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Note

STUDIES ON DOUBLE SELENATES. IX. THERMAL DECOMPOSITION OF LANTHANIDE OF YTTRIUM AND MAGNESIUM DOUBLE SELENATES

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ABSTRACT

The preparation and thermal decomposition of lanthanide selenates [1] and magnesium selenate [2,3] have been reported previously. However, no information is available in the literature concerning the thermal decomposition of lanthanide and magnesium double selenates.

EXPERIMENTAL

Magnesium selenate was obtained by adding 25% (v/v) of a freshly prepared aqueous solution of selenic acid to a hot suspension of magnesium carbonate in water [3]. Selenic acid [4], lanthanide and yttrium selenates [1,5] and lanthanide or yttrium and magnesium double selenates [6] were prepared following literature methods.

Lanthanide and yttrium ions were separated quantitatively from magnesium ions as hydroxides and determined by gravimetry as the corresponding oxides [7]. Isolation of magnesium ions was performed by complexometric titration with a standard solution of EDTA, using Erio T as indicator [8]. The water of crystallization and selenium contents were determined from the thermogravimetric (TG) curves. The TG and differential thermal analysis (DTA) curves were obtained as described in ref. 6.

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TABLE 1

Analytical and thermoanalytical (TG) results

Compound	Lanthanide (%)		Magnesium (%)		Selenium (%)		Water (%)	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$La_2(SeO_4)_3 \cdot MgSeO_4 \cdot 10H_2O$	26.35	26.35	2.31	2.17	29.96	29.78	17.09	16.41
$Ce_2(SeO_4)_3MgSeO_4 \cdot 8H_2O$	27.46	27.48	2.38	1.87	30.95	28.09	14.11	14.54
$Pr_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$	26.19	28.50	2.26	2.46	29.35	29.08	18.42	17.98
$Nd_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$	26.64	26.63	2.25	1.89	29.17	29.10	18.31	18.26
$Sm_2(SeO_4)_3 \cdot MgSeO_4 \cdot 17H_2O$	24.99	25.50	2.02	1.81	26.25	26.25	25.46	25.00
$Eu_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$	26.79	26.78	2.14	1.93	27.84	27.70	20.65	21.11
$Gd_2(SeO_4)_3 \cdot MgSeO_4 \cdot 15H_2O$	26.63	28.45	2.05	1.77	26.75	26.74	22.88	22.67
$Tb_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$	27.68	26.01	2.11	1.94	27.51	27.45	20.40	20.38
$Dy_2(SeO_4)_3 \cdot MgSeO_4 \cdot 17H_2O$	26.48	26.48	1.98	1.80	25.73	25.72	24.96	24.65
$Ho_2(SeO_4)_3 \cdot MgSeO_4 \cdot 15H_2O$	27.57	27.42	2.03	2.00	26.40	26.34	22.59	22.98
$Er_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$	28.72	27.80	2.09	2.18	27.11	26.22	20.10	20.48
$Tm_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$	28.92	28.92	2.08	2.03	27.04	27.01	20.05	20.02
$Yb_2(SeO_4)_3 \cdot MgSeO_4 \cdot 21H_2O$	26.21	30.21	1.84	2.03	23.92	23.84	28.65	28.80
$Lu_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$	30.58	30.51	2.12	2.03	27.60	27.36	17.32	17.11
$Y_2(SeO_4)_3 \cdot MgSeO_4 \cdot 12H_2O$	17.96	17.95	2.46	2.11	31.90	30.03	21.84	22.15

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds $Ln_2(SeO_4)_3 \cdot MgSeO_4 \cdot nH_2O$, where Ln = lanthanides and yttrium and $n = 6-21$.

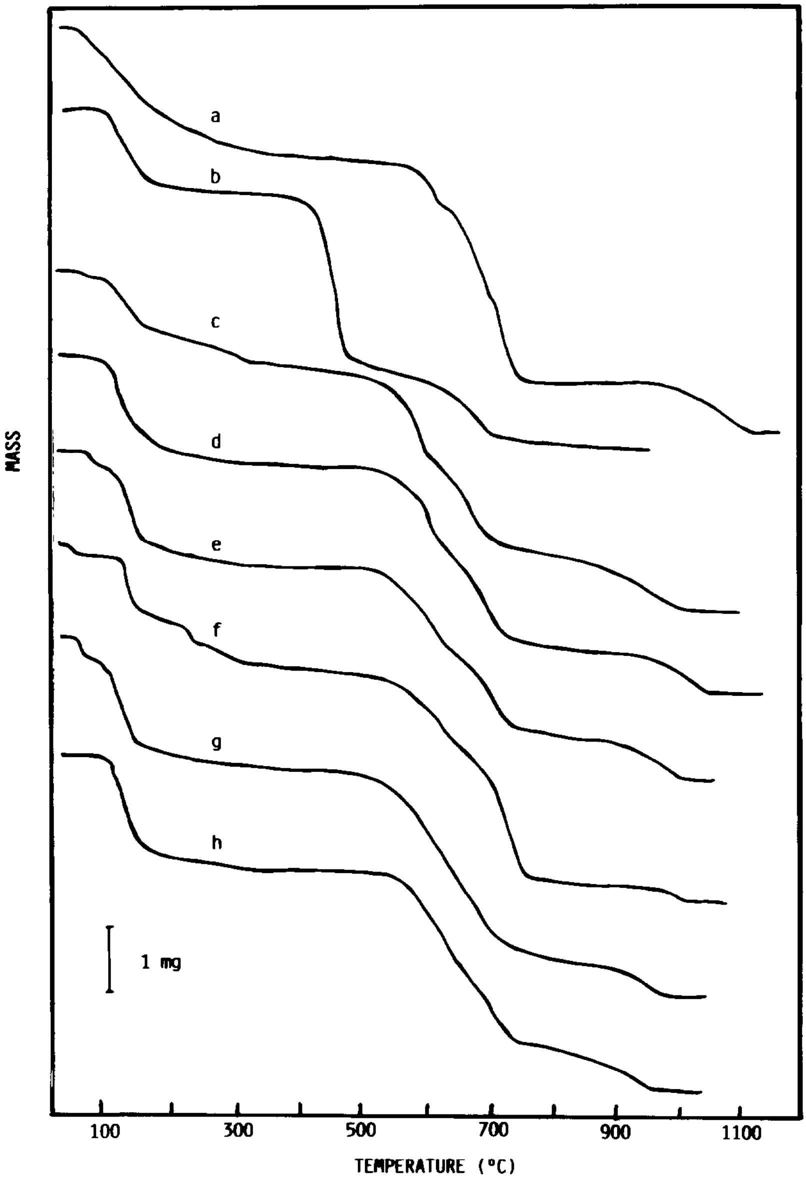

Fig. 1. TG curves of the La–Mg, Ce–Mg, Pr–Mg, Nd–Mg, Sm–Mg, Eu–Mg, Gd–Mg and Tb–Mg double selenates (heating rate, 6.25°C min^{-1}): a, $La_2(SeO_4)_3 \cdot MgSeO_4 \cdot 10H_2O$ (11.88 mg); b, $Ce_2(SeO_4)_3 \cdot MgSeO_4 \cdot 8H_2O$ (13.06 mg); c, $Pr_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$ (8.80 mg); d, $Nd_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$ (8.76 mg); e, $Sm_2(SeO_4)_3 \cdot MgSeO_4 \cdot 17H_2O$ (6.80 mg); f, $Eu_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$ (9.00 mg); g, $Gd_2(SeO_4)_3 \cdot MgSeO_4 \cdot 15H_2O$ (8.80 mg); h, $Tb_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$ (9.30 mg).

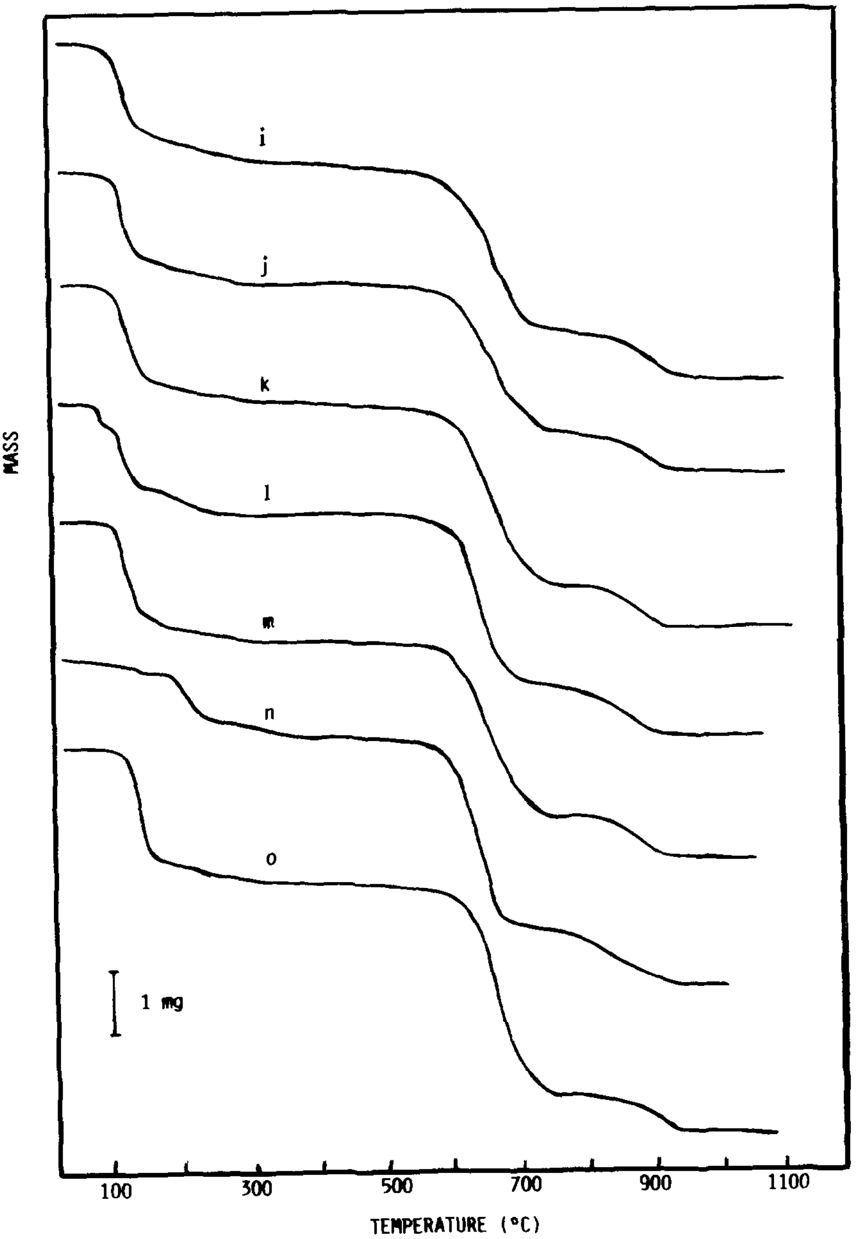

Fig. 2. TG curves of the Dy–Mg, Ho–Mg, Er–Mg, Tm–Mg, Yb–Mg, Lu–Mg and Y–Mg double selenates (heating rate, 6.25 °C min^{-1}): i, $Dy_2(SeO_4)_3 \cdot MgSeO_4 \cdot 17H_2O$ (7.30 mg); j, $Ho_2(SeO_4)_3 \cdot MgSeO_4 \cdot 15H_2O$ (6.96 mg); k, $Er_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$ (8.30 mg); l, $Tm_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$ (8.24 mg); m, $Yb_2(SeO_4)_3 \cdot MgSeO_4 \cdot 21H_2O$ (8.30 mg); n, $Lu_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$ (8.18 mg); o, $Y_2(SeO_4)_3 \cdot MgSeO_4 \cdot 12H_2O$ (8.80 mg).

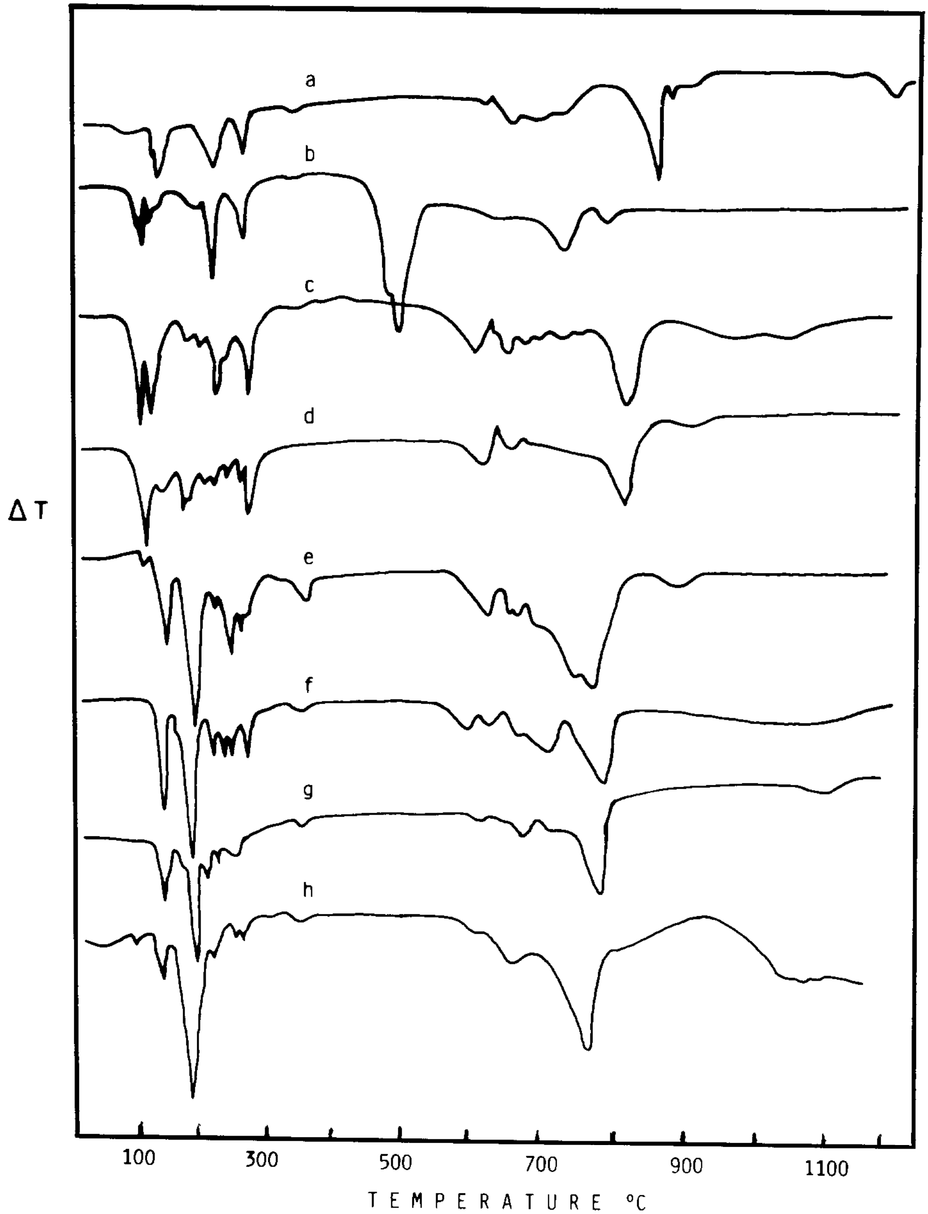

Fig. 3. DTA curves of the La–Mg, Ce–Mg, Pr–Mg, Nd–Mg, Sm–Mg, Eu–Mg, Gd–Mg and Tb–Mg double selenates, diluted at 20% in α-alumina (heating rate, 12.5 °C min^{-1}): a, $La_2(SeO_4)_3 \cdot MgSeO_4 \cdot 10H_2O$; b, $Ce_2(SeO_4)_3 \cdot MgSeO_4 \cdot 8H_2O$; c, $Pr_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$; d, $Nd_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$; e, $Sm_2(SeO_4)_3 \cdot MgSeO_4 \cdot 17H_2O$; f, $Eu_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$; g, $Gd_2(SeO_4)_3 \cdot MgSeO_4 \cdot 15H_2O$; h, $Tb_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$.

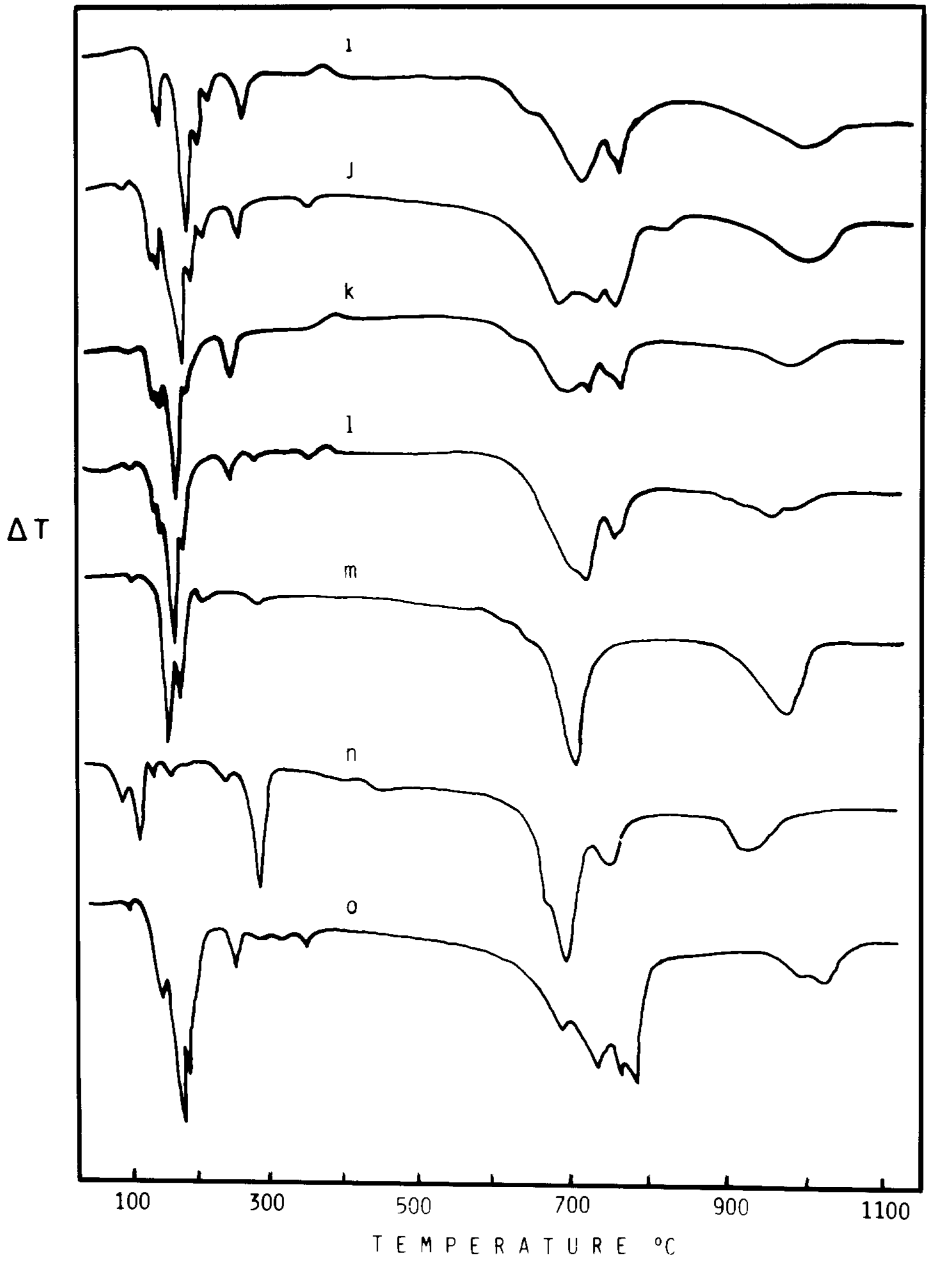

Fig. 4. DTA curves of Dy–Mg, Ho–Mg, Er–Mg, Tm–Mg, Yb–Mg, Lu–Mg and Y–Mg double selenates, diluted at 20% in α-alumina (heating rate, 12.5 °C min^{-1}): i, $Dy_2(SeO_4)_3 \cdot MgSeO_4 \cdot 17H_2O$; j, $Ho_2(SeO_4)_3 \cdot MgSeO_4 \cdot 15H_2O$; k, $Er_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$; l, $Tm_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$; m, $Yb_2(SeO_4)_3 \cdot MgSeO_4 \cdot 21H_2O$; n, $Lu_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$; o, $Y_2(SeO_4)_3 \cdot MgSeO_4 \cdot 12H_2O$.

It can be seen from the TG curves (Figs. 1 and 2) and DTA curves (Figs. 3 and 4) that the thermal decomposition of the double selenates occurs in a characteristic way for each compound. The reactions which occur on heating can be summarized as follows

$$\begin{aligned}
La_2(SeO_4)_3 \cdot MgSeO_4 \cdot 10H_2O &\xrightarrow{1} La_2(SeO_4)_3 \cdot MgSeO_4 \\
&\xrightarrow{2} La_2(SeO_3)_4 \cdot MgSeO_4 \\
&\xrightarrow{3} La_2O_2SeO_3 \cdot MgO \\
&\xrightarrow{4} La_2O_3 \cdot MgO
\end{aligned}$$

$$\begin{aligned}
Ce_2(SeO_4)_3 \cdot MgSeO_4 \cdot 8H_2O &\xrightarrow{1} Ce_2(SeO_4)_3 \cdot MgSeO_4 \\
&\xrightarrow{2} 2CeO_2 \cdot MgSeO_3 \\
&\xrightarrow{3} 2CeO_2 \cdot MgO
\end{aligned}$$

$$\begin{aligned}
3Pr_2(SeO_4)_3 \cdot 3MgSeO_4 \cdot 33H_2O &\xrightarrow{1} 3Pr_2(SeO_4)_3 \cdot 3MgSeO_4 \\
&\xrightarrow{2} 3Pr_2O_2SeO_3 \cdot 3MgSeO_4 \\
&\xrightarrow{3} 3Pr_2O_2SeO_3 \cdot 3MgO \\
&\xrightarrow{4} Pr_6O_{11} \cdot 3MgO
\end{aligned}$$

$$\begin{aligned}
2Tb_2(SeO_4)_3 \cdot 2MgSeO_4 \cdot 26H_2O &\xrightarrow{1} 2Tb_2(SeO_4)_3 \cdot 2MgSeO_4 \\
&\xrightarrow{2} 2Tb_2O_2SeO_3 \cdot 2MgSeO_4 \\
&\xrightarrow{3} 2Tb_2O_2SeO_3 \cdot 2MgO \\
&\xrightarrow{4} Tb_4O_7 \cdot 2MgO
\end{aligned}$$

$$\begin{aligned}
Ln_2(SeO_4)_3 \cdot MgSeO_4 \cdot nH_2O &\xrightarrow{1} Ln_2(SeO_4)_3 \cdot MgSeO_4 \\
&\xrightarrow{2} Ln_2O_2SeO_3 \cdot MgSeO_4 \\
&\xrightarrow{3} Ln_2O_2SeO_3 \cdot MgO \\
&\xrightarrow{4} Ln_2O_3 \cdot MgO
\end{aligned}$$

Ln = Nd, Gd, Ho, Er, Y

$$\begin{aligned}
Ln_2(SeO_4)_3 \cdot MgSeO_4 \cdot nH_2O &\xrightarrow{1} Ln_2(SeO_4)_3 \cdot MgSeO_4 \\
&\xrightarrow{2} Ln_2O_2SeO_3 \cdot MgO \\
&\xrightarrow{4} Ln_2O_3 \cdot MgO
\end{aligned}$$

Ln = Dy, Tm, Yb, Lu

TABLE 2

Reactions (1)–(4) and corresponding temperature ranges observed in the TG curves of the compounds $Ln_2(SeO_4)_3 \cdot MgSeO_4 \cdot nH_2O$

Compound	Temperature range of mass loss reactions (1)–(4) in the TG curves (°C)			
	(1)	(2)	(3)	(4)
$La_2(SeO_4)_3 \cdot MgSeO_4 \cdot 10H_2O$	50–350	550–600	600–750	950–1150
$Ce_2(SeO_4)_3 \cdot MgSeO_4 \cdot 8H_2O$	70–250	400–500	500–750	–
$Pr_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$	50–350	500–625	625–750	800–1050
$Nd_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$	80–250	500–625	625–750	900–1050
$Sm_2(SeO_4)_3 \cdot MgSeO_4 \cdot 17H_2O$	80–300	500–630	630–730	800–1000
$Eu_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$	100–325	480–630	630–730	830– 980
$Gd_2(SeO_4)_3 \cdot MgSeO_4 \cdot 15H_2O$	60–300	480–630	630–730	800– 970
$Tb_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$	100–250	500–640	640–730	800– 960
$Dy_2(SeO_4)_3 \cdot MgSeO_4 \cdot 17H_2O$	60–300	550–700	–	750– 940
$Ho_2(SeO_4)_3 \cdot MgSeO_4 \cdot 15H_2O$	60–300	550–670	670–720	800– 920
$Er_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$	80–300	550–670	670–720	760– 900
$Tm_2(SeO_4)_3 \cdot MgSeO_4 \cdot 13H_2O$	70–260	550–700	–	720– 900
$Yb_2(SeO_4)_3 \cdot MgSeO_4 \cdot 21H_2O$	80–250	550–670	–	670– 900
$Lu_2(SeO_4)_3 \cdot MgSeO_4 \cdot 11H_2O$	90–350	550–670	–	670– 900
$Y_2(SeO_4)_3 \cdot MgSeO_4 \cdot 12H_2O$	100–330	550–680	680–740	800– 950

For each compound, Table 2 gives the temperature ranges of the above reactions corresponding to the successive mass losses observed in the TG curves.

Table 3 gives the temperature of the DTA peaks corresponding to the dehydration, crystalline transitions and thermal decomposition reactions of the anhydrous salts.

The TG curves of Figs. 1 and 2 show that the thermal decomposition starts with dehydration at temperatures up to 300 °C. For the double selenates of La, Ce, Nd, Tb, Ho, Er, Y and Mg, dehydration occurs in one step, the last water molecules being lost more slowly. The TG curves of the other compounds show evidence of formation of unstable intermediate hydrates.

The second step in the TG curve is due to the first thermal decomposition of the anhydrous double salt formed in the first step. These mass losses occur between 480 and 750 °C and are due to the thermal decomposition of the lanthanide selenate to the (di)oxyselenite and magnesium selenate to magnesium oxide.

The reduction of selenate ion to (di)oxyselenite is evident only in the TG curve of the La–Mg double selenate. For the Dy–Mg, Tm–Mg and Yb–Mg double selenates, the formation of the corresponding lanthanide (di)oxyselenite occurs simultaneously with the thermal decomposition of magnesium selenate to magnesium oxide.

TABLE 3

Temperatures (°C) of the peaks observed in the DTA curves of the lanthanide or yttrium and magnesium double selenate hydrates

Double selenate	Dehydration, crystalline transition	Thermal decomposition of the anhydrous salts
La–Mg	90–140–230–270–350	630–670–700–870–890–1200
Ce–Mg	110–130–200–230–280–350	510–670–740–870
Pr–Mg	115–135–190–215–240–280–360	620–650–670–730–810–980
Nd–Mg	115–150–180–210–230–270	620–630–805–900
Sm–Mg	115–150–190–230–250–265–365	625–650–730–750–880
Eu–Mg	150–190–225–240–255–270–365	600–630–650–700–780
Gd–Mg	150–195–210–220–225–305	610–680–725–790–1100
Tb–Mg	105–150–195–210–255–260–305	605–670–780–1050
Dy–Mg	140–170–195–215–260–390 [a]	650–720–775–1000
Ho–Mg	100–145–150–170–195–215–255–355	690–740–775–995
Er–Mg	100–140–150–165–180–255–400 [a]	690–730–780–970
Tm–Mg	100–140–150–165–170–255–280–355–400 [a]	720–755–950
Yb–Mg	105–160–170–210–280	700–970
Lu–Mg	90–115–130–160–250–275–450	700–760–930
Y–Mg	100–150–170–180–255–275–310–355	690–730–760–790–1030

[a] Small exothermic peaks.

For the remaining double selenates, the inflexion that can be seen in the second step of the TG curve indicates that the formation of the (di)oxyselenite precedes the decomposition of magnesium selenate to magnesium oxide. For the Ce–Mg double selenate, the second mass loss occurring between 400 and 500°C corresponds to the total decomposition of cerium(III) selenate to cerium(IV) oxide without visible intermediate formation of (di)oxyselenite, probably due to the rapid oxidation of Ce^{III} to Ce^{IV}, as reported previously [1,9].

The final mass loss observed in the TG curves is due to the thermal decomposition of the lanthanide (di)oxyselenite to the corresponding oxide. The only exception is the final mass loss of the TG curve of the Ce–Mg compound which is due to thermal decomposition of magnesium selenate to magnesium oxide.

The DTA curves of Figs. 3 and 4 can be divided into two parts: one corresponding to dehydration of the double selenate hydrate and the other corresponding to the decomposition of the anhydrous double selenate. The endothermic and exothermic peaks are summarized in Table 3. The first part of the DTA curve is made up of a series of superimposed peaks between 100 and 350°C. Some of these peaks correspond to the inflexions observed in the TG curves, confirming the intermediate formation of unstable hydrates. The small endothermic peaks which appear at the end of the dehydration process and the small exothermic peaks in the Dy–Mg (390°C), Er–Mg

(400 ° C) and Tm–Mg (400 ° C) compounds are probably due to crystalline transitions.

CONCLUSIONS

The thermal behaviour of the lanthanide or yttrium and magnesium double selenate hydrates is different from that of the corresponding simple selenates.

The techniques used in the preparation of these compounds lead to the formation of double selenate hydrates with the formulae $Ln_2(SeO_4)_3 \cdot MgSeO_4 \cdot nH_2O$ (where Ln = lanthanides and yttrium).

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

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