Studies on double selenates.
Part 12. Thermal decomposition of ammonium selenate and of double selenates of lanthanide, and yttrium, and ammonium

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(Received 30 June 1993; accepted 10 December 1993)

Abstract

Thermogravimetry (TG) up to 900°C, differential thermal analysis (DTA) up to 1100°C and gravimetric data up to 1200°C, have been used to study the thermal decomposition of ammonium selenate and of the double selenates of lanthanides, and yttrium, and ammonium. The results provided the composition and thermal stability and also an interpretation of the thermal decomposition mechanisms.

INTRODUCTION

Several investigations have been carried out on the preparation and characterization of the double selenates of lanthanum, samarium, dysprosium, erbium, and yttrium, and ammonium [1, 2], and of cerium and ammonium [3]. The preparation and thermoanalytical studies of the lanthanum to gadolinium and ammonium double selenates have also been reported [4–7]. We have found no reference in the literature to the preparation and thermal decomposition of terbium, thulium, ytterbium, and lutetium, and ammonium double selenates. The present paper is primarily an extension of the work reported in refs. 4–7, including all lanthanide and ammonium double selenates, and also a part of our comprehensive study of the double selenates already described [8–18].

EXPERIMENTAL

Ammonium selenate was prepared from a solution of selenic acid neutralized with a solution of ammonia until a pH of 8.5 was reached. The selenic acid and the lanthanide and yttrium selenates were prepared as described

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previously [19]. The double selenates were prepared by mixing equimolar proportions of the corresponding lanthanide and yttrium selenates with ammonium selenate solution, and allowing the mixture to evaporate, as already described [8].

The lanthanide and yttrium ions were determined by complexometric titrations with EDTA standard solutions, using xylenol orange as an indicator [20, 21] and from the TG curves. The selenium contents were determined by the iodometric method [22] and from the furnace and TG curves. Ammonium and water of crystallization contents were determined from the TG curves.

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 $5 \ mm \ min^{-1}$ [9].

The differential thermal analysis (DTA) curves were obtained in an 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 $2.5 \ mm \ min^{-1}$ [9].

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds prepared, of formulae $Ln_2(SeO_4)_3 \cdot y(NH_4)_2SeO_4 \cdot nH_2O$, where Ln is lanthanide and yttrium, $y = 1–1.5$, and $n = 0–6$.

The TG and DTA curves for anhydrous ammonium selenate are shown in Fig. 1. The TG curve shows a mass loss in two steps between 200 and 400°C. The first step occurring up to 280°C is due to the thermal decomposition of the compound with the formation of Se (grey), Se (red), and SeO_2, and it was observed in the sample heated up to the temperature indicated by the TG curves. The second mass loss between 280 and 400°C is due to the sublimation of the grey selenium.

The first endothermic peak at 140°C observed in the DTA curve is due to the fusion of the compound. The sharp exotherm with two peaks at 285 and 300°C is ascribed to the thermal decomposition of the anhydrous ammonium selenate, and the large exotherm between 320 and 530°C, with a peak at 500°C, is ascribed to the sublimation of grey selenium. The attribution of

TABLE 1

Gravimetric (Gr), thermogravimetric (TG), complexometric and iodometric results of the compounds $Ln_2X_3 \cdot y(NH_4)_2X \cdot nH_2O$; X is SeO_4, $y = 1–1.5$, $n = 0–6$

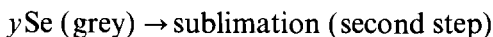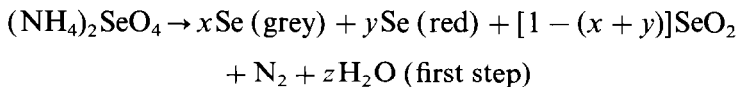| Compound	Lanthanides/%			Selenium/%			Ammonium/%		Water/%	
	Calcd.	Gr	EDTA	Calcd.	Gr	EDTA	Calcd.	TG	Calcd.	TG
$La_2X_3 \cdot (NH_4)_2X \cdot 4H_2O$	29.00	28.97	29.32	32.97	32.92	32.11	3.76	3.75	7.53	7.7
$Ce_2X_3 \cdot (NH_4)_2X \cdot 3.5H_2O$	29.46	29.69	30.12	32.20	32.43	32.01	3.80	3.72	6.63	6.8
$Pr_2X_3 \cdot (NH_4)_2X \cdot H_2O$	31.04	31.18	31.39	34.79	34.76	34.84	3.98	4.00	1.99	2.1
$Nd_2X_3 \cdot (NH_4)_2X \cdot H_2O$	30.94	30.91	30.78	33.87	33.78	33.08	3.87	3.84	3.87	4.1
$Sm_2X_3 1.3(NH_4)_2X \cdot H_2O$	30.67	30.58	30.59	34.63	34.56	34.81	4.79	4.86	1.84	2.0
$Eu_2X_3 \cdot (NH_4)_2X \cdot 6H_2O$	29.80	29.59	29.65	30.97	30.88	30.82	3.54	3.70	10.60	10.7
$Gd_2X_3 \cdot (NH_4)_2X \cdot 5H_2O$	31.06	31.29	31.40	31.19	31.15	31.32	3.57	3.52	8.90	8.7
$Tb_2X_3 \cdot (NH_4)_2X \cdot 5H_2O$	31.29	31.30	30.98	31.09	31.23	30.90	3.56	3.59	8.86	8.5
$Dy_2X_3 \cdot (NH_4)_2X \cdot 5H_2O$	31.77	31.83	31.60	30.87	31.15	31.62	3.52	3.41	8.81	8.5
$Ho_2X_3 \cdot (NH_4)_2X$	35.17	35.16	35.42	33.68	33.58	33.34	3.85	3.97	–	–
$Er_2X_3 1.5(NH_4)_2X \cdot 4H_2O$	30.30	30.53	29.95	32.18	32.24	32.12	4.90	5.05	6.53	6.3
$Tm_2X_3 1.25(NH_4)_2X$	34.11	34.46	33.78	33.88	33.57	33.75	4.56	4.61	–	–
$Yb_2X_3 1.4(NH_4)_2X$	33.74	33.41	33.50	33.87	34.05	33.12	4.93	5.00	–	–
$Lu_2X_3 1.4(NH_4)_2X$	33.99	33.82	33.75	33.75	33.97	33.47	4.91	4.79	–	–
$Y_2X_3 \cdot (NH_4)_2X \cdot 4.5H_2O$	20.51	20.43	20.04	36.44	36.67	36.82	4.16	4.10	9.35	9.2
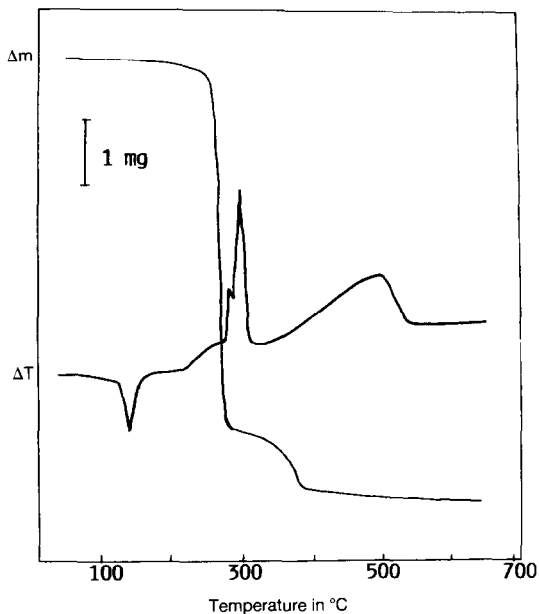
Fig. 1. TG and DTA curves of anhydrous ammonium selenate: m_i, 6.93 mg; heating rate, 20°C min^{-1}; air flow, ≈ 5 cm^3 min^{-1}.

the last exothermic peak at 500°C is in disagreement with the interpretation reported by Nabar and Paralkar [7].

The data obtained from the TG and DTA curves of the ammonium selenate suggest that the reactions occurring during the heating can be summarized by the equations

$$(NH_4)_2SeO_4 \rightarrow x\,Se\,(grey) + y\,Se\,(red) + [1 - (x + y)]SeO_2$$

$$+ N_2 + z\,H_2O \text{ (first step)}$$

$$y\,Se\,(grey) \rightarrow \text{sublimation (second step)}$$

This is in agreement with the literature data concerning the pyrolysis of ammonium selenate [23] and the decomposition of ammonium hydro-selenate [24].

The TG curves for the lanthanide, and yttrium, and ammonium double selenates are shown in Fig. 2. These curves show mass losses in three, four or five steps up to 900°C. The final thermal decomposition for all the compounds, except for the cerium and ammonium double selenate, was obtained in the furnace up to 1200°C.

For the lanthanum and ammonium double selenate (Fig. 2, curve a), the mass loss occurs in four steps. The first mass loss between 50 and 190°C is due to dehydration with losses of $4H_2O$. The second mass loss between 240 and 500°C is due to the thermal decomposition of the anhydrous compound, with the loss of ammonium selenate. The third step between 500 and

860°C is ascribed to the thermal decomposition of lanthanum selenate to (di)oxyselenite, $La_2O_2SeO_3$, as intermediate. The last mass loss (furnace) is due to the thermal decomposition of the intermediate to lanthanum oxide, La_2O_3.

For the cerium and ammonium double selenate (Fig. 2, curve b), the thermal decomposition occurs in three steps. The first step, between 50 and 200°C, is due to dehydration with the loss of $3.5H_2O$. The second step between 240 and 360°C is ascribed to the thermal decomposition of the anhydrous compound, with loss of ammonium selenate. The third step between 360 and 800°C is due to the thermal decomposition of cerium(III) selenate to cerium(IV) oxide, CeO_2.

For the praseodymium, and neodymium, and ammonium double selenates (Fig. 2, curves c and d), the mass losses occur in four steps. The first
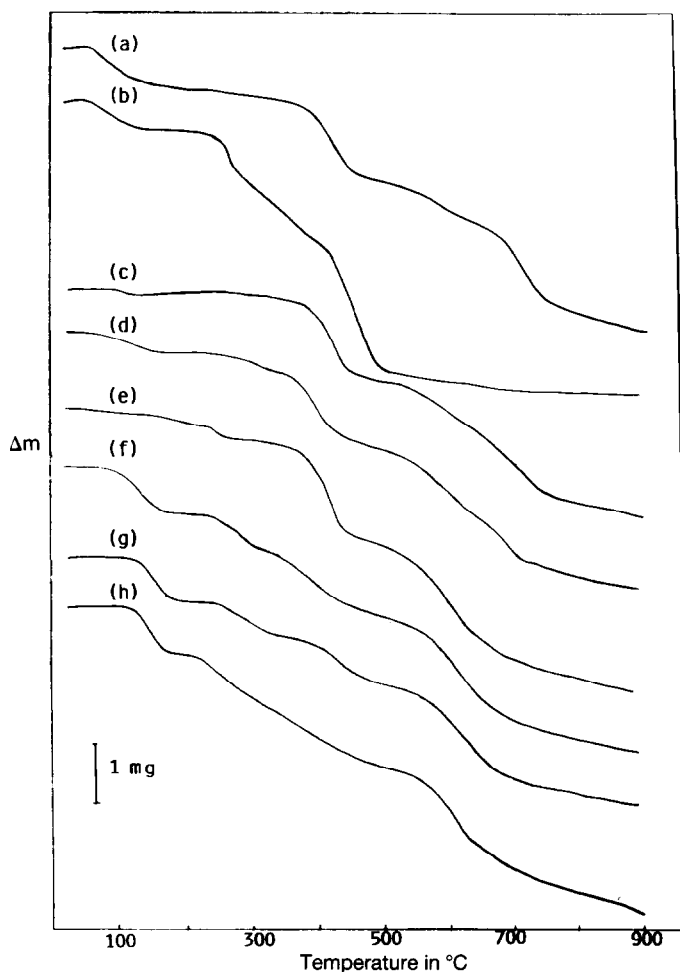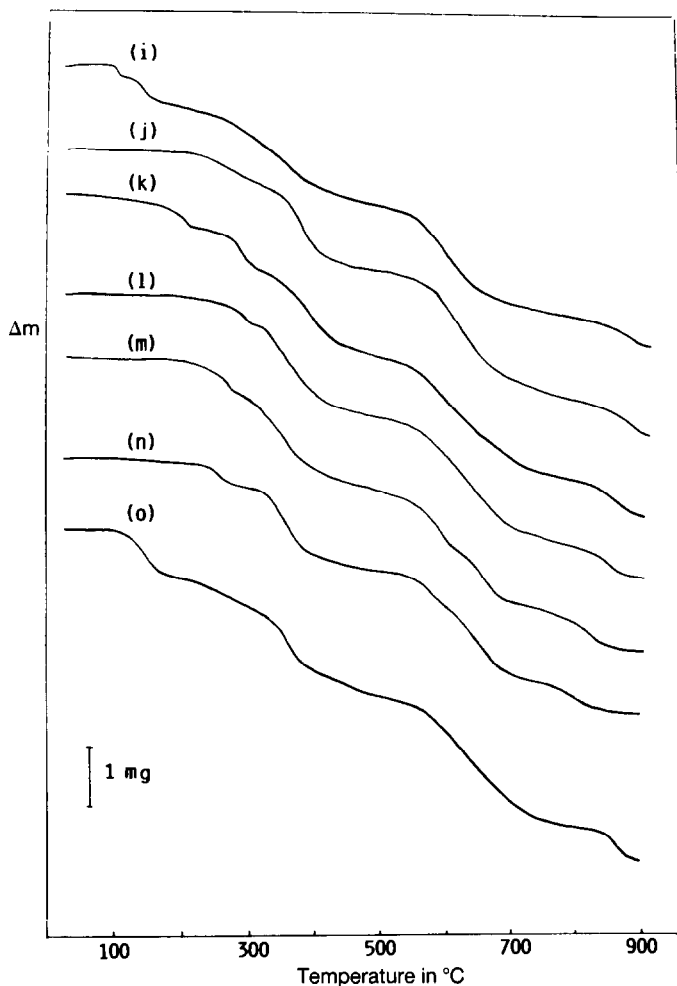

Fig. 2(a).

Fig. 2(b).

Fig. 2. TG curves for the double selenates: heating rate, 20°C min^{-1}; air flux, ≈ 5 cm^3 min^{-1}; platinum crucible. (a) La NH$_4$ (7.80 mg); (b) Ce–NH$_4$ (7.32 mg); (c) Pr–NH$_4$ (7.30 mg); (d) Nd–NH$_4$ (7.35 mg); (e) Sm–1.3NH$_4$ (7.67 mg); (f) Eu–NH$_4$ (7.91 mg); (g) Gd–NH$_4$ (7.43 mg); (h) Tb–NH$_4$ (8.15 mg); (i) Dy–NH$_4$ (7.09 mg); (j) Ho–NH$_4$ (7.87 mg); (k) Er–1.5NH$_4$ (7.99 mg); (l) Tm–1.25NH$_4$ (8.74 mg); (m) Yb–1.4NH$_4$ (8.07 mg); (n) Lu–1.4NH$_4$ (7.15 mg); and (o) Y–NH$_4$ (7.63 mg).

step between 50 and 140°C (Pr–NH$_4$), and between 50 and 150°C (Nd–NH$_4$), is due to the dehydration with losses of 1H$_2$O and 2H$_2$O, respectively. The second step between 270 and 480°C (Pr–NH$_4$), and between 240 and 460°C (Nd–NH$_4$), is due to the thermal decomposition of the anhydrous compounds, with loss of ammonium selenate. The third step between 480 and 810°C (Pr–NH$_4$), and between 460 and 820°C (Nd–NH$_4$), is ascribed to the thermal decomposition of the praseodymium and

neodymium selenate to the respective (di)oxyselenites, $Pr_2O_2SeO_3$ and $Nd_2O_2SeO_3$. The last step between 810 and $>900°C$ (Pr–NH$_4$), and between 820 and $>900°C$ (Nd–NH$_4$) (furnace), is due to the thermal decomposition of (di)oxyselenite to the oxides, Pr_6O_{11} and Nd_2O_3.

For the europium, gadolinum, terbium, and yttrium, and ammonium double selenates (Fig. 2, curves f, g, h and o), the mass losses also occur in four steps. The first step between 70 and 180°C (Eu–NH$_4$), between 120 and 180°C (Gd–NH$_4$), between 130 and 180°C (Tb–NH$_4$), and between 90 and 170°C (Y–NH$_4$), is due to dehydration with losses of $6H_2O$, $5H_2O$, $5H_2O$, and $4.5H_2O$, respectively. The second mass loss between 220 and 440°C (Eu–NH$_4$), between 220 and 480°C (Gd–NH$_4$), between 200 and 420°C (Tb–NH$_4$), and between 170 and 420°C (Y–NH$_4$), is ascribed to the thermal decomposition of the anhydrous compounds, with loss of ammonium selenate. The third mass loss between 440 and 740°C (Eu–NH$_4$), between 480 and 830°C (Gd–NH$_4$), between 420 and 730°C (Tb–NH$_4$), and between 420 and 760°C (Y–NH$_4$), is due to the thermal decomposition of the lanthanide selenates to the respective (di)oxyselenites, $Eu_2O_2SeO_3$, $Gd_2O_2SeO_3$, $Tb_2O_2SeO_3$ and $Y_2O_2SeO_3$. The last step between 740 and $>900°C$ (Eu), between 830 and $>900°C$ (Gd), between 730 and $>900°C$ (Tb), and between 760 and $>900°C$ (Y), is due to the thermal decomposition of the intermediates to the oxides, Eu_2O_3, Gd_2O_3, Tb_4O_7 and Y_2O_3, respectively.

For the dysprosium and ammonium double selenate (Fig. 2, curve i), the mass loss occurs in five steps. The first step, between 90 and 120°C, is due to partial dehydration, with loss of $1H_2O$. The second step, between 120 and 170°C, is due to the final dehydration with loss of $4H_2O$. The third step, between 200 and 300°C, is ascribed to the loss of ammonium selenate. The fourth step, between 380 and 670°C, is ascribed to the thermal decomposition of dysprosium selenate to the (di)oxyselenite, $Dy_2O_2SeO_3$. The last step, between 670 and $>900°C$, is due to the thermal decomposition of the (di)oxyselenite to dysprosium oxide, Dy_2O_3.

For the holmium and ammonium double selenate (Fig. 2, curve j), the mass loss occurs in three steps. The first step between 200 and 390°C is ascribed to loss of ammonium selenate. The second step, between 390 and 740°C, is due to the thermal decomposition of holmium selenate to the (di)oxyselenite, $Ho_2O_2SeO_3$. The third step, between 740 and $>900°C$, is due to the thermal decomposition of the intermediate to holmium oxide, Ho_2O_3.

In the compounds where the 1:1 stoichiometry was not obeyed, this was probably due to the addition of an excess of ammonium selenate.

For the samarium and erbium, and ammonium double selenates (Fig. 2, curves e and k), the mass losses occur in five steps. The first step between 50 and 160°C (Sm–NH$_4$), and between 100 and 220°C (Er–NH$_4$), is due to dehydration, with losses of $1H_2O$ and $4H_2O$, respectively. The second step,

TABLE 2

Mass losses and temperature ranges for the partial thermal decomposition steps observed in the TG curves and in the furnace for the compounds $Ln_2(SeO_4)_3 \cdot y(NH_4)_2SeO_4 \cdot nH_2O$; Ln is lanthanides and yttrium, $y = 1-1.5$, $n = 0-6$

Compound	$m_i/$ mg	$\Delta m/$ mg	$\Delta T/$ °C	Partial thermal decomposition	Calcd./ %	Exp./ %
La–NH$_4 \cdot$ 4H$_2$O	7.80	0.60	50–190	4H$_2$O	7.53	7.7
		1.45	240–500	(NH$_4$)$_2$SeO$_4$	18.6	18.6
		2.20	500–860	2SeO$_2$ + 1.5O$_2$	28.19	28.2
		0.90 [a]	860– > 900	SeO$_2$	11.58	11.5
Ce–NH$_4 \cdot$ 3.5H$_2$O	7.32	0.50	50–200	3.5H$_2$O	6.63	6.8
		1.35	240–360	(NH$_4$)$_2$SeO$_4$	18.82	18.4
		2.80	360–800	3SeO$_2$ + O$_2$	38.36	38.3
Pr–NH$_4 \cdot$ H$_2$O	7.30	0.15	50–140	H$_2$O	1.99	2.1
		1.45	270–480	(NH$_4$)$_2$SeO$_4$	19.73	19.9
		2.15	480–880	2SeO$_2$ + 1.5O$_2$	29.73	29.5
		0.80 [a]	880– > 900	SeO$_2$	12.22	11.0
Nd–NH$_4 \cdot$ 2H$_2$O	7.35	0.30	50–150	2H$_2$O	3.87	4.1
		1.40	240–460	(NH$_4$)$_2$SeO$_4$	19.20	19.0
		2.15	460–820	2SeO$_2$ + 1.5O$_2$	28.95	29.3
		0.85 [a]	820– > 900	SeO$_2$	11.90	11.6
Sm–1.3NH$_4 \cdot$ H$_2$O	7.67	0.15	50–160	H$_2$O	1.84	2.0
		0.40	160–320	0.3(NH$_4$)$_2$SeO$_4$	5.48	5.2
		1.45	320–480	(NH$_4$)$_2$SeO$_4$	18.26	18.9
		2.10	480–760	2SeO$_2$ + 1.5O$_2$	27.53	27.4
		0.85 [a]	760– > 900	SeO$_2$	11.32	11.1
Eu–NH$_4 \cdot$ 6H$_2$O	7.91	0.85	70–180	6H$_2$O	10.60	10.7
		1.45	220–440	(NH$_4$)$_2$SeO$_4$	17.56	18.3
		2.10	440–740	2SeO$_2$ + 1.5O$_2$	26.46	26.5
		0.80 [a]	740– > 900	SeO$_2$	10.88	10.1
Gd–NH$_4 \cdot$ 5H$_2$O	7.43	0.65	120–180	5H$_2$O	8.90	8.7
		1.30	230–480	(NH$_4$)$_2$SeO$_4$	17.68	17.5
		2.00	480–830	2SeO$_2$ + 1.5O$_2$	26.66	26.9
		0.80 [a]	830– > 900	SeO$_2$	10.96	10.8
Tb–NH$_4 \cdot$ 5H$_2$O	8.15	0.70	130–180	5H$_2$O	8.87	8.6
		1.45	200–420	(NH$_4$)$_2$SeO$_4$	17.63	17.8
		2.15	430–730	2SeO$_2$ + 1.5O$_2$	26.57	26.4
		0.85 [a]	730– > 900	SeO$_2$	10.92	10.4
Dy–NH$_4 \cdot$ 5H$_2$O	7.09	0.15	90–120	1H$_2$O	1.76	2.1
		0.45	120–170	4H$_2$O	7.05	6.4
		1.20	200–380	(NH$_4$)$_2$SeO$_4$	17.50	16.9
		1.90	380–670	2SeO$_2$ + 1.5O$_2$	26.38	26.8
		0.80 [a]	670– > 900	SeO$_2$	10.85	11.3
Ho–NH$_4$	7.87	1.55	200–390	(NH$_4$)$_2$SeO$_4$	19.09	19.7
		2.25	390–740	2SeO$_2$ + 1.5O$_2$	28.78	28.6
		0.90 [a]	740– > 900	SeO$_2$	11.83	11.4

TABLE 2 (continued)

Compound	$m_i/$ mg	$\Delta m/$ mg	$\Delta T/$ °C	Partial thermal decomposition	Calcd./ %	Exp./ %
Er–1.5NH$_4$ · 4H$_2$O	7.99	0.50	100–220	4H$_2$O	6.53	6.3
		0.65	220–310	0.5(NH$_4$)$_2$SeO$_4$	8.11	8.1
		1.35	310–470	1(NH$_4$)$_2$SeO$_4$	16.22	16.9
		1.90	470–750	2SeO$_2$ + 1.5O$_2$	24.45	23.8
		0.80 [a]	750– >900	SeO$_2$	10.05	10.0
Tm–1.35NH$_4$	8.74	0.55	220–320	0.35(NH$_4$)$_2$SeO$_4$	6.18	6.3
		1.45	320–460	(NH$_4$)$_2$SeO$_4$	17.76	16.6
		2.35	460–750	2SeO$_2$ + 1.5O$_2$	26.77	26.9
		0.95 [a]	750– >900	ScO$_2$	11.00	10.9
Yb–1.4NH$_4$	8.07	0.60	200–300	0.4(NH$_4$)$_2$SeO$_4$	6.98	7.4
		1.40	300–470	(NH$_4$)$_2$SeO$_4$	17.46	17.3
		2.10	470–750	2SeO$_2$ + 1.5O$_2$	26.32	26.0
		0.90 [a]	750– >900	SeO$_2$	10.82	11.2
Lu–1.4NH$_4$	7.15	0.35	200–280	0.3(NH$_4$)$_2$SeO$_4$	5.22	4.9
		1.35	300–470	1.1(NH$_4$)$_2$SeO$_4$	19.13	18.9
		1.90	470–760	2SeO$_2$ + 1.5O$_2$	26.22	26.6
		0.80 [a]	760– >900	SeO$_2$	10.78	11.2
Y–NH$_4$ · 4.5H$_2$O	7.63	0.70	90–170	4.5H$_2$O	9.35	9.2
		1.55	170–420	(NH$_4$)$_2$SeO$_4$	20.72	20.3
		2.40	420–760	2SeO$_2$ + 1.5O$_2$	31.14	31.5
		1.00	760– >900	SeO$_2$	12.80	13.1

[a] Gravimetric data.

between 160 and 320°C (Sm–NH$_4$), and between 220 and 310°C (Er–NH$_4$), is ascribed to the loss of 0.3(NH$_4$)$_2$SeO$_4$ and 0.5(NH$_4$)$_2$SeO$_4$, respectively. The third step, between 310 and 480°C (Sm–NH$_4$), and between 310 and 470°C (Er–NH$_4$), is due to the thermal decomposition of the rest of the ammonium selenate. The fourth step, between 480 and 760°C (Sm–NH$_4$), and between 470 and 750°C (Er–NH$_4$), is ascribed to the thermal decomposition of the samarium and erbium selenates to the (di)oxyselenites, Sm$_2$O$_2$SeO$_3$ and Er$_2$O$_2$SeO$_3$. The last step, between 760 and >900°C (Sm), and between 750 and >900°C, is ascribed to the thermal decomposition of the (di)oxyselenites to the oxides, Sm$_2$O$_3$ and Er$_2$O$_3$, respectively.

For the thulium, ytterbium and lutetium, and ammonium double selenates (Fig. 2, curves l, m, n), the mass losses occur in four steps. The first step, between 220 and 320°C (Tm–NH$_4$), between 200 and 300°C (Yb–NH$_4$), and between 200 and 280°C (Lu–NH$_4$), is due to losses of 0.35, 0.4 and 0.3 (NH$_4$)$_2$SeO$_4$, respectively. The second step, between 320 and 460°C (Tm–NH$_4$), between 300 and 470°C (Yb–NH$_4$), and between 280 and 470°C (Lu–NH$_4$), is ascribed to losses of 1(NH$_4$)$_2$SeO$_4$ (Tm–NH$_4$ and Yb–NH$_4$), and 1.1(NH$_4$)$_2$SeO$_4$ (Lu–NH$_4$). The third step, between 460 and

TABLE 3

Temperatures of the DTA peaks and their probable interpretations

Compound	Peak/°C (endo)	Loss	Peak/°C (exo)	Loss	Peak/°C (endo)	Loss
$La_2(SeO_4)_3 \cdot (NH_4)_2SeO_4 \cdot 4H_2O$	100, 110	$4H_2O$	350–580	$(NH_4)_2SeO_4$	890, 910, 1000	$2SeO_2$, $1.5O_2$
$Ce_2(SeO_4)_3 \cdot (NH_4)_2SeO_4 \cdot 3.5H_2O$	110	$3.5H_2O$	260	$(NH_4)_2SeO_4$	500	$3SeO_2$, O_2
$Pr_2(SeO_4)_3 \cdot (NH_4)_2SeO_4 \cdot H_2O$	110	H_2O	390, 540	$(NH_4)_2SeO_4$	800	$2SeO_2$, $1.5O_2$
$Nd_2(SeO_4)_3 \cdot (NH_4)_2SeO_4 \cdot 2H_2O$	140, 160	$2H_2O$	390, 600	$(NH_4)_2SeO_4$	850	$2SeO_2$, $1.5O_2$
$Sm_2(SeO_4)_3 \cdot 1.3(NH_4)_2SeO_4 \cdot H_2O$	90	H_2O	430, 650	$1.3(NH_4)_2SeO_4$	820, 960	$2SeO_2$, $1.5O_2$
$Eu_2(SeO_4)_3 \cdot (NH_4)_2SeO_4 \cdot 6H_2O$	60, 150	$6H_2O$	350, 650	$(NH_4)_2SeO_4$	750, 820	$2SeO_2$, $1.5O_2$
$Gd_2(SeO_4)_3 \cdot (NH_4)_2SeO_4 \cdot 5H_2O$	110, 240	$5H_2O$	390, 670	$(NH_4)_2SeO_4$	750, 820	$2SeO_2$, $1.5O_2$
$Tb_2(SeO_4)_3 \cdot (NH_4)_2SeO_4 \cdot 5H_2O$	170	$5H_2O$	350, 370, 660	$(NH_4)_2SeO_4$	700, 830	$2SeO_2$, $1.5O_2$
$Dy_2(SeO_4)_3 \cdot (NH_4)_2SeO_4 \cdot 5H_2O$	160, 190, 250	$5H_2O$	390, 620	$(NH_4)_2SeO_4$	730, 830; 780	$2SeO_2$, $1.5O_2$; $2SeO_2$, $1.5O_2$
$Ho_2(SeO_4)_3 \cdot (NH_4)_2SeO_4$	230	Structural rearrangement	340, 560	$(NH_4)_2SeO_4$	960	SeO_2
$Er_2(SeO_4)_3 \cdot 1.5(NH_4)_2SeO_4 \cdot 4H_2O$	100, 230 (Structural rearrangement)	$4H_2O$	380, 590	$1.5(NH_4)_2SeO_4$	700, 790	$2SeO_2$, $1.5O_2$
$Tm_2(SeO_4)_3 \cdot 1.25(NH_4)_2SeO_4$	290	Structural rearrangement	340, 590	$1.25(NH_4)_2SeO_4$	750, 810; 720, 760	$2SeO_2$, $1.5O_2$; $2SeO_2$, $1.5O_2$
$Yb_2(SeO_4)_3 \cdot 1.4(NH_4)_2SeO_4$	250	Structural rearrangement	340, 570	$1.4(NH_4)_2SeO_4$	920; 760	SeO_2; $2SeO_2$, $1.5O_2$
$Lu_2(SeO_4)_3 \cdot 1.4(NH_4)_2SeO_4$	260	Structural rearrangement	340, 350, 570	$1.4(NH_4)_2SeO_4$	920	SeO_2
$Y_2(SeO_4)_3(NH_4)_2SeO_4 \cdot 4.5H_2O$	120, 140, 220	$4.5H_2O$	340, 560	$(NH_4)_2SeO_4$	690, 800	$2SeO_2$, $1.5O_2$

750°C, 470 and 750°C, and 470 and 760°C, is ascribed, respectively, to the thermal decomposition of thulium, ytterbium and lutetium selenates to the (di)oxyselenites, $Tm_2O_2SeO_3$, $Yb_2O_2SeO_3$ and $Lu_2O_2SeO_3$. The last step, between 750 and 900°C (Tm and Yb), and between 760 and >900°C (Lu), is ascribed to the thermal decomposition of the intermediates to the oxides, Tm_2O_3, Yb_2O_3 and Lu_2O_3.

The mass losses and temperature ranges corresponding to the observed partial losses of the compounds for each step of the TG curve and in the furnace, are shown in Table 2.

The DTA curves of the prepared compounds are shown in Fig. 3. All curves show endothermic and exothermic peaks due to the dehydration, and thermal decomposition, respectively, and an endothermic peak due probably
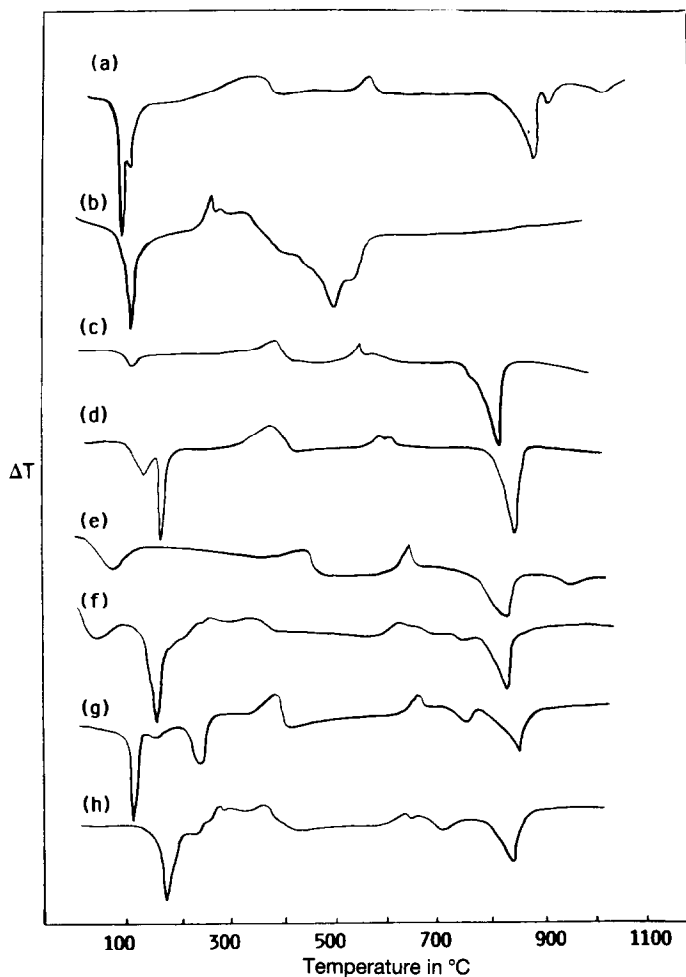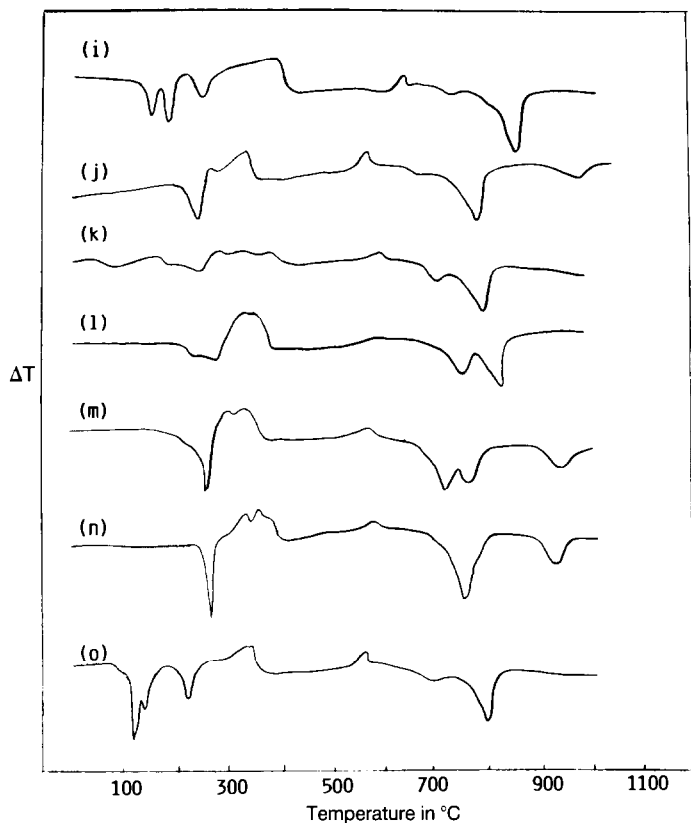

Fig. 3(a).

Fig. 3(b).

Fig. 3. DTA curves for the double selenates diluted to 40% in α-alumina: heating rate, $10°C$ min^{-1}. (a) La–NH_4; (b) Ce–NH_4; (c) Pr–NH_4; (d) Nd–NH_4; (e) Sm–$1.3NH_4$; (f) Eu–NH_4; (g) Gd–NH_4; (h) Tb–NH_4; (i) Dy–NH_4; (j) Ho–NH_4; (k) Er–$1.5NH_4$; (l) Tm–$1.25NH_4$; (m) Yb–$1.4NH_4$; (n) Lu–$1.4NH_4$; and (o) Y–NH_4.

to structural rearrangement. The literature does not report fusion for any of the double selenates prepared in this study.

The temperature of each DTA peak and its probable interpretation is summarized in Table 3.

CONCLUDING REMARKS

The thermal behaviour of the double selenates of lanthanides, and yttrium, and ammonium showed characteristic TG and DTA patterns.

For the compounds where the 1:1 stoichiometry was not obeyed, the loss of excess ammonium selenate occurs before the thermal decomposition of the anhydrous double selenates.

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