Journal of Thermal Analysis and Calorimetry, Vol. 73 (2003) 315–321

PHYSICOCHEMICAL STUDY OF THE COMPOUNDS IN THE THREE-COMPONENT SYSTEM Sc_2O_3–SeO_2–H_2O AT 100°C

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

[1]Prof. Assen Zlatarov University, Bourgas 80 10, Bulgaria
[2]Technological College, Razgrad 7200, Bulgaria

(Received November 19, 2002; in revised form March 8, 2003)

Abstract

The selenites of scandium are used as new materials in producing instrument and semi-conductor engineering. Like tellurites, they can also be applied as materials for making lasers. The process of producing scandium selenides by the reduction of the corresponding selenites has the advantage of taking place at relatively low temperatures and high rate. In this respect, it is necessary to command methods of obtaining high-purity selenites and to obtain data concerning their thermal stability.

A physicochemical study of the system Sc_2O_3–SeO_2–H_2O was carried out at 100°C in order to find solutions to these problems.

The possible compounds in the system at a given temperature were obtained. The compounds were identified by the Schreinemakers' method and also by chemical and X-ray phase analyses. The mechanism of thermal decomposition was determined by means of a derivatograph.

Keywords: scandium selenites, solubility isotherm, thermal analysis, X-ray pattern

Introduction

Nilson [1] first obtained amorphous scandium selenite by mixing equimolar solutions of scandium sulphate and sodium selenite. By heating it with selenious acid, scandium hydrogen selenite was obtained. Mayer *et al.* [2] obtained X-ray amorphous scandium selenite, calculated its enthalpy of formation and studied its thermal decomposition. Other authors [3] obtained $Sc_2(SeO_3)_3 \cdot 5H_2O$ by two methods: neutralization of a suspension of scandium hydroxide by a solution of selenious acid and also by an exchange reaction of a soluble scandium compound with a solution of alkaline selenite. The solubility of scandium selenite in a solution of H_2SeO_3 at 25°C was studied in reference [4]. By the Schreinemakers' method it was found that $Sc_2(SeO_3)_3 \cdot 5H_2O$ and $Sc(HSeO_3)_3$ were obtained.

$Sc_2O(SeO_3)_2 \cdot 3H_2O$ was obtained by mixing a solution of H_2SeO_3 and a suspension of $Sc(OH)_3$ in equimolar ratios [5]. The same authors suggested that $ScH(SeO_3)_2 \cdot H_2O$ should be obtained by mixing a solution of $ScCl_3$ containing $NaHSeO_3$ in a tenfold ex-

---

[*] Author for correspondence: stanislav@btu.bg

1388–6150/2003/ $ 20.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

cess. Scandium diselenite $ScH(SeO_3)_2 \cdot H_2O$ is a white crystalline substance slightly soluble in water.

Other authors [6] obtained anhydrous $Sc(HSeO_3)_3$ and determined the parameters of its crystal lattice.

The aim of the present work was to draw the solubility isotherm of the system, to determine the equilibrium fields of the compounds obtained and their composition, and also to determine and describe the mechanism of thermal decomposition of these compounds by derivatograph analysis.

Experimental

Materials

Sc_2O_3 with purity of 99.9999 mass% and H_2SeO_3 with purity of 99.999 mass% were used as initial compounds.

Methods

In order to study the system Sc_2O_3–SeO_2–H_2O at 100°C, samples were prepared in quartz ampules, each containing 2 g of Sc_2O_3 and varying concentrations of H_2SeO_3 (from 0 to 85%). The samples were placed in an air thermostat at 100 ± 0.5°C. They were periodically stirred. In order to determine the time needed to reach chemical equilibrium, kinetic curves of equilibrium were obtained. For that purpose, more samples with the same chemical composition were prepared and opened periodically. Equilibrium was considered to have been reached when the liquid and solid phases no longer changed their composition (determined by chemical analysis). Crystallographic equilibrium was reached when the intensity and interplanar distances of the X-ray patterns of the solid phases did not change any more. When equilibrium was reached, the ampules were opened, the liquid and solid phases were separated at the experimental temperature and were subjected to chemical, thermal and X-ray phase analyses.

Scandium was identified as Sc_2O_3 complexometrically [7], and SeO_2 was analysed iodometrically and gravimetrically [8].The concentration of Sc^{3+} in the liquid phase was determined spectrophotometrically on a Spekol-11 apparatus (Carl Zeiss, Jena, Germany) [9].

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. An OD-102 derivatograph (MOM, Hungary) was used for thermal analysis by heating the phases from 25 to 1000°C at a rate 5°C min^{-1} in ceramic crucibles. α-Al_2O_3 was used as a standard substance.

Results and discussion

The results from studying the system Sc_2O_3–SeO_2–H_2O at 100°C are presented in Fig. 1 and Table 1. Schreinemakers data show that 2 solid phases crystallize in this system: $Sc_2(SeO_3)_3 \cdot 4H_2O$ and $Sc_2(SeO_3)_3 \cdot 3H_2SeO_3$. The crystallization field of

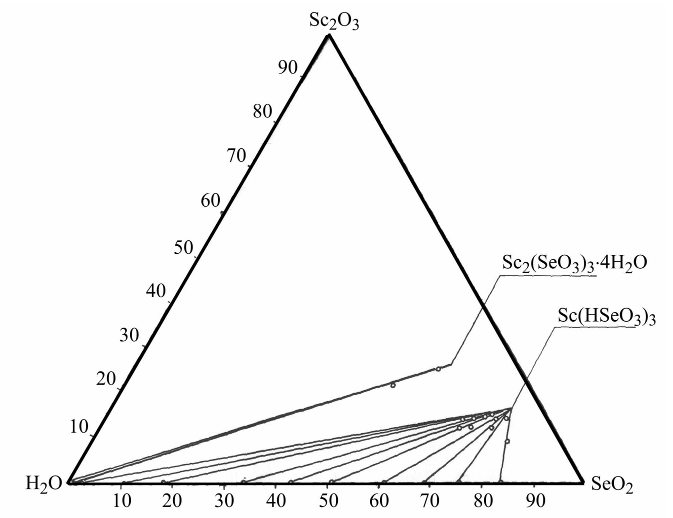

Fig. 1 Solubility isotherm of the system Sc_2O_3–SeO_2–H_2O at 100°C

$Sc_2(SeO_3)_3·3H_2SeO_3$ takes most of the diagram – from 0.75 to 83.20% of SeO_2 in the liquid phase. The eutonic point between $Sc_2(SeO_3)_3·4H_2O$ and $Sc_2(SeO_3)_3·3H_2SeO_3$ is at 0.75 mass% of SeO_2 and $2.1·10^{-3}$ mass% of Sc_2O_3.

Table 1 Solubility isotherm of the system Sc_2O_3–SeO_2–H_2O at 100°C

No.	Liquid phase/mass%		Solid phase/mass%		Formula composition
	$Sc_2O_3·10^3$	SeO_2	Sc_2O_3	SeO_2	
1	2.50	0.40	24.52	59.20	$Sc_2(SeO_3)_3·4H_2O$
2	2.80	0.75	21.60	51.59	$Sc_2(SeO_3)_3·4H_2O$
3	3.30	0.75	15.52	73.80	$Sc(HSeO_3)_3$
4	3.40	2.53	14.25	71.10	$Sc(HSeO_3)_3$
5	3.68	10.68	13.50	69.47	$Sc(HSeO_3)_3$
6	3.78	18.23	15.08	73.54	$Sc(HSeO_3)_3$
7	4.22	33.77	13.20	71.75	$Sc(HSeO_3)_3$
8	4.60	42.11	12.22	69.10	$Sc(HSeO_3)_3$
9	4.79	50.68	12.40	72.50	$Sc(HSeO_3)_3$
10	5.10	61.34	14.25	75.56	$Sc(HSeO_3)_3$
11	5.56	68.34	12.12	75.38	$Sc(HSeO_3)_3$
12	6.24	78.07	14.33	77.12	$Sc(HSeO_3)_3$
13	6.85	83.20	9.13	79.90	$Sc(HSeO_3)_3$

Thermal curves of $Sc_2(SeO_3)_3 \cdot 4H_2O$ is shown in Fig. 2. Normal scandium selenite is thermostable at 100°C and at that temperature adsorption water is completely liberated. In the temperature interval 100–280°C (the endothermal peak has a minimum at 195°C) one-stage liberation of 4 moles of crystalline water takes place. The mass loss during that transformation is 13.63 mass% compared with 14.44 mass% calculated from the TG curve. The deference of 0.81% is because of the liberation of adsorption water in the first stage of the process. The exothermal peak at 660°C is due to crystallization of the X-ray amorphous product. The X-ray pattern of the product heated at 400–630°C shows that it is amorphous, while the same product heated over 630°C is crystalline. Then, 2 moles of SeO_2 are liberated at 2 stages resulting in the consecutive formation of $Sc_2O_3 \cdot 2SeO_2$ ($Sc_2O(SeO_3)_2$) and an oxoselenite with composition $(ScO)_2SeO_3$. The latter reaction takes place at 920°C, the temperature at which the selenite is heated. The mass loss for the formation of this oxoselenite is 54.51 mass% corresponding to 55.0 mass% calculated from the TG curve. After heating the selenite for 2–3 h at 1100–1200°C, SeO_2 is completely liberated and Sc_2O_3 is obtained as a pure phase.

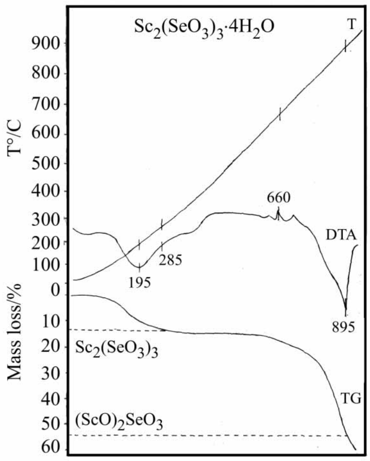

Fig. 2 Simultaneous TG and DTA curves of $Sc_2(SeO_3)_3 \cdot 4H_2O$

Figure 3 shows the thermal curves of $Sc_2(SeO_3)_3 \cdot 3H_2SeO_3$. The selenite is thermostable at 215°C. At 215–335°C, 3 moles of constitutionally bound water are liberated and it turns into $Sc_2(SeO_3)_3 \cdot 3SeO_2$. The TG curve shows that mass loss is 6.42 mass% (theoretical calculation for this transition is 6.30 mass%). The exothermal peak at 410°C is due to crystallization of X-ray amorphous scandium hexaselenite. This transformation was also proved by the X-ray patterns of the products obtained by heating at 380 and 450°C. Hexaselenite is thermostable at 500°C. Then, SeO_2 is liberated at several stages. At 500–580°C, 1 mole of SeO_2 is liberated and hexaselenite turns into pentaselenite. The mass loss is 19.18 mass% (theoretical calculation is 19.24 mass%). Pentaselenite loses 1 mole of SeO_2 and at 580–650°C it turns into tetraselenite. The mass loss is 32.02 mass%

Table 2 Chemical analysis of the products of thermal decomposition of scandium selenites

Phase	Experimental composition/%			Theoretical composition/%			Standard deviation/$S \cdot 10^2$		
	Sc_2O_3	SeO_2	H_2O	Sc_2O_3	SeO_2	H_2O	Sc_2O_3	SeO_2	H_2O
$Sc_2(SeO_3)_3 \cdot 3H_2SeO_3$	16.10	77.63	5.57	16.08	77.62	5.60	1.58	6.08	8.03
$Sc_2(SeO_3)_3 \cdot 3SeO_2$	17.14	82.81	–	17.16	82.84	–	3.81	3.24	–
$Sc_2(SeO_3)_3 \cdot 2SeO_2$	19.91	80.10	–	19.90	80.10	–	8.51	2.00	–
$Sc_2(SeO_3)_3 \cdot SeO_2$	23.70	76.30	–	23.71	76.29	–	2.55	2.00	–
$Sc_2(SeO_3)_3$	29.25	70.72	–	29.27	70.70	–	3.08	3.08	–
$Sc_2O_3 \cdot 2SeO_2$	38.32	61.62	–	38.33	61.67	–	4.95	4.36	–
$Sc_2O_3 \cdot SeO_2$	55.44	44.57	–	55.42	44.58	–	4.00	2.64	–
Sc_2O_3	99.92	–	–	100	–	–	3.08	–	–

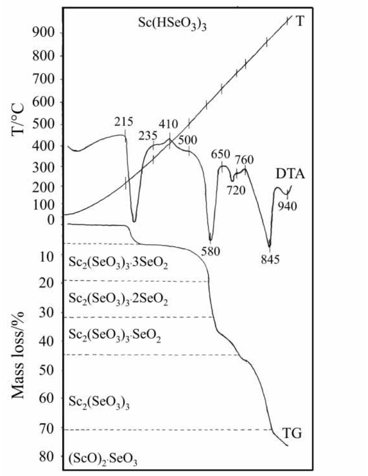

Fig. 3 Simultaneous TG and DTA curves of $Sc_2(SeO_3)_3·3H_2SeO_3/Sc(HSeO_3)_3/$

(theoretical calculation is 32.15 mass%). The small endothermal peak at 650–720°C is due to a mass loss 1 mole of SeO_2 and a transition of tetraselenite into normal scandium selenite. The mass loss is 45.22 mass% (theoretical calculation is 45.14 mass%). $Sc_2(SeO_3)_3$ decomposes at several stages, too. At 720–760°C 1 mole of SeO_2 is liberated and oxoselenite $Sc_2O_3·2SeO_2$ is obtained, which then turns into $Sc_2O_3·SeO_2$ at 760–845°C. The mass loss is 71.12 mass% (theoretical calculation is 71.04 mass%). Complete decomposition of selenite and its transformation into Sc_2O_3 do not take place. At 940°C, the temperature at which the product is heated, the mass loss is 78.0 mass% (theoretical calculation is 83.98 mass%).

The mechanism of the thermal decomposition of the two compounds was proved by gravimetric analysis and also by isolating the intermediate products and subjecting them to chemical and X-ray phase analyses.

Table 2 presents the data from chemical analysis and the theoretical calculations for the corresponding compounds. The good agreement between them is a proof of the correctness of the suggested scheme. X-ray phase analysis also confirms the identity of the new phases obtained.

Conclusions

The solubility isotherm of the system Sc_2O_3–SeO_2–H_2O at 100°C was studied. The compounds in the system are identified by Schreinemakers' method, and also by chemical, derivatograph and X-ray phase analyses after isolating them in the pure state.

References

1 L. F. Nilson, Berichte, 13 (1880) 1439.
2 A. I. Mayer, L. Ia. Suponickii and M. H. Karapetianc, Izv. ANSSSR, Neorgan. Materiali, 4 (1968) 921.

3 A. S. Znamenskaia, L. N. Komisarova and V. I. Spicin, Zh. Neorgan. Khimii, 17 (1972) 1828.
4 A. S. Znamenskaia and L. N. Komisarova, Zh. Neorgan. Khimii, 18 (1973) 873.
5 L. N. Komisarova and A. S. Znamenskaia, Zh. Neorgan. Khimii, 19 (1974) 295.
6 J. Valkonen and M. Leskelä, Acta Crystallogr., 34B (1978) 1323.
7 V. Umland, A. Jansen, P. Tierg and C. Winsch, Teorie und Praktische Anwendung von Comlexbildern, Dechema, Frankfurt am Main 1971.
8 I. I. Nazarenko and E. I. Ernakov, Analyticheskaia Khimia Selena i Tellura, Nauka, Moskow 1974, pp. 5 and 59.
9 A. N. Ermakov, Zbornik nauchnih troudov. Analyticheskaia khimia,redkih elementov, Nauka, Moskow 1988.
10 G. G. Gospodinov, M. G. Stancheva, J. Therm. Anal. Cal., 55 (1999) 221.
11 G. G. Gospodinov, M. G. Stancheva, J. Therm. Anal. Cal., 65 (2001) 275.
12 G. G. Gospodinov, M. G. Stancheva, J. Therm. Anal. Cal., 67 (2002) 463.