$
8	$7.2 \cdot 10^{-3}$	24.50	25.40	39.51	$DyH(SeO_3)_2 \cdot 2H_2O$
9	$7.8 \cdot 10^{-3}$	28.26	31.45	43.68	$DyH(SeO_3)_2 \cdot 2H_2O$
10	$8.2 \cdot 10^{-3}$	34.62	34.20	46.70	$DyH(SeO_3)_2 \cdot 2H_2O$
11	$8.3 \cdot 10^{-3}$	41.91	34.86	47.82	$DyH(SeO_3)_2 \cdot 2H_2O$
12	$8.7 \cdot 10^{-3}$	51.47	30.04	49.52	$DyH(SeO_3)_2 \cdot 2H_2O$
13	$9.4 \cdot 10^{-3}$	56.04	25.68	52.11	$DyH(SeO_3)_2 \cdot 2H_2O$
14	$1.2 \cdot 10^{-2}$	61.56	28.70	53.10	$DyH(SeO_3)_2 \cdot 2H_2O$
15	$1.3 \cdot 10^{-2}$	63.19	28.95	53.54	$DyH(SeO_3)_2 \cdot 2H_2O$
16	$1.5 \cdot 10^{-2}$	68.35	27.12	55.90	$DyH(SeO_3)_2 \cdot 2H_2O$

The mass loss, according to the TG curve, is 9.20 wt% (theoretical value 9.25 wt%). Chemical analysis of a sample heated at 600°C gave the concentration of Dy_2O_3 as 52.82 wt%, and that of SeO_2 as 47.21 wt%. The concentrations calculated theoretically were 52.84 wt% and 47.16 wt%, respectively. At 715°C an exothermal peak is observed corresponding to crystallization of the anhydrous salt obtained. A confirmation of the crystallinity of the final product is the fact that the X-ray pattern of a sample obtained below this temperature only shows the main halo without any peaks, while the X-ray pattern of a sample heated slightly above this temperature shows a number of peaks. The anhydrous dysprosium selenite formed is stable at 815°C. At a higher temperature 2 moles of SeO_2 are liberated and the selenite is transformed into a basic salt with the composition $Dy_2O_3 \cdot SeO_2$ or $(DyO)_2 \cdot SeO_2$.

The mass loss resulting from this decomposition reaction is 37.70 wt% (theoretical value 37.78 wt%). Chemical analysis of a sample heated at 980°C gave the concentration of Dy_2O_3 as 77.10 wt% and that of SeO_2 as 22.99 wt%. The concentration calculated theoretically were 77.07 wt% and 22.93 wt%, respectively. Complete decomposition of the selenite with liberation of the last mole of SeO_2 is observed only at temperatures over 1200°C. Chemical and X-ray phase analyses proved that the pure phase Dy_2O_3 was obtained (Dy –87.20 wt%; theoretical value 87.30 wt%).

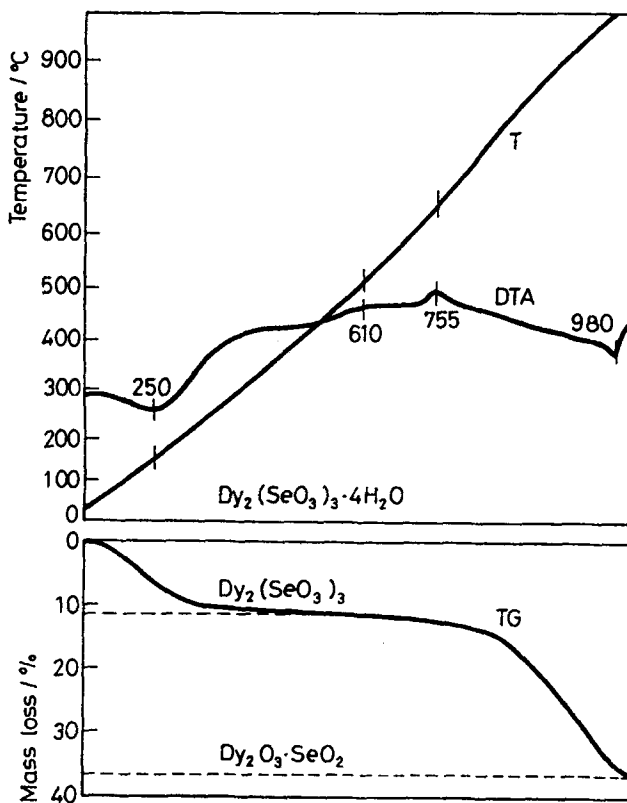**Fig. 3** TG, DTG and DTA curves of $Dy_2(SeO_3)_3 \cdot 4H_2O$

The TG, DTG and DTA curves of $Dy_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O$ (Fig. 4) shows that in the temperature interval 170–400°C, crystallization and constitutional water is liberated and hydrogen selenite is transformed to $Dy_2(SeO_3)_3 \cdot SeO_2$ (Fig. 2c). The mass loss is 10.12 wt% (theoretical value 9.96 wt%). Chemical analysis of a sample heated at 350°C gave the concentration of Dy_2O_3 as 45.71 wt% and that of SeO_2 as 35.32 wt%. The concentration calculated theoretically were 45.66 wt% and 54.34 wt%, respectively.

In the temperature interval 430–720°C, 1 mole of SeO_2 is liberated and the tetraselenite transforms into normal dysprosium selenite, $Dy_2(SeO_3)_3$, (Fig. 2d). The mass loss due to this decomposition reaction is 22.21 wt% (theoretical values 22.16 wt%). Chemical analysis of a sample heated at 750–800°C gave the concentration of Dy_2O_3 as 52.88 wt% and that of SeO_2 as 47.18 wt%. The concentrations calculated theoretically were 52.86 wt% and 47.15 wt%, respectively.

In the temperature interval 835–945°C, dysprosium selentie $Dy_2(SeO_3)_3$ decomposes, liberating 2 moles of SeO_2, and $Dy_2O_3 \cdot SeO_2$ or $(DyO)_2 \cdot SeO_3$ is obtained. The mass loss is 46.67 wt% (the mass loss calculated for the corresponding transition is 48.67 wt%). Chemical analysis of a sample heated at 945°C gave the con-
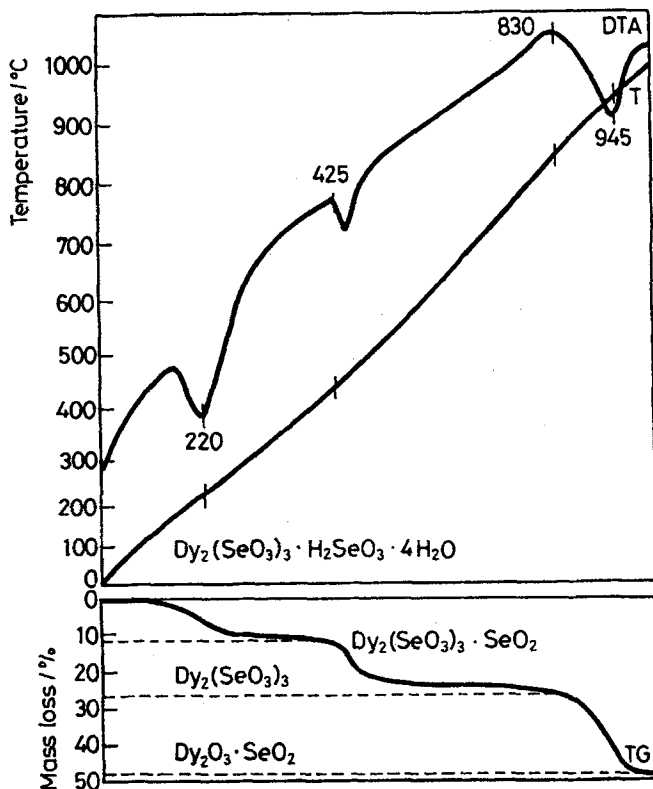
Fig. 4 TG, DTG and DTA curves of $Dy_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O$

centration of Dy_2O_3 as 77.15 wt% and that of SeO_2 as 23.03 wt%. The concentrations calculated theoretically for this phase were 77.07 wt% and 22.92 wt%, respectively. Complete decomposition of dysprosium selenite with liberation of the last mole of SeO_2 takes place only after heating the sample for 3 or 4 h at 1100–1200°C (Fig. 2e). The concentration of Dy in the final product is 87.21 wt% (theoretical value 83.13 wt%).

Thus, besides using the data from the TG curves obtained by TG, DTG and DTA analysis, the compositions of the by-products of thermal decomposition were proved by isolating them in the pure state modelling the conditions of thermal analysis as well as by chemical and X-ray phase analyses of these products.

References

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