THERMAL DECOMPOSITION OF HYDRATED SELENITES OF HEAVIER TRIVALENT LANTHANIDES AND YTTRIUM CONTAINING SELENIOUS ACID

Lázaro Moscardini D'ASSUNÇÃO*
Marcelo Reis DA COSTA**
Massao IONASHIRO***

▪ ABSTRACT: Hydrated heavier lanthanides(III) and yttrium(III) selenites, contend selenious acid were prepared. Thermogravimetry and differential thermogravimetry (TG-DTG), X-ray diffraction and other methods of analysis have been used in the characterization 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 mechanism.

▪ KEYWORDS: Heavier lanthanides; yttrium; selenites; thermal decomposition.

Introduction

Preparation and study on the thermal stability of lanthanides(III) and yttrium(III) selenites have been described.[1,2,4-7,9-10] Preparation and thermal decomposition of complex selenites of rare earth elements have also been described.[3]

This paper presents the results of the reaction of a light excess of selenious acid with the corresponding heavier lanthanides and yttrium hydroxides, in an attempt to isolate the selenites in a crystalline form. Actually, crystalline substances were isolated, but compounds which showed the general formula $Ln_2(SeO_3)_3.xH_2SeO_3.nH_2O$.

These compounds were characterised and studied by employing complexometric methods, TG-DTG, and X-ray diffraction powder patterns. The data obtained allowed us to acquire information about the thermal stability of the compounds and of their decomposition products.

* Escola de Farmácia e Odontologia de Alfenas – 37130-000 – EFOA – Alfenas – MG – Brasil.
** Instituto de Ciências Químicas e Farmacêuticas – UNIFENAS – 37130-000 – Alfenas – MG – Brasil.
*** Instituto de Química – UNESP – 14800-900 – Araraquara – SP – Brasil.

Experimental

Selenious acid solution was obtained by dissolving the appropriate amount of selenium dioxide in water. Heavier lanthanides(III) and yttrium(III) hydroxides were prepared by reaction of the aqueous solution of ammonia with an aqueous solution of the corresponding lanthanide or yttrium chloride. The precipitates obtained were washed until elimination of chloride ions.

The compounds were prepared by addition of the aqueous solution of selenious acid, with constant stirring to suspensions of the respective lanthanides or yttrium hidroxides. The precipitates obtained were washed and filtered through sintered glass crucibles and kept in a desiccator over anhydrous calcium chloride until a constant weight was attained.

Lanthanides(III) and yttrium(III) ions were determined in accordance with already described procedures.[4,8] Selenious acid, selenite ions and the water contents of the compounds were determined by TG-DTG curves.

The TG-DTG curves were recorded on a Perkin-Elmer TGA-7 thermogravimetric system. A sample of about 25 mg of each material was put into platinum crucible and heated in air (flow of 20 mL min^{-1}) with a heating rate of 10 $Kmin^{-1}$ at atmospheric pressure.

Diffraction patterns were obtained using HGZ 4/B horizontal diffractometer (Germany) as previously described.[9]

Results and discussion

Table 1 presents the analytical and thermoanalytical data of the prepared compounds of general formula $Ln_2(SeO_3)_3.xH_2SeO_3.nH_2O$, where Ln = Eu – Lu and Y, x = 0.2 – 0.8 and n = 4.0 – 5.0.

The X-ray powder diffraction patterns show that the compounds have a low symmetry crystalline structure and form a isomorphous series. The more characteristic lines obtained by the powder diffraction method are presented in Table 2.

The TG-DTG curves are shown in Figure 1. These curves show mass losses in steps characteristic of each compound.

For the europium compound Figure 1a the thermal decomposition occurs in six consecutive steps between 30°C and 1100°C. The first and second mass losses up to 360°C, that occur through consecutive steps, are due to the dehydration with losses of $2H_2O$ in each step. The third mass loss between 390°C and 480°C is ascribed to the elimination of $0.2H_2SeO_3$. The fourth and fifth steps between 480°C and 800°C are due to the thermal decomposition of the anhydrous europium selenite with formation of the (di) oxyselenite, $Eu_2O_2SeO_3$, an intermediate compound. The last step between 800°C and 1100°C is due to the thermal decomposition of the intermediate to the europium oxide, Eu_2O_3.

Table 1 – Analytical and thermoanalytical results

Compound	Lanthanide (%)			Selenium (%)		Selenious acid (%)		Water (%)	
	Calcd.	TG	EDTA	Calcd.	TG	Calcd.	TG	Calcd.	TG
$Eu_2A_3 0.2B.4H_2O$	38.83	39.24	39.20	30.27	30.13	3.30	3.25	9.21	9.34
$Gd_2A_3 0.6B.4.5H_2O$	36.83	36.68	36.60	27.74	27.67	9.06	9.23	9.50	9.48
$Tb_2A_3 0.6B.5H_2O$	36.69	37.28	37.40	27.35	26.98	8.93	9.99	10.40	10.45
$Dy_2A_3 0.8B.5H_2O$	36.14	36.54	36.23	26.34	26.03	11.48	11.20	10.02	10.30
$Ho_2A_3 0.4B.4.5H_2O$	39.11	39.84	38.40	28.09	27.99	6.12	6.06	9.61	9.72
$Er_2A_3 0.5B4.5H_2O$	38.85	39.52	38.47	27.51	27.50	7.49	7.78	9.42	9.24
$Tm_2A_3 0.6B.4.5H_2O$	38.52	38.64	39.19	27.00	26.98	8.82	8.99	9.24	9.28
$Yb_2A_3 0.8B.5H_2O$	37.61	37.89	37.72	25.74	25.60	11.20	11.18	9.79	9.72
$Lu_2A_3 0.7B.4.5H_2O$	39.79	39.85	39.89	26.26	26.19	10.01	9.72	8.99	8.97
$Y_2A_3 0.7B.4.5H_2O$	24.36	24.74	24.89	32.45	32.51	12.37	12.15	11.11	11.18

Key: A means selenite; B means selenious acid.

Table 2 – X-ray powder patterns of the hydrated heavier lanthanides and yttrium contend selenious acid

Eu		Gd		Tb		Dy		Ho		Er		Tm		Yb		Lu		Y	
d(■)	I/I_o	d(■)	I/I_o	d(■)	I/Io	d(■)	I/Io	d(■)	I/Io	d(■)	I/Io	d(■)	I/Io	d(■)	I/Io	d(■)	I/Io	d(■)	I/Io
8.13	10	8.03	10	8.03	10	8.03	10	8.10	10	8.10	10	8.08	10	8.03	10	8.10	10	8.08	10
		6.06	0.5	6.06	1.47	6.06	0.5	6.04	1.2	6.03	1.2	6.02	1.1	6.02	6.8	6.02	1.0	5.18	1.1
4.11	1.4			4.08	4.0	4.06	2.1	4.07	1.0	4.06	2.3	4.05	2.4	4.05	3.0	4.06	2.0		
3.49	1.1	3.40	1.8	3.44	0.7	3.45	1.0	3.46	0.6	3.45	1.2	3.45	1.1	3.45	1.4	3.55	1.3	3.44	1.4
3.42	1.4	3.38	1.2	3.37	1.8	3.38	0.8	3.38	0.5	3.37	1.0	3.36	0.9	3.35	1.0	3.34	4.1	3.36	2.5
2.99	1.1	2.90	0.4	2.94	2.2	2.95	1.2	2.95	0.6	2.94	1.4	2.92	2.0	2.92	0.9	2.92	5.5	2.92	3.0
2.97	1.2	2.89	0.5	2.89	4.0	2.90	1.8	2.90	1.1	2.90	2.0	2.89	2.1	2.88	2.0	2.88	5.5	2.90	1.0
2.73	1.1	2.71	1.5	2.70	1.3	2.71	0.5	2.71	0.5	2.71	1.7	2.71	1.5	2.70	1.0	-	-	2.70	0.9

For the gadolinium compound (Figure 1b) the thermal decomposition also occurs in six steps between 40°C and 1100°C. The first, second and third steps up to 320°C are due to the dehydration with losses of 2.0; 2.0 and $0.5H_2O$ respectively. The fourth step between 370°C and 480°C is ascribed to the elimination of $0.6H_2SeO_3$. The fifth step between 520°C and 800°C is ascribed to the thermal decomposition of the gadolinium selenite with formation of the intermediate (di) oxyselenite, $Gd_2O_2SeO_3$. The last step between 800°C and 1100°C is due to the thermal decomposition of the intermediate to the gadolinium oxide, Gd_2O_3.

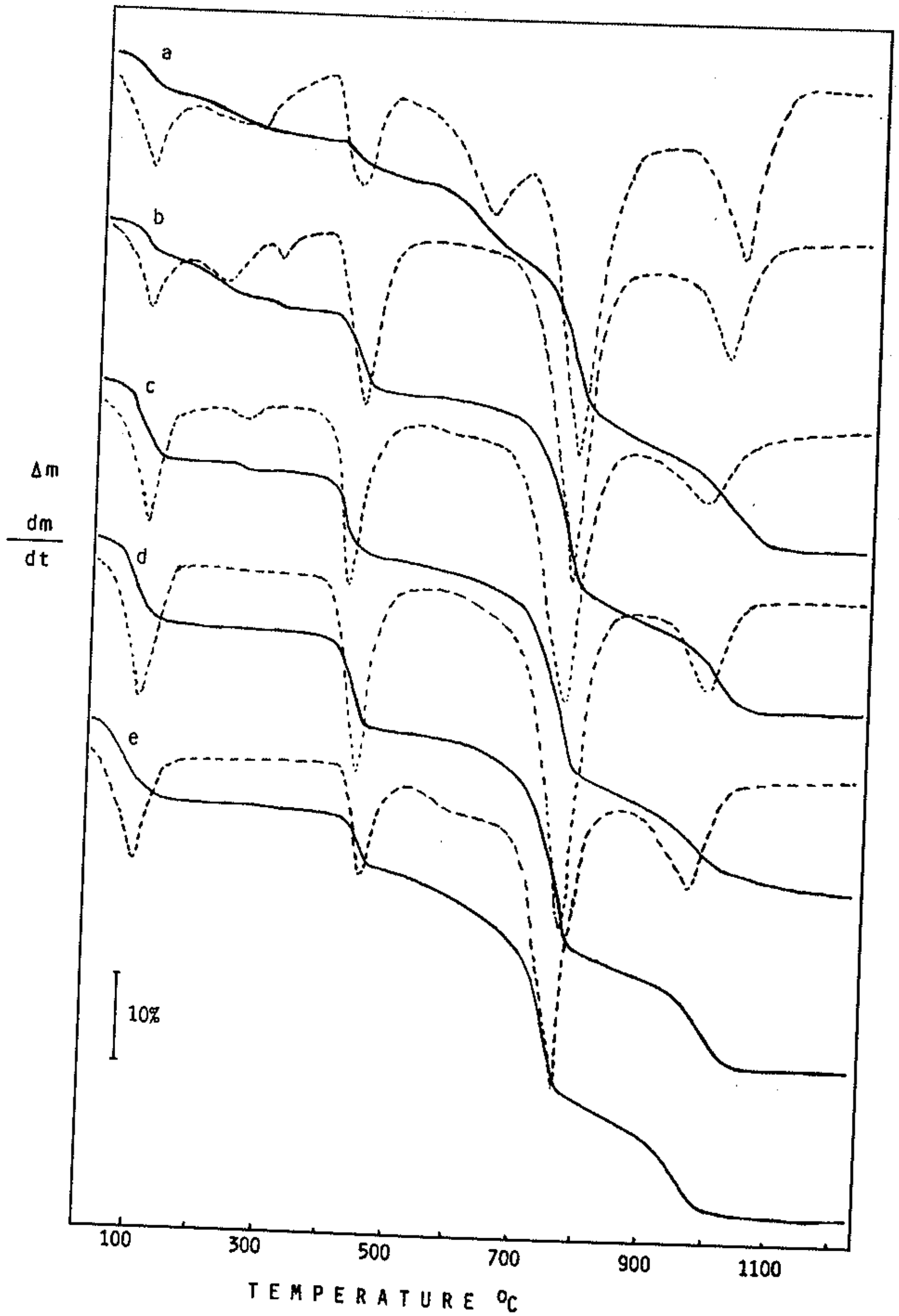

FIGURE 1 – TG-DTG curves of hydrated selenites, contend selenious acid. Heating rate 10°C min^{-1}; air flux ± 20 mL min^{-1}; a) Eu; b) Gd; c) Tb; d) Dy; e) Ho.

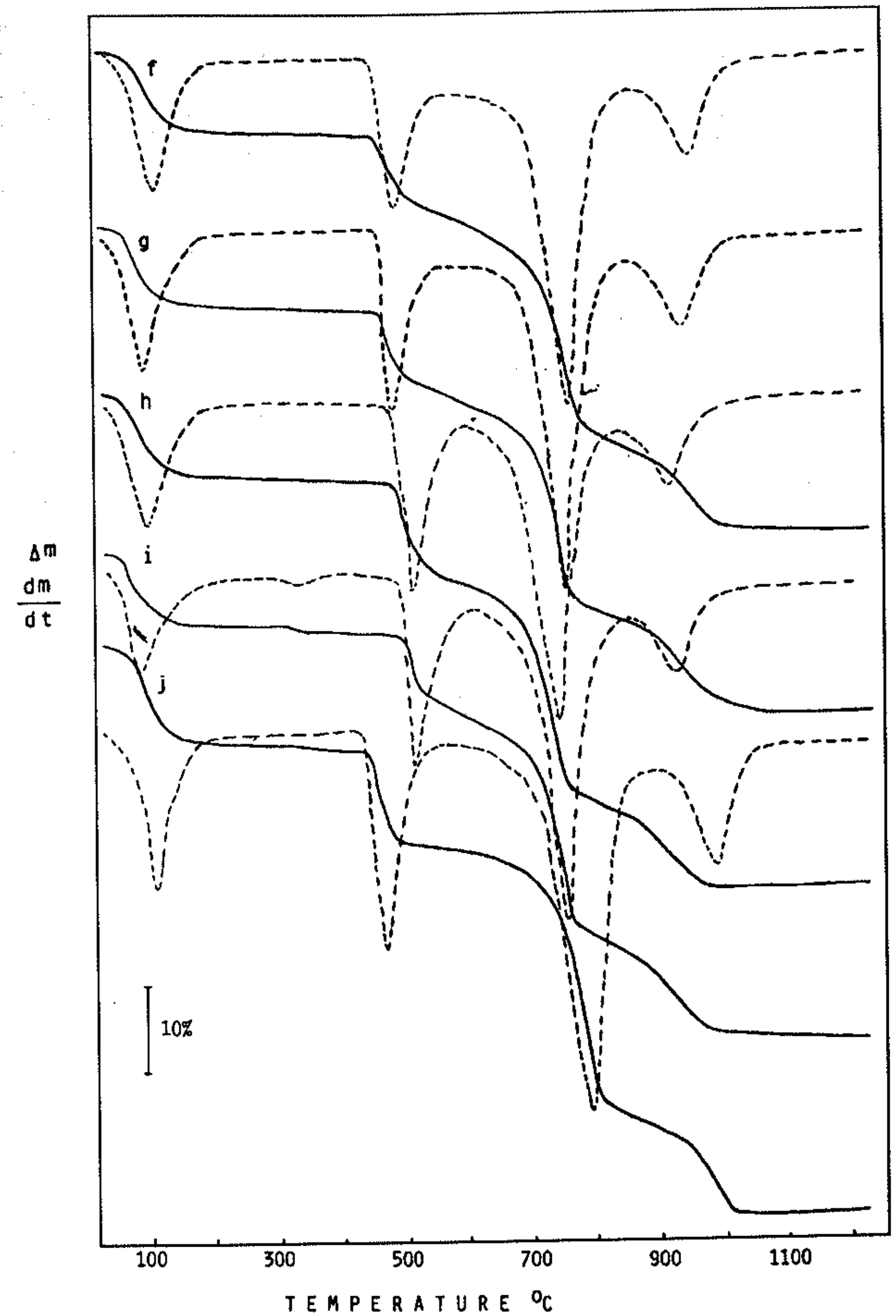

FIGURE 2 – TG-DTG curves of hydrated selenites, contend selenious acid. Heating rate 10°C min^{-1}; air flux ± 20 mL min^{-1}; f) Er; g) Tm; h) Yb; i) Lu and j) Y.

For the terbium and lutetium compounds (Figures 1c and 1i), the thermal decomposition occur in five steps, between 30°C and 1100°C. The first step between 30°C and 150°C (Tb); 40°C and 200°C (Lu) are due to the losses of 4.5 and 4.0H_2O respectively. The second step between 200°C and 290°C (Tb); 250°C and 340°C (Lu) are due to the final dehydration with loss of 0.5H_2O. The third step between 330°C and 490°C (Tb); 450°C and 550°C (Lu) are due to the elimination of 0.6 and 0.7H_2SeO_3 respectively. The fourth step between 490°C and 780°C (Tb); 550°C and 750°C (Lu) are due to the thermal decomposition of the terbium and lutetium selenites with formation of the respectives (di) oxyselenites, $Tb_2O_2SeO_3$ and $Lu_2O_2SeO_3$, as intermediate compounds. The last step between 780°C and 1100°C (Tb); 750°C and 1000°C (Lu) are ascribed to the thermal decomposition of these intermediate compounds to the respective oxide, Tb_4O_7 or Lu_2O_3.

For the other compounds (Dy-Yb and Y), Figures 1d-h and j, the thermal decompositions occur in four steps between 30°C and 1100°C, with the TG-DTG curves showing a great similary. The first mass loss in all curves is due to the dehydration and it occurs in one single step. The second mass loss is ascribed to the elimination of the selenious acid. The third mass loss is due to the thermal decomposition of the anhydrous lanthanide selenites to the (di) oxyselenites. The last mass loss is due to the thermal decomposition of these intermediate compounds to the respective oxides, Ln_2O_3.

The temperature ranges associated with the mass losses observed in the TG-DTG curves are shown in Table 3.

Table 3 – Temperature range (K) and partial mass loss observed in the TG curves

Compound	ΔT(K)	Partial thermal decomposition	Mas loss %	
			Theor.	Exp.
$Eu_2(SeO_3)_3 0.2H_2SeO_3.4H_2O$	30- 120	$2H_2O$	4.60	4.65
	120- 360	$2H_2O$	4.60	4.69
	390- 480	$0.2H_2SeO_3$	3.30	3.25
	480- 800	$2SeO_2$	28.35	28.23
	800-1100	$1SeO_2$	14.18	14.11
$Gd_2(SeO_3)_3 0.6H_2SeO_3.4.5H_2O$	40- 120	$2H_2O$	4.22	4.25
	120- 250	$2H_2O$	4.22	4.21
	250- 320	$0.5H_2O$	1.06	1.02
	370- 480	$0.6H_2SeO_3$	9.06	9.23
	520- 800	$2SeO_2$	25.99	25.93
	800-1100	$1SeO_2$	12.99	12.96

Continuação

Compound	ΔT(K)	Partial thermal decomposition	Mas loss %	
			Theor.	Exp.
$Tb_2(SeO_3)_3 0.6H_2SeO_3.5H_2O$	30- 150	$4.5H_2O$	9.36	9.24
	200- 290	$0.5H_2O$	1.04	1.21
	330- 490	$0.6H_2SeO_3$	8.93	8.99
	490- 780	$2SeO_2$	25.62	25.32
	780-1100	$1SeO_2$	12.81	12.60
$Dy_2(SeO_3)_3 0.8H_2SeO_3.5H_2O$	30- 150	$5H_2O$	10.02	9.97
	340- 490	$0.8H_2SeO_3$	11.48	11.18
	510- 770	$2SeO_2$	24.68	24.66
	770-1100	$1SeO_2$	12.34	12.28
$Ho_2(SeO_3)_3 0.4H_2SeO_3 4.5H_2O$	30- 190	$4.5H_2O$	9.61	9.48
	350- 500	$0.4H_2SeO_3$	6.12	6.31
	500- 790	$2SeO_2$	26.31	26.24
	790-1100	$1SeO_2$	13.16	13.10
$Er_2(SeO_3)_3 0.5H_2SeO_3 4.5H_2O$	40- 190	$4.5H_2O$	9.42	9.24
	400- 520	$0.5H_2SeO_3$	7.49	7.78
	520-780	$2SeO_2$	25.78	25.82
	780-1050	$1SeO_2$	12.8	12.82
$Tm_2(SeO_3)_3 0.6H_2SeO_3 4.5H_2O$	30- 190	$4.5H_2O$	9.24	9.28
	400- 540	$0.6H_2SeO_3$	8.82	8.99
	540- 770	$2SeO_2$	25.30	25.42
	770-1050	$1SeO_2$	12.65	12.50
$Yb_2(SeO_3)_3 0.8H_2SeO_3 5H_2O$	30- 190	$5H_2O$	9.79	9.72
	400- 530	$0.8H_2SeO_3$	11.21	11.18
	530- 720	$2SeO_2$	24.11	23.97
	720-1000	$1SeO_2$	12.06	12.00
$Lu_2(SeO_3)_3 0.7H_2SeO_3 4.5H_2O$	40- 200	$4H_2O$	7.99	8.00
	250- 340	$0.5H_2O$	1.00	0.97
	450- 550	$0.7H_2SeO_3$	10.01	9.72
	550- 750	$2SeO_2$	24.60	24.57
	750-1000	$1SeO_2$	12.30	12.23
$Y_2(SeO_3)_3 0.7H_2SeO_3 4.5H_2O$	30- 180	$4.5H_2O$	11.11	11.18
	380- 500	$0.7H_2SeO_3$	12.37	12.15
	520- 800	$2SeO_2$	30.40	30.36
	800-1100	$1SeO_2$	15.20	15.33

Calculations based on the mass losses observed in the TG curves are consistent with the following thermal decomposition mechanisms:

$Ln_2(SeO_3)_3.xH_2SeO_3.nH_2O \rightarrow Ln_2(SeO_3)_3.xH_2SeO_3 + nH_2O$

$Ln_2(SeO_3)_3.xH_2SeO_3 \rightarrow Ln_2(SeO_3)_3 + xH_2SeO_3$

$Ln_2(SeO_3)_3 \rightarrow Ln_2O_2SeO_3 + 2SeO2$

$Ln_2O_2SeO_3 \rightarrow Ln_2O_3 + SeO_2$

(In the case of Tb, Tb_4O_7 is the final residue)

Concluding remarks

The method used for the preparation of the investigated compounds do not permitted to obtain compounds with the general formula $Ln_2(SeO_3)_3.nH_2O$, but compounds contend selenious acid.

The TG-DTG curves established the stoichiometry of the compounds and also provided information about the thermal stability of the compounds and that of the intermediate compounds.

Acknowledgements

The authors are thankful to FAPESP (Proc. 90/2932-4) and CNPq (Proc. 30.0610/92-0 and 80.0238/92-3).

D'ASSUNÇÃO, L. M., DA COSTA, M. R., IONASHIRO, M. Termodecomposição de selenitos de lantanídeos mais pesados e ítrio hidratados, contendo ácido selenioso. *Ecl. Quím. (São Paulo)*, v.20, p.69-77, 1995.

■ *RESUMO: Foram preparados selenitos de lantanídeos mais pesados e ítrio, contendo ácido selenioso. Na caracterização, bem como no estudo da decomposição térmica desses compostos, foram utilizados termogravimetria e termogravimetria derivada (TG-DTG), difração de raios X e outros métodos de análise. Os resultados levaram à obtenção da composição e estabilidade térmica dos compostos. É proposto um mecanismo para a termodecomposição dos compostos sintetizados.*

■ *PALAVRAS-CHAVE: Lantanídeos mais pesados; ítrio; selenitos; decomposição térmica.*

References

1 GIESBRECHT, E., GIOLITO, I. Thermal decomposition of the selenites of some rare earth elements. II – yttrium, cerium, terbium, dysprosium, holmium, erbium, thulium, ytterbium and lutetium selenites. *An. Acad. Bras. Ciênc.*, v.39, p.233-9, 1967.

2 GIESBRECHT, E., PERRIER, M., WENDLANDT, W. W. Thermal decomposition of the selenites of some rare earth elements. *An. Acad. Bras. Ciênc.*, v.34, p.37-43, 1962.

3 GIESBRECHT, E., VICENTINI, G., BARBIERI, L. Complex selenites of rare earth elements. *An. Acad. Bras. Ciênc.*, v.40, p.453-9, 1968.

4 IONASHIRO, M. et al. Thermal decomposition of hydrated selenites of trivalent lanthanides and yttrium. *Thermochim. Acta*, v.168, p.223-32, 1990.

5 MAIER, A. I., SUPONITSKII, Yu. I., KARAPET'YANTS, M. Kh. Thermal decomposition of selenites of rare earth elements, scandium and yttrium. *Khim. Khim.Tekhnol.*, v.14, p.3-7, 1971.

6 MARKOVSKII, L. Ya., SAFINA, R. A. Composition and thermal stability of lanthanum selenites. *Zh. Prikl. Khim.*, v.41, p.693, 1968.

7 ______ . Thermal stability of selenites of Ce(IV) and Ce(III). *Zh. Prikl. Khim.*, v.41, p.2537-40, 1968.

8 OLIVEIRA, C. N., IONASHIRO, M., GRANER, C. A. F. Titulação complemétrica de zinco, cobre e cobalto. *Ecl. Quím.*, v.10, p.7-10, 1985.

9 SAVCHENKO, G. S., TANANAEV, I. V., VOLODINA, A. N. Formation composition and thermal properties of selenites of some rare earth elements and yttrium. *Neorg. Mater.*, v.4, p.1097-107, 1968.

10 SUPONITSKII, Yu. L. et al. Thermal decomposition of corium, praseodymium and neodymium selenites. *Tr. Mosk. Khim. Tekhnol. Inst.*, v.54, p.27-9, 1967.

Recebido em 15.2.1995.
Aceito em 28.3.1995.