Thermochimica Acta, 168 (1990) 223–232
Elsevier Science Publishers B.V., Amsterdam

THERMAL DECOMPOSITION OF HYDRATED SELENITES OF TRIVALENT LANTHANIDES AND YTTRIUM

M. IONASHIRO *, C.B. MELIOS, C.A. RIBEIRO and M. SPIRANDELI CRESPI

Instituto de Química, Universidade Estadual Paulista, Araraquara, São Paulo, C.P. 355, CEP. 14.800 (Brazil)

I. GIOLITO

Instituto de Química, Universidade de São Paulo, São Paulo (Brazil)

(Received 26 February 1990)

ABSTRACT

Hydrated lanthanide(III) and yttrium(III) selenites were prepared. Simultaneous thermogravimetric and differential thermal analysis, classical differential thermal analysis , X-ray diffraction and other methods of analysis have been used in the characterisation as well as in the study of the thermal decomposition of these compounds. The results led to the composition and thermal stability and also to interpretations concerning the thermal decomposition mechanisms.

INTRODUCTION

Communications on the preparation of lanthanide(III) and yttrium(III) selenites were published in 1874 by Nilson, Berzelius, Clève and Jolin (see ref. 1) and in 1911 by Espil [2].

The first study on the thermal stability of these compounds was carried out by Giesbrecht and coworkers [3,4], up to 960 ° C. Other investigations of the thermal decomposition of several lanthanide(III) and yttrium(III) selenites have also been described [5–10].

In this work, all lanthanide(III) (except for promethium) and yttrium(III) selenites were prepared. These compounds were characterised and studied by employing iodometric and complexometric methods, TG–DTA, DTA and X-ray diffraction powder patterns. The data obtained allowed us to acquire information as yet absent from the literature about the thermal decomposition of the aforementioned compounds.

---

* Author to whom correspondence should be addressed.

0040-6031/90/$03.50

EXPERIMENTAL

Sodium selenite, lanthanide(III) and yttrium(III) chlorides and selenites were prepared in accordance with already-described procedures [3].

Lanthanide(III) and yttrium(III) ions were determined both by complexometric back titrations with standard EDTA and $ZnSO_4$ solutions, using xylenol orange as indicator [11], and by TG curves. Selenite ions were determined by both iodometry [12] and TG curves. The water contents of the compounds were determined by TG curves.

Simultaneous TG–DTA curves were obtained with Rigaku Denki Co. (Japan) equipment, α-Al_2O_3 being used as the reference material; samples of about 20 mg were placed in a platinum crucible and heated at a rate of $10\,^\circ C\ min^{-1}$ in an argon atmosphere (flow rate $\approx 20\ ml\ min^{-1}$), at ambient pressure.

DTA curves were recorded on BP-engenharia equipment (Campinas, Brazil). α-Al_2O_3 was used as the reference material. The samples were diluted to 20% (by weight) with α-Al_2O_3 and tightly and homogeneously packed in the cylindrical holes of the nickel block of the specimen-holder assembly. The heating rate was $10\,^\circ C\ min^{-1}$ under a static air atmosphere at ambient pressure.

Diffraction patterns were obtained with an HGZ 4/B horizontal diffractometer (G.D.R.) equipped with a proportional counter and pulse height

TABLE 1

Analytical and thermoanalytical (TG) results

Compound	Lanthanide (%)			Selenium (%)			Water (%)	
	Theoretical	EDTA	TG	Theoretical	Iodometric	TG	Theoretical	TG
$La_2(SeO_3)_3 \cdot 3H_2O$	38.98	39.87	38.58	33.23	32.73	33.05	7.59	7.75
$Ce_2(SeO_3)_3 \cdot 4H_2O$	38.22	38.97	37.04	32.31	31.75	31.67	9.83	10.0
$Pr_2(SeO_3)_3 \cdot 4H_2O$	38.35	38.71	38.07	32.24	31.77	32.34	9.81	10.0
$Nd_2(SeO_3)_3 \cdot 4H_2O$	38.91	39.53	38.35	31.95	31.10	31.45	9.72	9.94
$Sm_2(SeO_3)_3 \cdot 4H_2O$	39.90	40.75	40.96	31.43	29.95	30.60	9.56	9.50
$Eu_2(SeO_3)_3 \cdot 4H_2O$	40.15	41.02	41.01	31.30	30.60	30.24	9.52	9.75
$Gd_2(SeO_3)_3 \cdot 4H_2O$	40.98	40.73	40.78	30.87	29.50	30.59	9.39	9.50
$Tb_2(SeO_3)_3 \cdot 4H_2O$	41.24	41.49	41.21	30.73	29.47	30.62	9.35	9.50
$Dy_2(SeO_3)_3 \cdot 4H_2O$	41.78	42.16	41.39	30.45	29.27	30.24	9.27	9.50
$Ho_2(SeO_3)_3 \cdot 4H_2O$	42.14	43.15	41.47	30.26	29.47	30.23	9.21	9.50
$Er_2(SeO_3)_3 \cdot 4H_2O$	42.48	43.99	42.20	30.08	29.05	29.88	9.15	9.75
$Tm_2(SeO_3)_3 \cdot 4H_2O$	42.72	43.01	42.25	29.95	29.37	29.88	9.11	9.25
$Yb_2(SeO_3)_3 \cdot 3H_2O$	44.31	44.23	43.91	30.33	29.99	30.24	6.92	7.00
$Lu_2(SeO_3)_3 \cdot 4H_2O$	43.58	44.56	43.53	29.50	29.53	29.18	8.98	9.00
$Y_2OH(SeO_3)_{2.5} \cdot 3H_2O$ [a]	31.40	29.88	33.07	34.86	34.43	34.45	9.55	9.00

[a] $[OH]_T = 3.0\%$; $[OH]_{TG} = 2.5\%$.

discriminator. The Bragg–Brentano arrangement was adopted using Cu Kα radiation ($\lambda = 1.541$ Å) and settings of 38 kV and 20 mA.

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the prepared compounds having the general formulae $Ln_2(SeO_3)_3 \cdot nH_2O$, where Ln ≡ lanthanide and $n = 3$ or 4, and $Y_2OH(SeO_3)_{2.5} \cdot 3H_2O$.

In the simultaneous TG–DTA curves (Figs. 1–3), the mass losses observed up to 250 °C, corresponding to endothermic peaks, are due to hydration water. Only in the yttrium compound is a small mass loss corresponding to the endothermic peak observed over the range 300–350 °C, and this is ascribed to the "hydroxyl" water loss.

For anhydrous lanthanum selenite (Fig. 1a), no mass loss is observed between 250 and 700 °C, but the DTA curve shows an exothermic peak at 550 °C. For the anhydrous selenites of praseodymium to samarium (Figs. 1c,

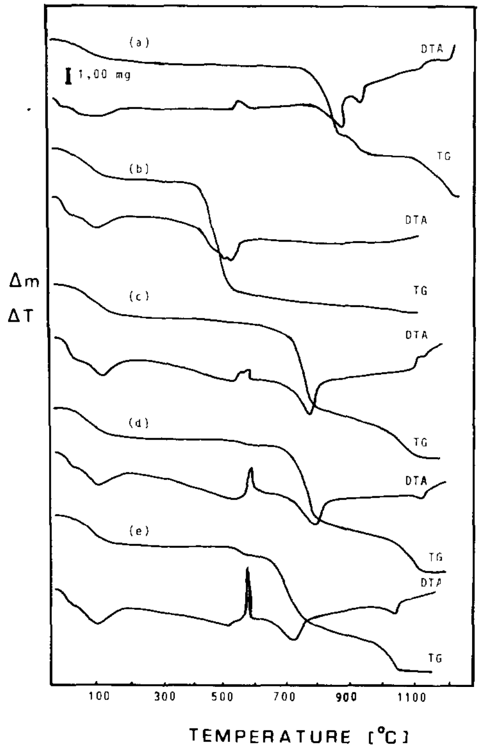

Fig. 1. Simultaneous TG–DTA curves of lanthanide selenite hydrates (heating rate, 10 °C min^{-1}): a, $La_2(SeO_3)_3 \cdot 3H_2O$ (20.05 mg); b, $Ce_2(SeO_3)_3 \cdot 4H_2O$ (20.00 mg); c, $Pr_2(SeO_3)_3 \cdot 4H_2O$ (20.12 mg); d, $Nd_2(SeO_3)_3 \cdot 4H_2O$ (20.12 mg); e, $Sm_2(SeO_3)_3 \cdot 4H_2O$ (20.00 mg).

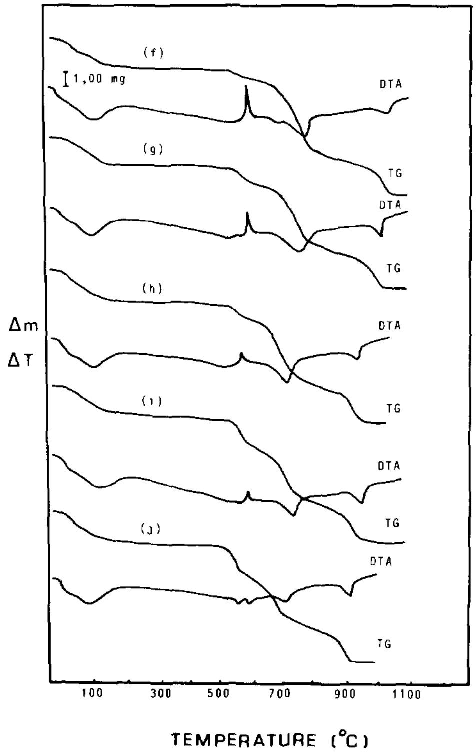

Fig. 2. Simultaneous TG–DTA curves of lanthanide selenite tetrahydrates ($m = 20.00$ mg; heating rate, 10 °C min^{-1}): f, $Eu_2(SeO_3)_3 \cdot 4H_2O$; g, $Gd_2(SeO_3)_3 \cdot 4H_2O$; h, $Tb_2(SeO_3)_3 \cdot 4H_2O$; i, $Dy_2(SeO_3)_3 \cdot 4H_2O$; j, $Ho_2(SeO_3)_3 \cdot 4H_2O$.

1d and 1e), europium to dysprosium (Figs. 2f, 2g, 2h and 2i) and yttrium (oxy)selenite (Fig. 3o), the exothermic peak occurs at ≈ 590 °C, with a small mass loss which increases with the atomic number of the lanthanide. This mass loss is probably due the exothermic reaction associated with the decrease of the thermal stability of these compounds as the atomic number increases. For the anhydrous selenites of holmium (Fig. 2j) and erbium to lutetium (Figs. 3k, 3l, 3m and 3n) the exothermic peak was not observed, suggesting that the heat evolved in the exothermic reaction is spent in the thermal decomposition, prevailing over the endothermic peak. Furthermore, this was confirmed by the classical DTA curves (Figs. 4 and 5), where all compounds (except that of cerium) present exothermic peaks. No doubt this is due to the diluting and packing of the samples, which promotes a temperature increase of the thermal decomposition.

The X-ray powder patterns show that the compounds are amorphous up to ≈ 500 °C and in the crystalline state for temperature higher than ≈ 650 °C (Fig. 6), showing that the exothermic peak is due to the crystallisa-

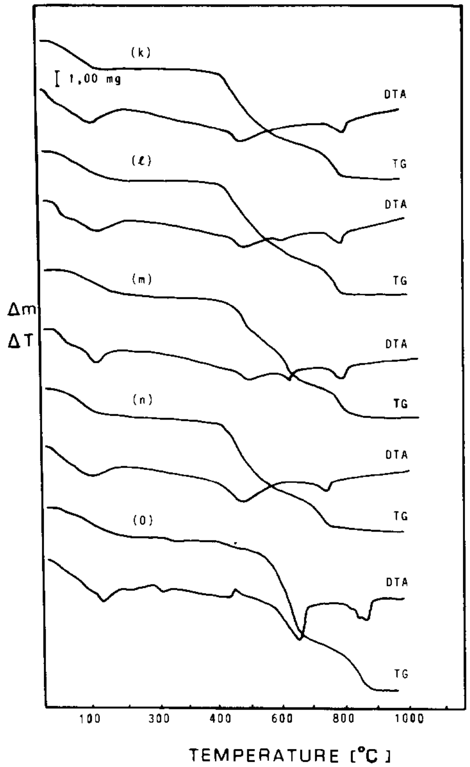

Fig. 3. Simultaneous TG–DTA curves of lanthanide and yttrium selenite hydrates ($m = 20.00$ mg; heating rate, 10 °C min^{-1}): k, $Er_2(SeO_3)_3 \cdot 4H_2O$; l, $Tm_2(SeO_3)_3 \cdot 4H_2O$; m, $Yb_2(SeO_3)_3 \cdot 3H_2O$; n, $Lu_2(SeO_3)_3 \cdot 4H_2O$; o, $Y_2(OH)(SeO_3)_{2.5} \cdot 3H_2O$.

tion process. For cerium(III) selenite, the exothermic peak is not observed; this is probably due to the lower thermal stability of this compound.

The thermal decomposition of anhydrous lanthanum selenite occurs in three steps, the following intermediate compounds being formed: $La_2O_{1.5}(SeO_3)_{1.5}$ (unique form among the currently investigated compounds), $La_2O_2SeO_3$ and the final product La_2O_3. For anhydrous cerium(III) selenite, the thermal decomposition occurs in a single step, with the final formation of CeO_2. The lower stability of cerium(III) selenite is probably due to the oxidation reaction Ce(III) → Ce(IV) (exothermic). The lower stability of the cerium(III) compounds were also observed in previous studies [13,14].

For the anhydrous selenites of praseodymium to holmium and ytterbium, the thermal decomposition occurs with the formation of the following intermediates: $Ln_2O_x(SeO_3)_{3-x}$ and $Ln_2O_2SeO_3$; the final residue is Ln_2O_3, except for praseodymium (Pr_6O_{11}) and terbium (Tb_4O_7). For the first intermediate x values increase over the range 0.1–1 with the increase of the atomic number of the lanthanide ion.

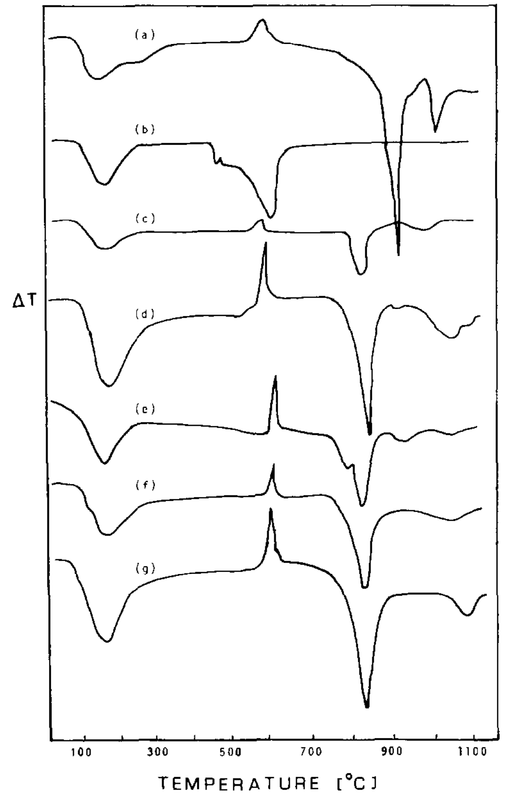

Fig. 4. DTA curves of lanthanide selenite hydrates, diluted to 20% (by weight) with α-alumina (heating rate, 10 °C min^{-1}): a, $La_2(SeO_3)_3 \cdot 3H_2O$; b, $Ce_2(SeO_3)_3 \cdot 4H_2O$; c, $Pr_2(SeO_3)_3 \cdot 4H_2O$; d, $Nd_2(SeO_3)_3 \cdot 4H_2O$; e, $Sm_2(SeO_3)_3 \cdot 4H_2O$; f, $Eu_2(SeO_3)_3 \cdot 4H_2O$; g, $Gd_2(SeO_3)_3 \cdot 4H_2O$.

For the thermal decomposition of the anhydrous selenites of erbium, thulium and lutetium single intermediates, $Ln_2O_2SeO_3$, are formed which decompose to the corresponding oxides Ln_2O_3. For the basic selenite of yttrium, the thermal decomposition of $Y_2O_{0.5}(SeO_3)_{2.5}$ occurs with the formation of two intermediates, $Y_2O_{0.65}(SeO_3)_{2.35}$ and $Y_2O_2SeO_3$; the final residue is Y_2O_3.

The temperature ranges associated with the mass losses observed in the TG curves are shown in Table 2.

Calculations based on the mass losses observed in the TG curves as well as information obtained from the DTA curves are consistent with the following thermal decomposition mechanisms:

$$
\begin{aligned}
(1)\ & La_2(SeO_3)_3 \cdot 3H_2O && \rightarrow La_2(SeO_3)_3 + 3H_2O \\
& La_2(SeO_3)_3 && \rightarrow La_2O_{1.5}(SeO_3)_{1.5} + 1.5SeO_2 \\
& La_2O_{1.5}(SeO_3)_{1.5} && \rightarrow La_2O_2SeO_3 + 0.5SeO_2 \\
& La_2O_2SeO_3 && \rightarrow La_2O_3 + SeO_2
\end{aligned}
$$

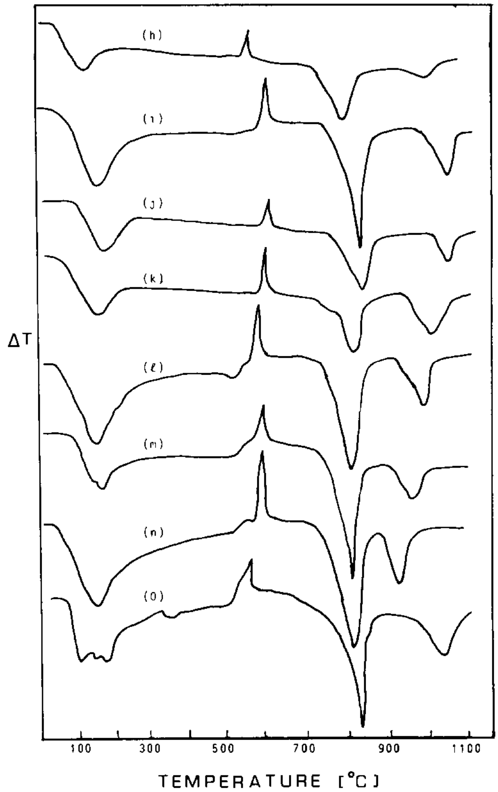

Fig. 5. DTA curves of lanthanide and yttrium selenite hydrates, diluted to 20% (by weight) with α-alumina (heating rate, 10 °C min^{-1}): h, $Tb_2(SeO_3)_3\cdot 4H_2O$; i, $Dy_2(SeO_3)_3\cdot 4H_2O$; j, $Ho_2(SeO_3)_3\cdot 4H_2O$; k, $Er_2(SeO_3)_3\cdot 4H_2O$; l, $Tm_2(SeO_3)_3\cdot 4H_2O$; m, $Yb_2(SeO_3)_3\cdot 3H_2O$; n, $Lu_2(SeO_3)_3\cdot 4H_2O$; o, $Y_2(OH)(SeO_3)_{2.5}\cdot 3H_2O$.

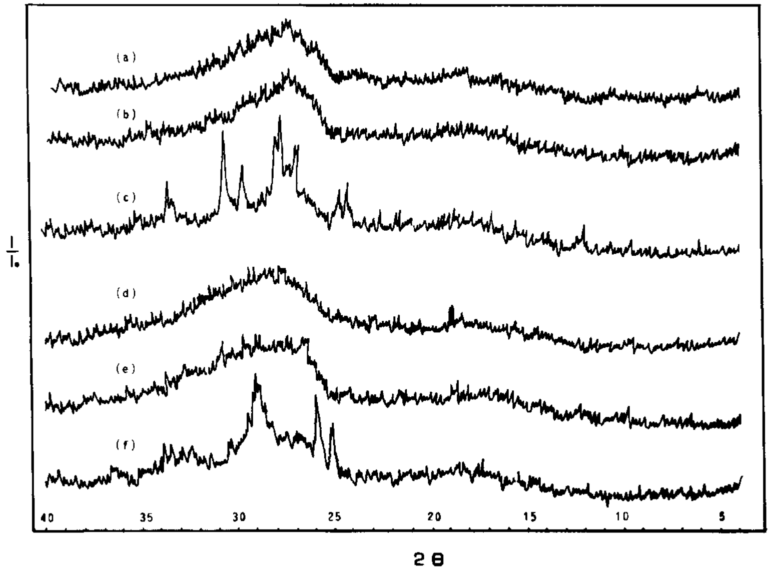

Fig. 6. X-ray powder patterns of: a, $La_2(SeO_3)_3\cdot 3H_2O$; b, $La_2(SeO_3)_3$ (400 °C); c, $La_2(SeO_3)_3$ (750 °C); d, $Yb_2(SeO_3)_3\cdot 3H_2O$; e, $Yb_2(SeO_3)_3$ (400 °C); f, $Yb_2(SeO_3)_3$ (750 °C

TABLE 2

Temperature range (° C) and mass loss (mg) observed in the TG curves

Sele-nite	Dehydration		Thermal decomposition of the anhydrous compound					
	ΔT (° C)	(Δm (mg))	ΔT (° C)	(Δm (mg))	ΔT (° C)	(Δm (mg))	ΔT (° C)	(Δm (mg))
La	50–250	(1.55)	720–880	(4.8)	880–960	(1.5)	1070–1240	(3.1)
Ce	50–200	(2.0)	420–600	(8.9)				
Pr	50–200	(2.0)	500–590	(0.3)	650–820	(5.6)	820–1130	(2.9)
Nd	50–200	(2.0)	500–590	(0.3)	650–820	(5.7)	820–1130	(3.0)
Sm	50–200	(1.9)	500–590	(0.3)	630–800	(5.4)	800–1070	(2.9)
Eu	50–200	(1.9)	500–590	(0.6)	630–800	(5.1)	800–1040	(2.9)
Gd	50–200	(1.9)	500–590	(0.8)	590–815	(5.0)	815–1030	(2.9)
Tb	50–200	(1.9)	500–590	(0.8)	590–800	(4.8)	800– 970	(2.8)
Dy	50–200	(1.9)	500–590	(1.4)	590–780	(4.3)	780– 960	(2.9)
Ho	50–180	(1.9)	500–590	(2.0)	590–760	(3.7)	760– 950	(2.9)
Ev	50–210	(1.85)	500–800	(5.7)			800– 940	(2.8)
Tm	50–200	(1.85)	500–800	(5.7)			800– 925	(2.8)
Yb	50–220	(1.4)	500–630	(2.8)	630–760	(2.9)	760– 925	(2.9)
Lu	50–220	(1.8)	500–760	(5.5)			760– 920	(2.8)
Y	50–210	(1.8)	500–570	(0.4)	600–770	(5.5)	770– 970	(2.9)
	300–350	(0.5)						

$$\begin{aligned}
(2)\ & Ce_2(SeO_3)_3 \cdot 4H_2O && \rightarrow Ce_2(SeO_3)_3 + 4H_2O \\
& Ce_2(SeO_3)_3 && \rightarrow 2CeO_2 + 3SeO_2
\end{aligned}$$

$$\begin{aligned}
(3)\ & 3Pr_2(SeO_3)_3 \cdot 4H_2O && \rightarrow 3Pr_2(SeO_3)_3 + 12H_2O \\
& 3Pr_2(SeO_3)_3 && \rightarrow 3Pr_2O_{0.1}(SeO_3)_{2.9} + 0.3SeO_2 \\
& 3Pr_2O_{0.1}(SeO_3)_{2.9} && \rightarrow 3Pr_2O_{2+y}SeO_3 + 5.7SeO_2 \\
& 3Pr_2O_{2+y}SeO_3 && \rightarrow Pr_6O_{11} + 3SeO_2
\end{aligned}$$

$$\begin{aligned}
(4)\ & 2Tb_2(SeO_3)_3 \cdot 4H_2O && \rightarrow 2Tb_2(SeO_3)_3 + 8H_2O \\
& 2Tb_2(SeO_3)_3 && \rightarrow 2Tb_2O_{0.3}(SeO_3)_{2.7} + 0.6SeO_2 \\
& 2Tb_2O_{0.3}(SeO_3)_{2.7} && \rightarrow 2Tb_2O_{2+y}SeO_3 + 3.4SeO_2 \\
& 2Tb_2O_{2+y}SeO_3 && \rightarrow Tb_4O_7 + SeO_2
\end{aligned}$$

$$\begin{aligned}
(5)\ & Ln_2(SeO_3)_3 \cdot nH_2O && \rightarrow Ln_2(SeO_3)_3 + nH_2O \\
& Ln_2(SeO_3)_3 && \rightarrow Ln_2O_x(SeO_3)_{3-x} + xSeO_2 \\
& Ln_2O_x(SeO_3)_{3-x} && \rightarrow Ln_2O_2SeO_3 + (2-x)SeO_2 \\
& Ln_2O_2SeO_3 && \rightarrow Ln_2O_3 + SeO_2
\end{aligned}$$

Ln ≡ Nd, Sm, Eu, Gd, Dy, Ho, Yb

n = 4 (except for Yb, $n = 3$)

x = 0.1 (Nd, Sm), 0.2 (Eu), 0.3 (Gd), 0.5 (Dy), 0.7 (Ho) or 1.0 (Yb)

$$\begin{aligned}
(6)\ & Ln_2(SeO_3)_3 \cdot 4H_2O && \rightarrow Ln_2(SeO_3)_3 + 4H_2O \\
& Ln_2(SeO_3)_3 && \rightarrow Ln_2O_2SeO_3 + 2SeO_2 \\
& Ln_2O_2SeO_3 && \rightarrow Ln_2O_3 + SeO_2
\end{aligned}$$

Ln ≡ Er, Tm, Lu

$$\begin{aligned}
(7)\ & Y_2OH(SeO_3)_{2.5} \cdot 3H_2O && \rightarrow Y_2OH(SeO_3)_{2.5} + 3H_2O \\
& Y_2OH(SeO_3)_{2.5} && \rightarrow Y_2O_{0.5}(SeO_3)_{2.5} + 0.5H_2O \\
& Y_2O_{0.5}(SeO_3)_{2.5} && \rightarrow Y_2O_{0.65}(SeO_3)_{2.35} + 0.15SeO_2 \\
& Y_2O_{0.65}(SeO_3)_{2.35} && \rightarrow Y_2O_2SeO_3 + 1.35SeO_2 \\
& Y_2O_2SeO_3 && \rightarrow Y_2O_3 + SeO_2
\end{aligned}$$

CONCLUDING REMARKS

The method used for the preparation of the currently investigated compounds, starting from trivalent lanthanide and yttrium chlorides, leads to quantitative yield; however, losses were observed in the process of washing carried out in order to obtain chloride-free precipitates.

The thermal stability of these compounds (except for cerium(III) selenite) decreases with the increase of the atomic number of the lanthanides.

TG–DTA, DTA and X-ray powder patterns provided information about the thermal decomposition mechanisms which have not yet been reported in the literature.

ACKNOWLEDGMENTS

The authors wish to acknowledge the cooperation of Dr. Wilson Cervi da Costa (Laboratório de Processos (Minerais–CNEN-MG, Brazil) for providing all facilities concerned with the recording of the simultaneous TG–DTA curves.

REFERENCES

1 J.W. Mellor, A Comprehensive Treatise on Inorganic and Theoretical Chemistry, Vol. X (S, Se), Longmans, Green and Co., London, 1947, pp. 830–832.
2 R.L. Espil, Comptes Rendus, 152 (1911) 378.
3 E. Giesbrecht, M. Perrier and W.W. Wendlandt, An. Acad. Bras. Cienc., 34 (1962) 37.
4 E. Giesbrecht and I. Giolito, An. Acad. Bras. Cienc., 39 (1967) 233.
5 Yu.L. Suponitskii, A.I. Maier, V.Ya. Kryuchkova and M.Kh. Karapet'yants, Tr. Mosk. Khim. Tekhnol. Inst., 54 (1967) 27.
6 L.Ya. Markovskii and R.A. Safina, Zh. Prikl. Khim., 41 (1968) 693.
7 L.Ya. Markovskii and R.A. Safina, Zh. Prikl. Khim., 41 (1968) 2537.
8 Yu.B. Perkovskaya, Zh. Khim., 8 (1968) 24; Chem. Abstr., 69 (1968) no. 56571.
9 G.S. Savchenko, I.V. Tananaev and A.N. Volodina, Neorg. Mater., 4 (1968) 1097.
10 A.I. Maier, Yu.L. Suponitskii and M.Kn. Karapet'yants, Khim. Khim. Tekhnol., 14 (1971) 3.
11 C.N. Oliveira, M. Ionashiro and C.A.F. Graner, Ecl. Quim., 10 (1985) 7.

12 T.E. Green and P.R. Maxturlley, Selenium and Tellurium, in I.M. Kolthoff and P. Elving (Eds.), Treatise on Analytical Chemistry, Vol. 7, Part II, Interscience, New York, 1961, p. 175.
13 I. Giolito and E. Giesbrecht, An. Acad. Bras. Cienc., 41 (1969) 517.
14 I. Giolito and M. Ionashiro, Thermochim. Acta, 46 (1981) 77.