Monatshefte für Chemie 133, 1381–1386 (2002)
DOI 10.1007/s00706-002-0506-7

Monatshefte für Chemie
Chemical Monthly
Printed in Austria

Chemistry of the Thermal Decomposition of Lutetium Selenities

Georgy G. Gospodinov[1] and **Miluvka G. Stancheva**[2]

[1] Prof. Assen Zlatarov University, BG-8010 Bourgas, Bulgaria
[2] Technological College, BG-7200 Razgrad, Bulgaria

Received February 27, 2002; accepted (revised) April 26, 2002
Published online September 19, 2002

Summary. The solubility isotherm of the system Lu_2O_3–SeO_2–H_2O was studied at 100°C. The compounds of the three-component system were identified by *Schreinemakers*' method and chemical, derivatograph and X-ray phase analyses after separation in the pure state: $Lu_2(SeO_3)_3 \cdot 4H_2O$ and $LuH(SeO_3)_2 \cdot 2H_2O$.

Keywords. Lutetium selenites; Solubility isotherm; Thermal analysis; Lattice parameters.

Introduction

Studies of lutetium selenites are limited to two publications concerning the synthesis of two salts and a description of the schemes of dehydration and complete decomposition of the normal salt to Lu_2O_3.

In Ref. [1], the authors described the synthesis of normal selenite with composition $Lu_2(SeO_3)_3 \cdot 4H_2O$ from the reaction of $LuCl_3$ with Na_2SeO_3. The crystallohydrate obtained was found to be X-ray amorphous.

Immonen et al. [2] obtained an acid salt with composition $Lu_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 5H_2O$ by mixing an aqueous solution of $LuCl_3$, containing NH_3, with selenous acid. It was found that this selenite is isomorphous to the series of acid selenites of the elements analogous to lanthanides with a similar composition.

Nowadays *de Pedro* [3] synthesized anhydrous selenites of lutetium by the method of solid phase synthesis and determined the parameters of the crystal lattice of $Lu_2Se_3O_9$ and Lu_2SeO_5 [4].

Experimental

In order to study the system Lu_2O_3–SeO_2–H_2O at 100°C, 20 samples were prepared each containing 2 g Lu_2O_3 and varying amounts of selenous acid (from 0 to 85 mass%). The samples were sealed in glass ampoules and placed in an air thermostat at 100.0 ± 0.1°C for two months. They were periodically shaken. To determine the necessary time for reaching the chemical equilibrium, kinetic curves

were obtained. For that purpuse, more ampoules with the same composition were prepared and opened periodically. Equilibrium was reached when chemical analysis showed that the liquid and the solid phases did not change their composition. It was considered that crystallographic equilibrium was established when the peak intensities and the interplanar distances in the X-ray patterns no longer changed. After chemical and X-ray equilibrium was reached, the liquid and solid phases were separated at the experimental temperature and subjected to chemical, crystalloopitcal, thermal and X-ray phase analyses.

Chemical analysis for Lu^{3+} in the solid phase was done complexometrically [5]. Selenite ions were analyzed iodometrically and gravimetrically [6]. The accuracy of the determinations was ± 0.01 mass%. The concentration of Lu^{3+} in the liquid phase was determined spectrophotometrically on a Specol-11 apparatus (Karl Zeiss, Germany) [7]. X-ray analysis was performed on an URD-6 apparatus (Germany) at Cu anode, K_α-emission, and a Ni filter for β-emission. An OD-102 derivatograph (MOM, Hungary) was used for the thermal analysis. Crystallooptical analyses were done on a Dokuval optical microscope (Karl Zeiss, Jena).

Results and Discussion

The results from studying the system Lu_2O_3–SeO_3–H_2O are presented in Table 1 and Fig. 1. *Schreinemakers*' method shows that two solid phases, $Lu_2(SeO_3)_3 \cdot 4H_2O$ and $Lu_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O$, which are incongruently soluble, crystallize in the system. The largest part of the diagram is occupied by the field of crystallization of hydrogen selenites (from 0.82 to 85.0 mass% SeO_2). The composition of the solution in the eutonic point is $3.2 \cdot 10^{-4}$ mass% Lu_2O_3 and 0.82 mass% SeO_2. Besides *Schreinemakers*' method, other methods of physicochemical analysis were used to identify the phases obtained. The powder diffractograms of the solid phases of points 2 and 4–13 confirm the identity of the compounds $Lu_2(SeO_3)_3 \cdot 4H_2O$ and $Lu_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O/LuH(SeO_3)_2 \cdot 2H_2O/$(Fig. 1 and Table 1).

Derivatographic analyses of $Lu_2(SeO_3)_3 \cdot 4H_2O$ and $LuH(SeO_3)_2 \cdot 2H_2O$ were carried out. The thermal dissociation of $Lu_2(SeO_3)_3 \cdot 4H_2O$ occurs according to

Table 1. Solubility isotherm of the system Lu_2O_3–SeO_2–H_2O at 100°C

N	Liquid phase mass%		Solid phase mass%		Formula composition
	Lu_2O_3	SeO_2	Lu_2O_3	SeO_2	
1	$3.1 \cdot 10^{-4}$	0.16	45.26	36.67	$Lu_2(SeO_3)_3 \cdot 4H_2O$
2	$3.2 \cdot 10^{-4}$	0.82	44.42	36.12	$Lu_2(SeO_3)_3 \cdot 4H_2O$
3	$3.2 \cdot 10^{-4}$	0.82	36.40	41.08	$LuH(SeO_3)_2 \cdot 2H_2O$
4	$5.3 \cdot 10^{-4}$	1.09	27.16	32.34	$LuH(SeO_3)_2 \cdot 2H_2O$
5	$5.6 \cdot 10^{-4}$	4.61	30.16	38.50	$LuH(SeO_3)_2 \cdot 2H_2O$
6	$6.2 \cdot 10^{-4}$	12.20	34.15	42.18	$LuH(SeO_3)_2 \cdot 2H_2O$
7	$6.8 \cdot 10^{-4}$	20.41	31.23	42.30	$LuH(SeO_3)_2 \cdot 2H_2O$
8	$7.5 \cdot 10^{-4}$	38.09	30.60	46.37	$LuH(SeO_3)_2 \cdot 2H_2O$
9	$8.1 \cdot 10^{-4}$	46.50	34.92	47.53	$LuH(SeO_3)_2 \cdot 2H_2O$
10	$8.8 \cdot 10^{-4}$	54.08	29.34	53.00	$LuH(SeO_3)_2 \cdot 2H_2O$
11	$9.4 \cdot 10^{-4}$	66.15	30.82	53.89	$LuH(SeO_3)_2 \cdot 2H_2O$
12	$1.2 \cdot 10^{-3}$	72.20	31.49	54.22	$LuH(SeO_3)_2 \cdot 2H_2O$
13	$2.2 \cdot 10^{-3}$	83.40	30.52	57.14	$LuH(SeO_3)_2 \cdot 2H_2O$

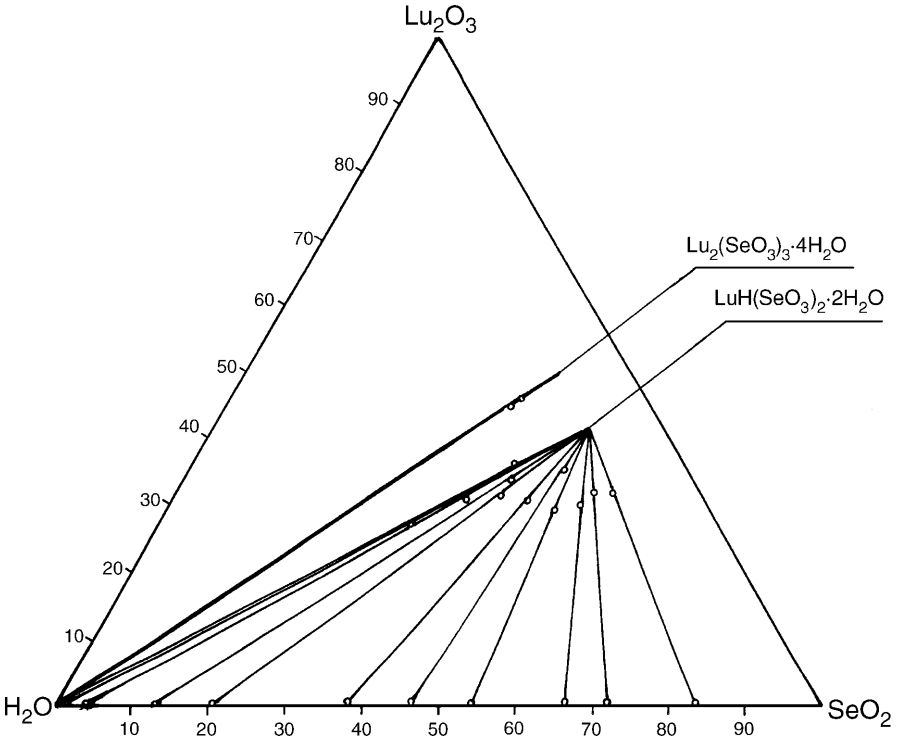

Fig. 1. Solubility isotherm of the system Lu_2O_3–SeO_2–H_2O at 100°C

the schemes:

$$Lu_2(SeO_3)_3 \cdot 4H_2O \xrightarrow[-4H_2O]{100-260^\circ C} \text{amorph. } Lu_2(SeO_3)_3 \xrightarrow{410-705^\circ C}$$
$$\text{cryst. } Lu_2(SeO_3)_3 \xrightarrow[-SeO_2]{705-873^\circ C} Lu_2O_3 \cdot 2SeO_2 \xrightarrow[-SeO_2]{873-910^\circ C} Lu_2O_3 \cdot SeO_2$$

Table 2. Chemical analysis of the products of thermal decomposition of lutetium selenites

Phase	Content of ... (theoretically)			Content of ... (experimentally)		
	Lu_2O_3	SeO_2	H_2O	Lu_2O_3	SeO_2	H_2O
$LuH(SeO_3)_2 \cdot 2H_2O$						
$Lu_2(SeO_3)_3 \cdot H_2SeO_3$	46.28	51.61	2.09	46.50	51.72	2.12
$Lu_2(SeO_3)_3 \cdot SeO_2$	47.27	52.71	–	47.41	53.01	–
$Lu_2(SeO_3)_3$	54.45	45.54	–	54.52	45.63	–
$Lu_2O_3 \cdot 2SeO_2$	64.20	35.80	–	64.50	35.78	–
$Lu_2(SeO_3)_3 \cdot 4H_2O$						
$Lu_2(SeO_3)_3$	54.45	45.54	–	54.98	45.48	–
$Lu_2O_3 \cdot 2SeO_2$	64.20	35.80	–	64.73	36.00	–
$Lu_2O_3 \cdot SeO_2$	78.20	21.80	–	78.39	22.00	–

Table 3. Crystallographic data of lutetium selenites

Compound	Crystal system	Space group	Lattice parameters			$V_{cell}/Å^3$	Z	$\rho_{x/g\,cm^{-3}}$
			$a/Å$	$b/Å$	$c/Å$			
$Lu_2(SeO_3)_3$	monoclinic	$P2_1/c$	16.8509	9.6512	11.8114 $\beta = 106.20$	18.4460	4	2.630
$LuH(SeO_3)_2 \cdot 2H_2O$	orthorombic	$P2_12_12_1$	6.4771	6.8520	16.2551	720.00	4	4.296
$Lu_2Se_4O_{11}$	monoclinic	$P2_1/m$	16.1561	7.0400	7.5811 $\beta = 100.37$	848.17	4	6.589
Lu_2SeO_5	orthorombic	Imma	18.7943	12.9792	5.4621	1332.42	8	5.072

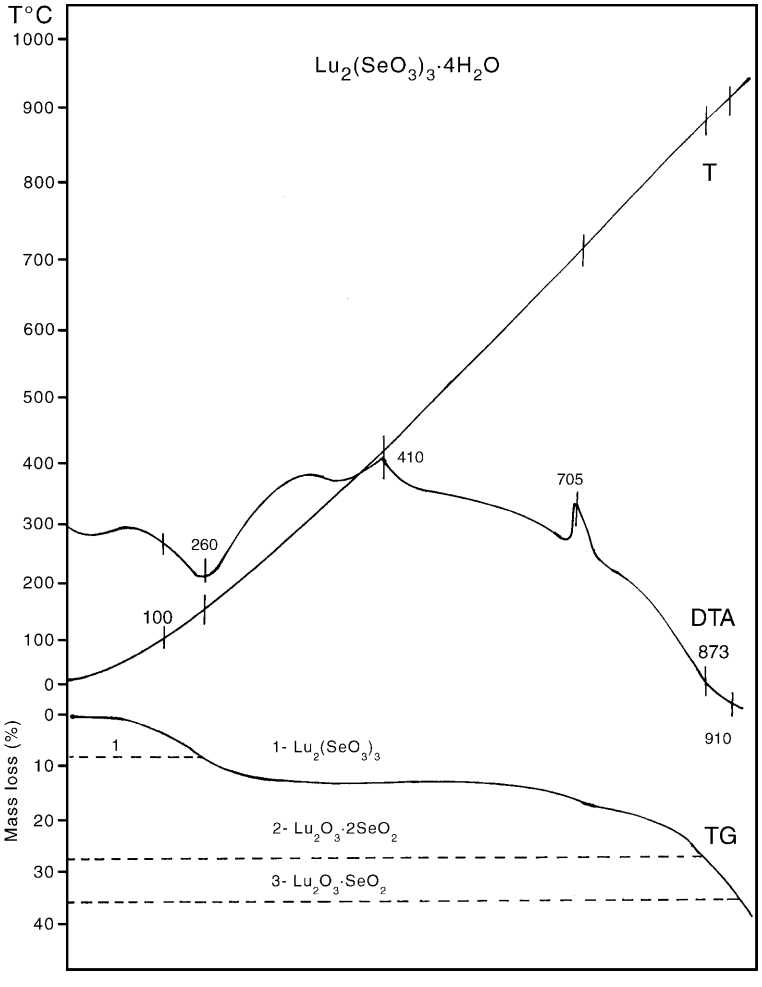

Fig. 2. Derivatogram of $Lu_2(SeO_3)_3 \cdot 4H_2O$

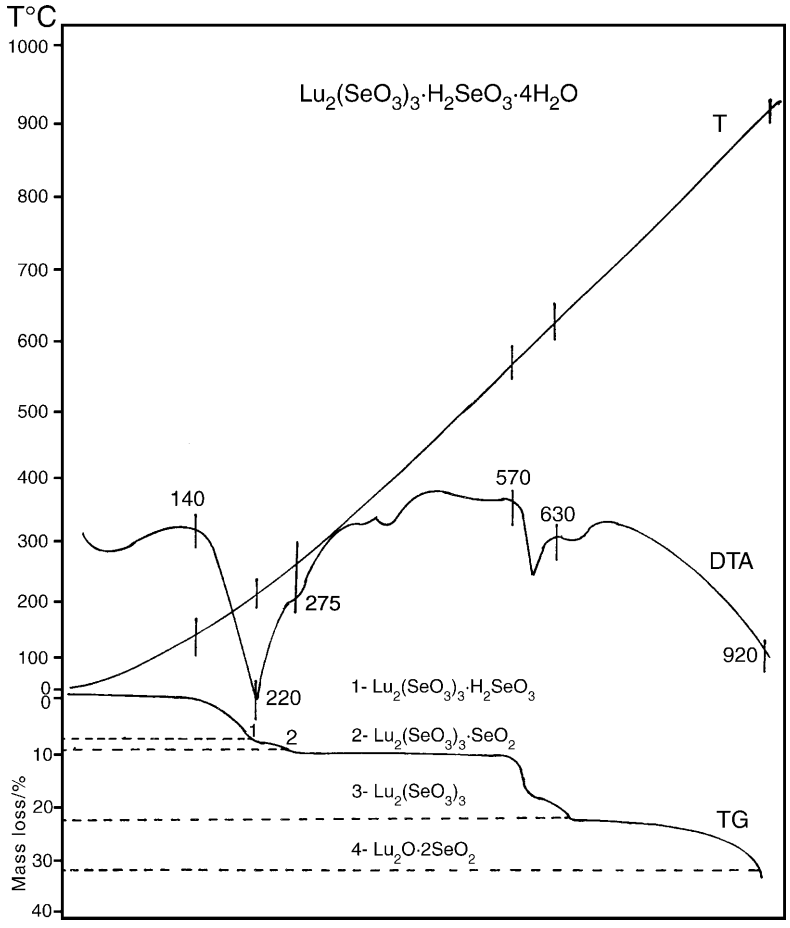

Fig. 3. Derivatogram of $Lu_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O$

and

$$Lu_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O \xrightarrow[-4H_2O]{140-220^\circ C} Lu_2(SeO_3)_3 \cdot H_2SeO_3 \xrightarrow[-H_2O]{220-275^\circ C}$$
$$Lu_2(SeO_3)_3 \cdot SeO_2 \xrightarrow[-SeO_2]{570-630^\circ C} Lu_2(SeO_3)_3 \xrightarrow[-SeO_2]{630-920^\circ C} Lu_2O_3 \cdot 2SeO_2$$

These decomposition steps are also confirmed by the results of the chemical analysis of samples from the compounds heated at conditions appropriately selected from the thermogram (Table 2). When the sample is heated at 940°C, the decomposition of the selenite is negligible. Complete decomposition takes place after continuous heating at 1330°C. The intermediate phases obtained by thermal decomposition of $Lu_2(SeO_3)_3 \cdot H_2SeO_3 \cdot 4H_2O$ were also identified by X-ray phase analysis.

The lattice parameters of the unit cells of all the selenites obtained were determined (Table 3). Our calculations for parameters of the unit cells of $Lu_2(SeO_3)_3$ and Lu_2SeO_5 are in good agreement with those reported in Refs. [3, 4], and the parameters of the unit cells of $LuH(SeO_3)_2 \cdot 2H_2O$ and $Lu_2Se_4O_{11}$ have been determined by the authors of the present work for the first time.

References

[1] Giesbrecht E, Giolito I (1967) An da Acad Brasileira de Ciencias **39**: 233
[2] Immonen E, Koskenlinna M, Ninisto L, Pakkanen T (1976) Finn Chem Lett **3**: 67
[3] De Pedro M, Rasines I, Castro A (1993) J Mat Sci Lett **12**: 1637
[4] De Pedro M, Trombe JC, Castro A (1995) J Mat Sci Lett **14**: 1637
[5] Umlang V, Iansen A, Tierg P, Winsh C (1971) Theorie und Praktische Anwendung von Komplexbildnern. Dechema, Frankfurt am Main
[6] Nazarenko II, Ermakov EI (1974) Analiticheskaia Khimia Selena I Tellura. Nauka, Moskow. pp 5, 59
[7] Riabchikov DI, Riabuhin VA (1966) Analiticheskaia Khimia Redkozemelnyih Elementov I Itria. Nauka, Moskow, p 187
[8] Koskenlinna M, Mutikanen I, Leskela M, Ninisto L (1994) Acta Cryst **C50**: 1384