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Note

STUDIES ON DOUBLE SELENATES. XI. THERMAL DECOMPOSITION OF LANTHANIDES OF THE CERIC GROUP AND LITHIUM DOUBLE SELENATES

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A previous communication [1] described the preparation of the double selenates of lanthanum and the alkali metals; the La–Li compound has the formula $La_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 8H_2O$. Subsequent reports [2–4] have shown that it was not possible to prepare the Ce–Li, Pr–Li, Nd–Li and Sm–Li double selenates, using the same method [1].

It was possible to isolate the double selenates of all the ceric group lanthanides and lithium not previously described and, also, a La–Li double selenate having a different stoichiometry, using a modified preparation technique.

EXPERIMENTAL

Selenic acid [5] and the hydrated basic carbonates of La–Sm [6] were prepared as described previously. The double selenates were prepared by mixing each hydrated basic carbonate of the ceric group lanthanide with analytical grade lithium carbonate in a molar proportion of 1 : 2. These mixtures were suspended in hot water and were treated with a 25% (v/v) aqueous solution of recently prepared selenic acid to almost total solubilization.

The solutions, still containing a small residue of undissolved carbonates, were filtered through finely porous sintered glass crucibles. The clear filtrates were evaporated in a steam bath to near-dryness and the crystals formed

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were removed from the mother liquor and kept in a dessicator over anhydrous calcium chloride until a constant weight was attained.

Lanthanide ions were determined by complexometric titrations with EDTA standard solution, using xylenol orange as an indicator [7,8], and also by thermogravimetric (TG) curves and gravimetric data obtained by heating the samples in a muffle furnace. Lithium ions were determined by flame emission photometry in a Corning model 400 flame photometer.

The water of crystallization was determined from the TG curves. Selenium contents were determined from the TG curves and from the gravimetric data obtained by heating the samples in a muffle furnace.

The TG curves were obtained in a Perkin–Elmer thermobalance model TGS-2 equipped with a furnace operating from ambient temperature up to 900 °C. Samples of about 8 mg were placed in a 0.2 ml platinum crucible and heated at a rate of 20.0 °C min^{-1}, in a dynamic air atmosphere at ambient pressure, using a recorder speed of 5 mm min^{-1}.

The differential thermal analysis (DTA) curves were obtained in a RB-12 DTA system from BP-Engenharia Indústria e Comércio Ltda (São Paulo, Brazil) equipped with a furnace operating from ambient temperature up to 1200 °C. Chromel–alumel differential thermocouples and a block thermocouple protected by nickel tubes were used. α-Alumina was used as the reference material. The samples were diluted to 40% (m/m) in α-alumina, and about 400 mg of these dilutions and of the reference material were tightly and homogeneously packed in the cylindrical holes of the nickel block of the specimen-holder assembly. The heating rate was 10.0 °C min^{-1} under a static air atmosphere and ambient pressure using a recorder speed of 2.5 mm min^{-1}.

The X-ray powder diffraction patterns were obtained in a HGZ 4/B horizontal diffractometer in a Bragg–Brentano arrangement using Cu $K\alpha$ radiation ($\lambda = 1.541$ Å), with proportional counter and pulse-height discriminator.

RESULTS AND DISCUSSION

The analytical and thermoanalytical (TG) data of Table 1 show that the compounds prepared had a content of lithium selenate a little higher than the molar stoichiometry of 1 : 1 observed in the lanthanides of the yttrium group and the lithium double selenate reported previously [9–12]. The higher contents of lithium selenate in these double selenates probably result from the molar proportion of lithium carbonate being double that of the La, Ce, Pr, Nd and Sm hydrated basic carbonates. It has already been mentioned that only in the case of lanthanum was it possible to crystallize a double selenate hydrate by using equimolar solutions of lithium selenate and of the ceric group lanthanide selenate.

TABLE 1

Analytical and thermoanalytical (TG) results

Compound	Lanthanides (%)			Lithium (%)		Selenium (%)		Water (%)	
	Theoretical	Experimental		Theoretical	Experimental flame emission photometry	Theoretical	Experimental TG	Theoretical	Experimental TG
		TG	EDTA titration						
$La_2(SeO_4)_3 \cdot 1.2Li_2SeO_4 \cdot 18H_2O$	22.79	22.53	22.36	1.37	1.34	27.20	28.65	26.60	26.74
$Ce_2(SeO_4)_3 \cdot 1.4Li_2SeO_4 \cdot 25H_2O$	20.32	19.00	20.33	1.41	1.43	25.19	25.16	32.66	32.72
$Pr_2(SeO_4)_3 \cdot 1.4Li_2SeO_4 \cdot 22H_2O$	21.24	22.48	20.60	1.46	1.41	26.19	26.48	29.88	29.85
$Nd_2(SeO_4)_3 \cdot 1.2Li_2SeO_4 \cdot 20H_2O$	22.79	23.13	22.61	1.32	1.30	26.20	25.90	29.47	29.23
$Sm_2(SeO_4)_3 \cdot 1.3Li_2SeO_4 \cdot 20H_2O$	23.24	23.17	24.14	1.39	1.47	26.24	25.45	27.85	28.69

TABLE 2

X-ray powder diffraction patterns data of the double selenates of the ceric group lanthanides and lithium

La–Li 1:1.2		Ce–Li 1:1.4		Pr–Li 1:1.4		Nd–Li 1:1.2		Sm–Li 1:1.3	
I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)
10	8.03	10	8.03	10	8.84	10	8.72	10	8.84
1.18	4.92	2.39	4.86	1.29	3.90	0.22	6.65	0.84	4.41
2.36	3.53	1.94	4.31	1.84	3.77	0.40	4.61	0.66	3.86
6.92	3.46	4.03	3.46	1.06	3.68	0.95	4.43	1.07	3.77
3.84	3.20	5.97	3.18	1.11	3.48	0.70	3.91	0.67	3.24
0.91	2.97	3.58	2.95	1.11	3.27	1.39	3.78	1.23	2.95
0.55	2.86	4.92	2.85	2.95	2.87	0.84	3.27	1.25	2.86
0.51	2.69			1.38	2.73	0.84	2.95	0.85	2.72
				0.55	2.29	1.92	2.88		
						1.17	2.73		

The data given in Table 1 also show that the results of complexometric titrations of the lanthanide ions are in agreement with the data obtained from the TG curves.

The X-ray powder diffraction data given in Table 2 suggest that all compounds described in the present report form an isomorphous series.

The TG curves shown in Fig. 1 and the analytical data given in Table 1 show that all double selenates have a high degree of hydration. The loss of the first water molecule starts at 100 ° C and the dehydration process continues up to 325 ° C (450 ° C in the case of the La–Li compound), the last water molecule being lost very slowly. The first mass losses in the TG curves for the Pr–Li, Nd–Li and Sm–Li double selenates also show the formation of unstable intermediate hydrates.

The thermal decomposition of all anhydrous double selenates starts at about 570 ° C, except in the case of the Ce–Li double selenate: the mass loss ocurring between 580–720 ° C is due to the thermal decomposition of cerium(III) selenate to cerium(IV) oxide.

The anhydrous La–Li double selenate$_2$ undergoes the following thermal decomposition between 580 ° C and 720 ° C: the lanthanum selenate decomposes to lanthanum (di)oxyselenite with simultaneous reduction of lithium selenate to lithium selenite. The final leveling, corresponding to the residue $La_2O_2SeO_3 \cdot Li_2SeO_3$, is not visible in the TG curves because these reactions end at a temperature higher than 900 ° C.

After dehydration the other double selenates undergo thermal decomposition in two steps: the first is the formation of the corresponding (di)oxyselenite with simultaneous reduction of lithium selenate to lithium selenite, and the second is the decomposition of these intermediate lanthanide compounds to the corresponding oxides.

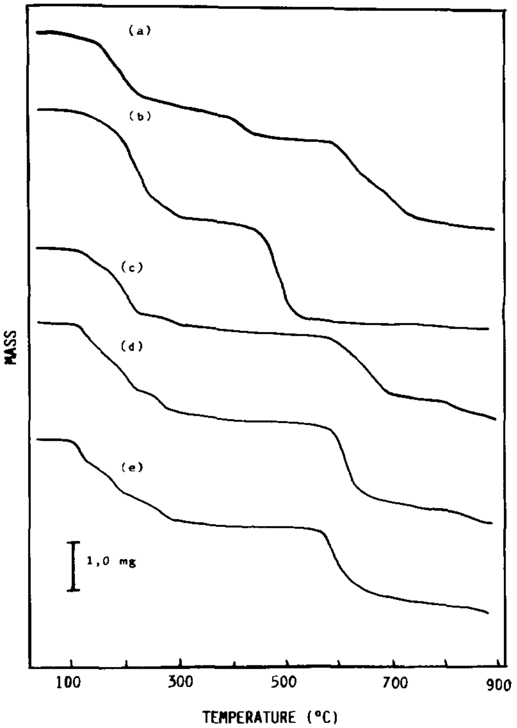

Fig. 1. TG curves for the double selenates (heating rate 20°C min^{-1}): (a) $La_2(SeO_4)_3 \cdot 1.2Li_2SeO_4 \cdot 18H_2O$, (8.44 mg); (b) $Ce_2(SeO_4)_3 \cdot 1.4Li_2SeO_4 \cdot 25H_2O$, (7.64 mg); (c) $Pr_2(SeO_4)_3 \cdot 1.4Li_2SeO_4 \cdot 22H_2O$, (6.70 mg); (d) $Nd_2(SeO_4)_3 \cdot 1.2Li_2SeO_4 \cdot 20H_2O$, (6.04 mg); and (e) $Sm_2(SeO_4)_3 \cdot 1.3Li_2SeO_4 \cdot 20H_2O$, (6.97 mg).

Samples of all double selenates were heated in small platinum crucibles in a muffle furnace up to 1150°C and mantained at that temperature for 30 min. The final residue was formed by the corresponding oxides (Ln_2O_3, CeO_2 and Pr_6O_{11}) showing that lithium selenite (or lithium oxide) underwent total thermal decomposition without leaving a residue, even in the case of the La–Li compound. In a previous report [1] the residue of the La–Li double selenate at 1160°C contained La_2O_3 and about 70% of the theoretical amount of Li_2O.

All double selenates described in the present note were also heated in porcelain crucibles in a muffle furnace at 1150°C for 30 min. It was observed, except for the Ce–Li compound, that the intermediate compounds having the formula $Ln_2O_2SeO_3 \cdot Li_2SeO_3$ persisted unchanged as final residues, probably because of the interactions of those substances with the enamel used in the vitrification of the porcelain crucibles. In the case of the Pr–Li compound, the samples heated at 1150°C for 30 min still had the characteristic green colour of the Pr^{III} ion with no evidence of the black oxide Pr_6O_{11}. In all cases the final masses corresponded to mixtures of

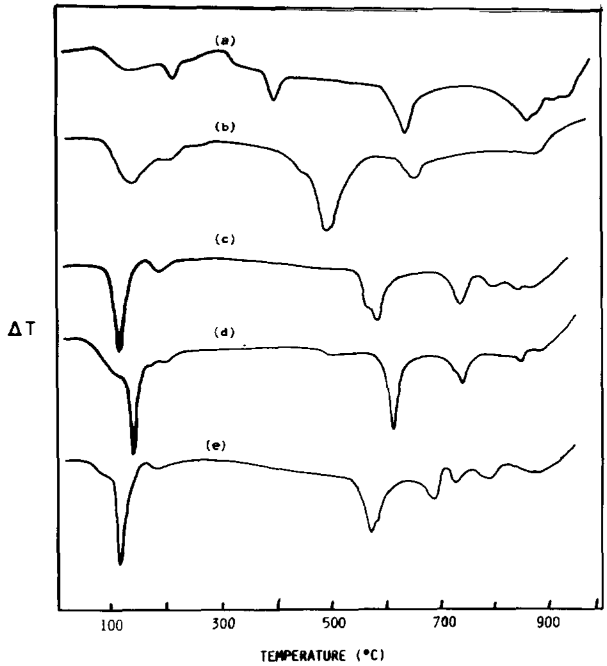

Fig. 2. DTA curves for the double selenates, diluted to 40% in α-alumina (heating rate 10 °C min^{-1}): (a) $La_2(SeO_4)_3 \cdot 1.2Li_2SeO_4 \cdot 18H_2O$; (b) $Ce_2(SeO_4)_3 \cdot 1.4Li_2SeO_4 \cdot 25H_2O$; (c) $Pr_2(SeO_4)_3 \cdot 1.4Li_2SeO_4 \cdot 22H_2O$; (d) $Nd_2(SeO_4)_3 \cdot 1.2Li_2SeO_4 \cdot 20H_2O$; and (e) $Sm_2(SeO_4)_3 \cdot 1.3Li_2SeO_4 \cdot 20H_2O$.

lanthanide (di)oxyselenites with lithium selenite. In the case of the Ce–Li compound the final residue was a mixture of cerium(IV) oxide and lithium selenite.

The endothermic peaks of the DTA curves shown in Fig. 2 up to 400 °C can be attributed to the dehydration processes. After dehydration, the endothermic peaks correspond with the mass losses observed in the TG curves.

The data obtained from the TG and DTA curves, and also those obtained by heating the sample in platinum crucibles in a muffle furnace, permit the suggestion that the reactions occurring during the heating of these compounds can be summarized by the following groups of equations.

Group I

$$Ln_2(SeO_4)_3 \cdot xLi_2SeO_4 \cdot nH_2O \rightarrow Ln_2(SeO_4)_3 \cdot xLi_2SeO_4 + nH_2O$$
$$Ln_2(SeO_4)_3 \cdot xLi_2SeO_4 \rightarrow Ln_2O_2SeO_3 \cdot xLi_2SeO_3 + 2SeO_2 + (1.5 + x)O_2$$
$$Ln_2O_2SeO_3 \cdot xLi_2SeO_3 \rightarrow Ln_2O_3 \cdot xLi_2SeO_3$$
$$Ln_2O_3 \cdot Li_2SeO_3 \rightarrow Ln_2O_3 + [xLi_2SeO_3]$$

Ln ≡ La, Pr, Nd or Sm; Ln_2O_3 ≡ La, Nd or Sm; Pr ≡ Pr_6O_{11}; $x = 1.2$ (La–Li, Nd–Li), 1.3 (Sm–Li) or 1.4 (Pr–Li).

Group II

$$Ce_2(SeO_4)_3 \cdot 1.4Li_2SeO_4 \cdot nH_2O \rightarrow Ce_2(SeO_4)_3 \cdot 1.4Li_2SeO_4 + nH_2O$$

$$Ce_2(SeO_4)_3 \cdot 1.4Li_2SeO_4 \rightarrow 2CeO_2 \cdot 1.4Li_2SeO_4 + 3SeO_2$$

$$2CeO_2 \cdot 1.4Li_2SeO_4 \rightarrow 2CeO_2 \cdot 1.4Li_2SeO_3 + 0.7O_2$$

$$2CeO_2 \cdot 1.4Li_2SeO_3 \rightarrow 2CeO_2 + [1.4Li_2SeO_3]$$

CONCLUDING REMARKS

The technique used in the preparation of the double selenates of the ceric group lanthanides and lithium has led to the formation of compounds having a higher lithium selenate content.

The thermal behaviour of these compounds, not yet described, is quite similar to that of the double selenates of the yttric group lanthanides and lithium already reported.

Each compound can be characterized by the simultaneous examination of its TG and DTA curves.

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