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Note

STUDIES ON DOUBLE SELENATES. X. THERMAL DECOMPOSITION OF LANTHANIDE, YTTRIUM AND CALCIUM DOUBLE SELENATES

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The preparation and thermal decomposition of lanthanide selenates [1], calcium selenate [2], and lanthanum and alkali metal double selenates [3] have been described in previous works. No reference to the thermal behaviour of lanthanides and calcium selenates was found in the literature.

EXPERIMENTAL

Selenic acid [4], lanthanides and yttrium selenates [1,5], calcium selenate [2], and the lanthanides, yttrium and calcium double selenates were prepared following procedures reported previously [3].

Lanthanide and yttrium ions were separated quantitatively from calcium ions as hydroxides and determined gravimetrically as the corresponding oxides [6]. After each isolation, the amount of calcium ions was determined by complexometric titration with EDTA standard solution, using Calcon as indicator [7]. Water of crystallization and selenium content were determined from thermogravimetric (TG) curves. TG and differential thermal analysis (DTA) curves were obtained according to the procedure described in a previous work [3].

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RESULTS AND DISCUSSION

Table 1 presents analytical and thermoanalytical (TG) data for the compounds prepared, which were of the formula $Ln_2(SeO_4)_3 \cdot CaSeO_4 \cdot nH_2O$ (Ln = lanthanides and yttrium, n varying between 6 and 16).

The TG curves (Figs. 1 and 2) and DTA curves (Figs. 3 and 4) show that the thermal decomposition of the double selenates considered in the present work occurs in a characteristic way for each compound. The reactions occurring during the heating of these compounds can be summarized by the following group of equations.

$$\begin{aligned}&La_2(SeO_4)_3 \cdot CaSeO_4 \cdot 9H_2O \xrightarrow{1} La_2(SeO_4)_3 \cdot CaSeO_4\\&\xrightarrow{2} La_2(SeO_3)_3 \cdot CaSeO_4 \xrightarrow{3} La_2O_2SeO_3 \cdot CaSeO_3\\&\xrightarrow{4} La_2O_3 \cdot CaSeO_3 \xrightarrow{5} La_2O_3 \cdot CaO \qquad (1)\end{aligned}$$

$$\begin{aligned}&Ce_2(SeO_4)_3 \cdot CaSeO_4 \cdot 6H_2O \xrightarrow{1} Ce_2(SeO_4)_3 \cdot CaSeO_4\\&\xrightarrow{3} 2CeO_2 \cdot CaSeO_4 \xrightarrow{4} 2CeO_2 \cdot CaSeO_3\\&\xrightarrow{5} 2CeO_2 \cdot CaO \qquad (2)\end{aligned}$$

$$\begin{aligned}&3Pr_2(SeO_4)_3 \cdot 3CaSeO_4 \cdot 24H_2O \xrightarrow{1} 3Pr_2(SeO_4)_3 \cdot 3CaSeO_4\\&\xrightarrow{3} 3Pr_2O_2SeO_3 \cdot 3CaSeO_4 \xrightarrow{5} Pr_6O_{11} \cdot 3CaO \qquad (3)\end{aligned}$$

TABLE 1

Analytical and thermoanalytical (TG) results

Compound	Lanthanides (%)		Calcium (%)		Selenium (%)		Water (%)	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$La_2(SeO_4)_3 \cdot CaSeO_4 \cdot 9H_2O$	26.41	26.41	3.81	3.50	30.03	28.02	15.42	15.41
$Ce_2(SeO_4)_3 \cdot CaSeO_4 \cdot 6H_2O$	28.02	28.00	4.01	3.64	31.58	30.34	10.81	10.57
$Pr_2(SeO_4)_3 \cdot CaSeO_4 \cdot 8H_2O$	27.15	26.60	3.86	3.87	30.43	28.01	13.89	13.86
$Nd_2(SeO_4)_3 \cdot CaSeO_4 \cdot 8H_2O$	27.62	27.55	3.84	3.59	30.24	28.58	13.80	14.01
$Sm_2(SeO_4)_3 \cdot CaSeO_4 \cdot 10H_2O$	27.52	27.18	3.67	3.35	28.90	27.70	16.49	16.36
$Eu_2(SeO_4)_3 \cdot CaSeO_4 \cdot 10H_2O$	27.73	27.22	3.66	3.39	28.82	26.56	16.44	16.77
$Gd_2(SeO_4)_3 \cdot CaSeO_4 \cdot 12H_2O$	27.52	26.65	3.51	3.32	27.64	26.37	18.92	18.81
$Tb_2(SeO_4)_3 \cdot CaSeO_4 \cdot 12H_2O$	27.73	26.91	3.50	3.20	27.56	24.23	18.87	18.87
$Dy_2(SeO_4)_3 \cdot CaSeO_4 \cdot 9H_2O$	29.77	28.98	3.65	3.42	28.74	26.07	14.76	14.98
$Ho_2(SeO_4)_3 \cdot CaSeO_4 \cdot 14H_2O$	27.63	27.16	3.36	3.30	26.45	25.97	21.13	21.11
$Er_2(SeO_4)_3 \cdot CaSeO_4 \cdot 12H_2O$	28.77	28.21	3.45	3.31	27.16	25.25	18.60	18.68
$Tm_2(SeO_4)_3 \cdot CaSeO_4 \cdot 16H_2O$	27.29	27.28	3.24	3.20	25.51	25.50	23.29	23.52
$Yb_2(SeO_4)_3 \cdot CaSeO_4 \cdot 10H_2O$	30.41	28.97	3.52	3.38	27.75	26.13	15.83	16.08
$Lu_2(SeO_4)_3 \cdot CaSeO_4 \cdot 16H_2O$	27.99	26.85	3.21	3.27	25.26	24.40	23.06	22.96
$Y_2(SeO_4)_3 \cdot CaSeO_4 \cdot 13H_2O$	17.36	17.30	3.91	3.77	30.84	30.20	22.88	22.92

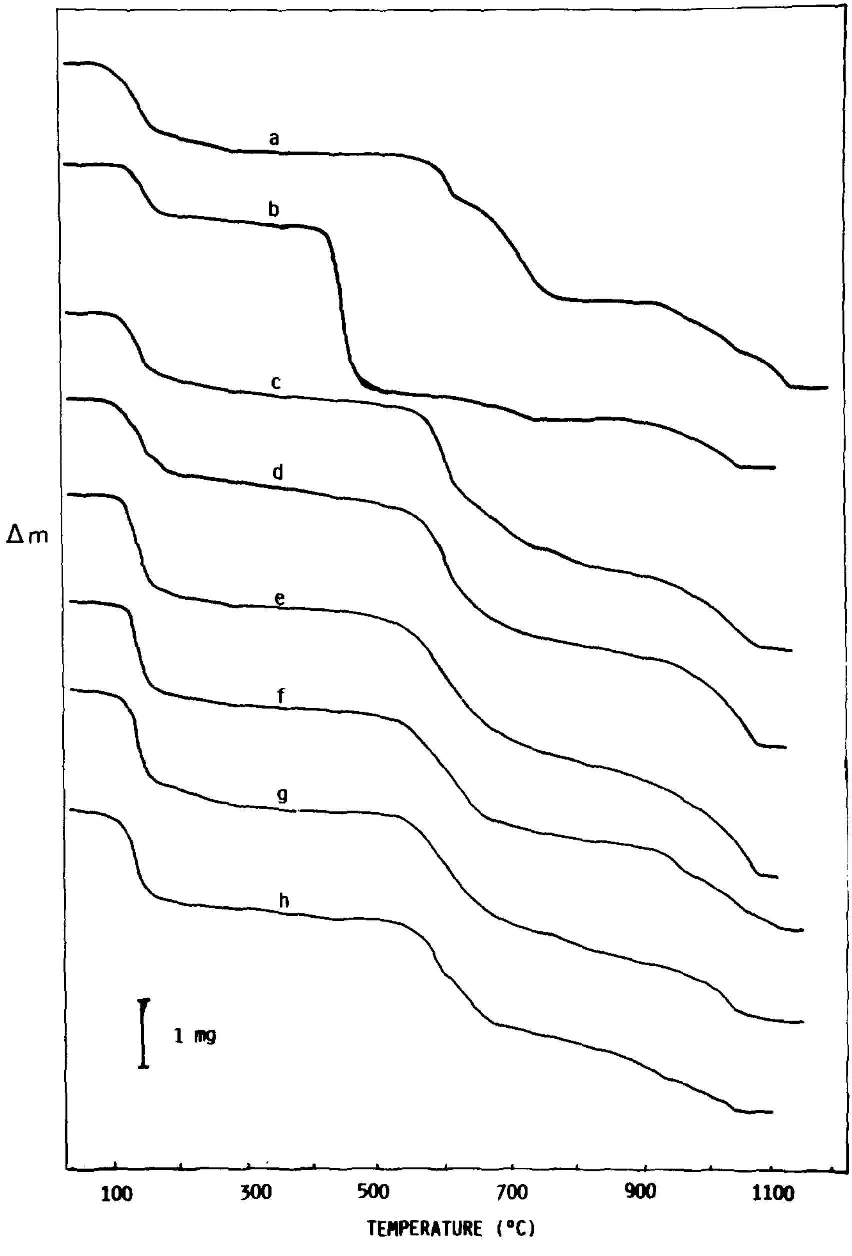

Fig. 1. TG curves for the double selenates of La–Tb and calcium (heating rate, 6.25°C min^{-1}): a, $La_2(SeO_4)_3 \cdot CaSeO_4 \cdot 9H_2O$ (8.76 mg); b, $Ce_2(SeO_4)_3 \cdot CaSeO_4 \cdot 6H_2O$ (8.04 mg); c, $Pr_2(SeO_4)_3 \cdot CaSeO_4 \cdot 8H_2O$ (9.34 mg); d, $Nd_2(SeO_4)_3 \cdot CaSeO_4 \cdot 8H_2O$ (8.92 mg); e, $Sm_2(SeO_4)_3 \cdot CaSeO_4 \cdot 10H_2O$ (9.78 mg); f, $Eu_2(SeO_4)_3 \cdot CaSeO_4 \cdot 10H_2O$ (9.24 mg); g, $Gd_2(SeO_4)_3 \cdot CaSeO_4 \cdot 12H_2O$ (9.04 mg); and h, $Tb_2(SeO_4)_3 \cdot CaSeO_4 \cdot 12H_2O$ (8.48 mg).

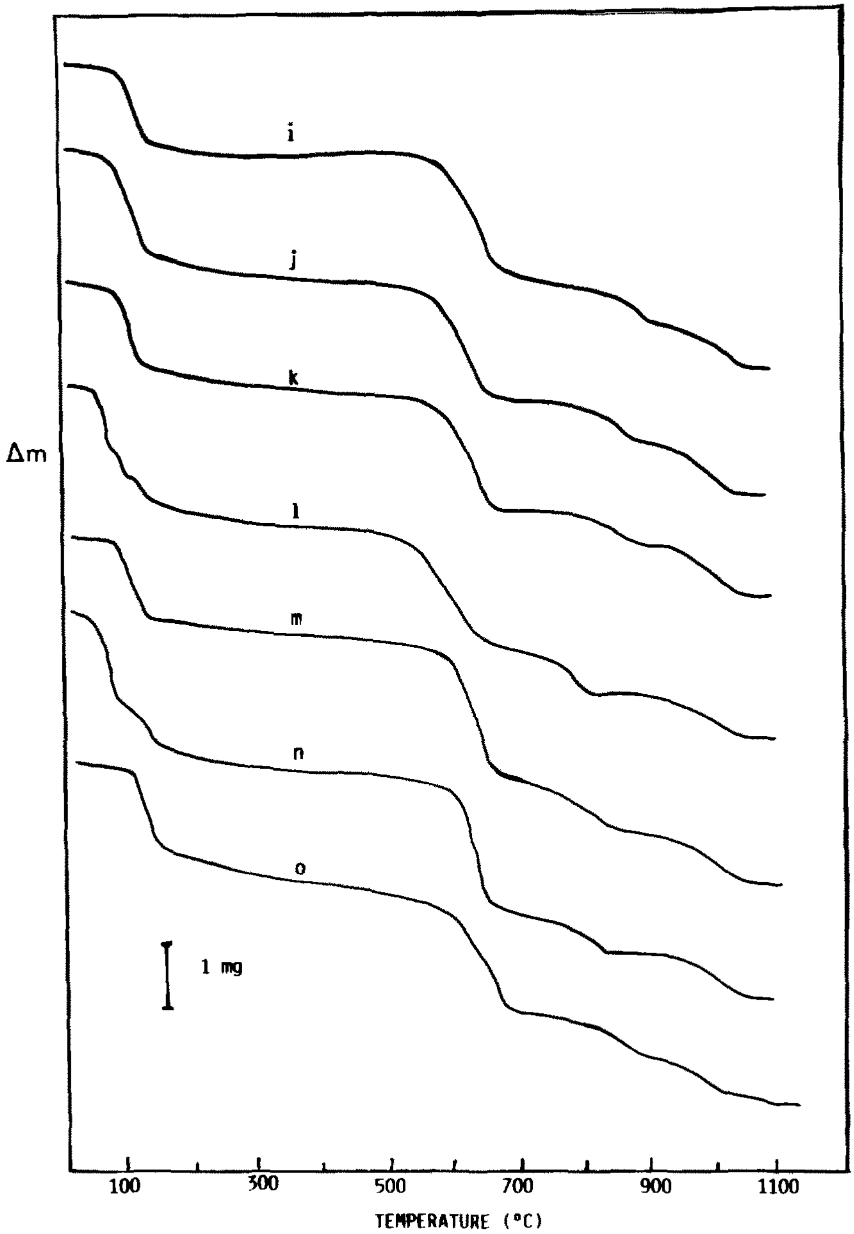

Fig. 2. TG curves for the double selenates of Dy–Lu, Y and calcium (heating rate, 6.25 °C min^{-1}): i, $Dy_2(SeO_4)_3 \cdot CaSeO_4 \cdot 9H_2O$ (8.68 mg); j, $Ho_2(SeO_4)_3 \cdot CaSeO_4 \cdot 14H_2O$ (8.62 mg); k, $Er_2(SeO_4)_3 \cdot CaSeO_4 \cdot 12H_2O$ (8.46 mg); l, $Tm_2(SeO_4)_3 \cdot CaSeO_4 \cdot 16H_2O$ (8.50 mg); m, $Yb_2(SeO_4)_3 \cdot CaSeO_4 \cdot 10H_2O$ (9.04 mg); n, $Lu_2(SeO_4)_3 \cdot CaSeO_4 \cdot 16H_2O$ (9.80 mg); and o, $Y_2(SeO_4)_3 \cdot CaSeO_4 \cdot 13H_2O$ (7.20 mg).

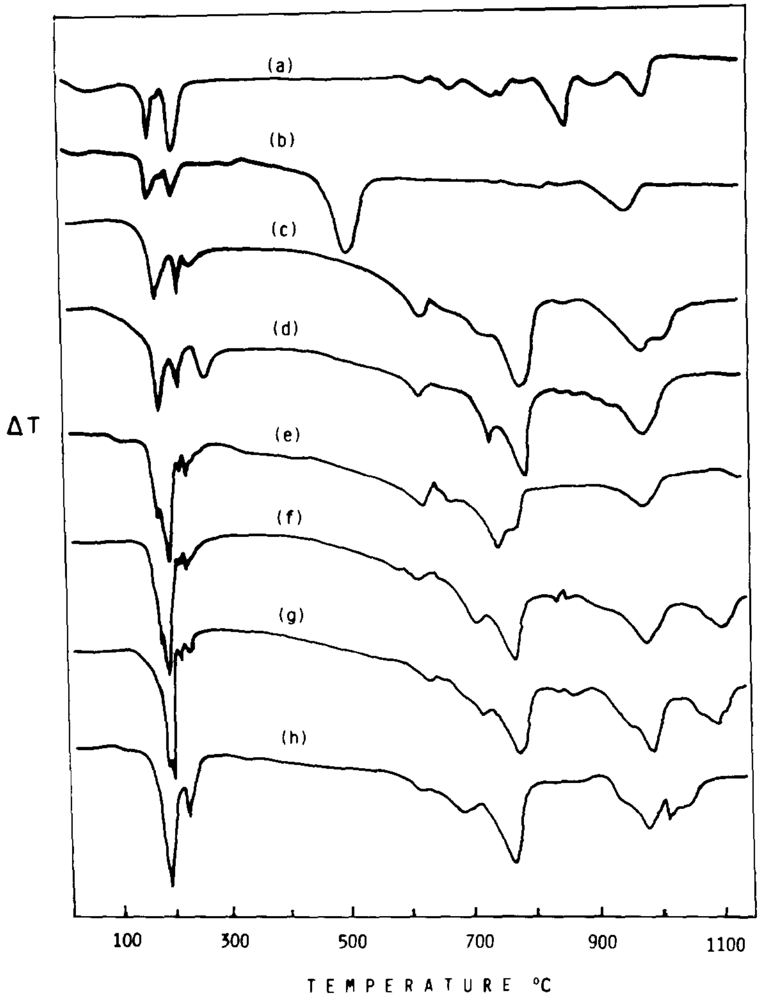

Fig. 3. DTA curves for the double selenates of La–Tb and calcium, diluted at 20% (m/m) in α-alumina (heating rate, 12.5 °C min^{-1}): a, $La_2(SeO_4)_3 \cdot CaSeO_4 \cdot 9H_2O$; b, $Ce_2(SeO_4)_3 \cdot CaSeO_4 \cdot 6H_2O$; c, $Pr_2(SeO_4)_3 \cdot CaSeO_4 \cdot 8H_2O$; d, $Nd_2(SeO_4)_3 \cdot CaSeO_4 \cdot 8H_2O$; e, $Sm_2(SeO_4)_3 \cdot CaSeO_4 \cdot 10H_2O$; f, $Eu_2(SeO_4)_3 \cdot CaSeO_4 \cdot 10H_2O$; g, $Gd_2(SeO_4)_3 \cdot CaSeO_4 \cdot 12H_2O$; and h, $Tb_2(SeO_4)_3 \cdot CaSeO_4 \cdot 12H_2O$.

$$\begin{aligned} &2Tb_2(SeO_4)_3 \cdot 2CaSeO_4 \cdot 24H_2O \xrightarrow{1} 2Tb_2(SeO_4)_3 \cdot 2CaSeO_4 \\ &\xrightarrow{3} 2Tb_2O_2SeO_3 \cdot 2CaSeO_4 \xrightarrow{4} Tb_4O_7 \cdot 2CaSeO_3 \xrightarrow{5} Tb_4O_7 \cdot 2CaO \end{aligned} \tag{4}$$

$$\begin{aligned} &Ln_2(SeO_4)_3 \cdot CaSeO_4 \cdot nH_2O \xrightarrow{1} Ln_2(SeO_4)_3 \cdot CaSeO_4 \\ &\xrightarrow{3} Ln_2O_2SeO_3 \cdot CaSeO_3 \xrightarrow{5} Ln_2O_3 \cdot CaO \end{aligned} \tag{5}$$

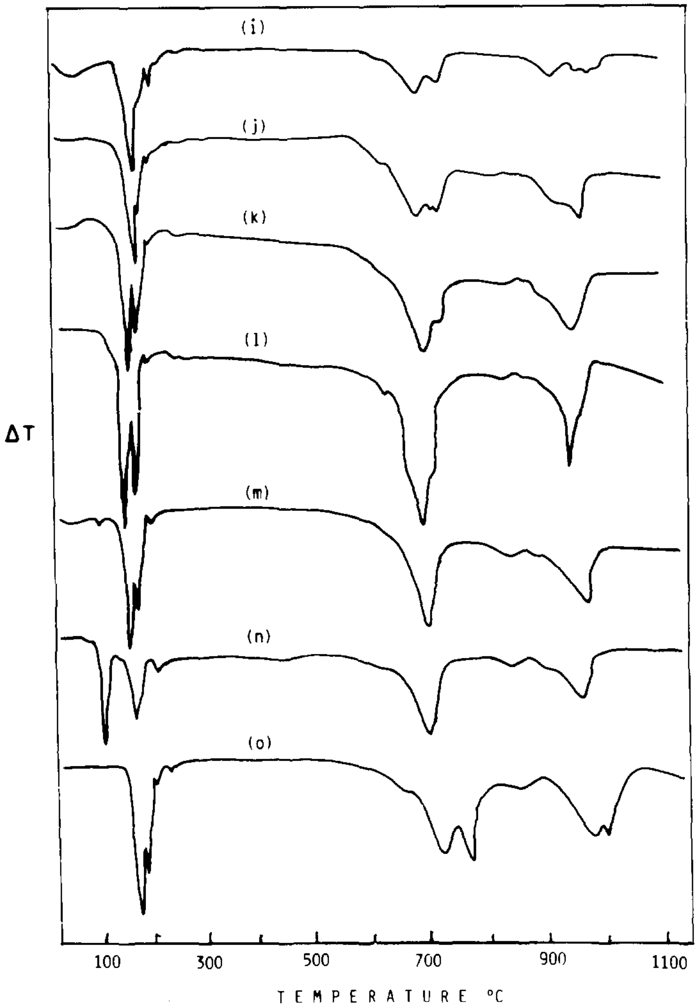

Fig. 4. DTA curves for the double selenates of Dy–Lu, Y and calcium, diluted at 20% (m/m) in α-alumina (heating rate, 12.5°C min^{-1}): i, $Dy_2(SeO_4)_3 \cdot CaSeO_4 \cdot 9H_2O$; j, $Ho_2(SeO_4)_3 \cdot CaSeO_4 \cdot 14H_2O$; k, $Er_2(SeO_4)_3 \cdot CaSeO_4 \cdot 12H_2O$; l, $Tm_2(SeO_4)_3 \cdot CaSeO_4 \cdot 16H_2O$; m, $Yb_2(SeO_4)_3 \cdot CaSeO_4 \cdot 10H_2O$; n, $Lu_2(SeO_4)_3 \cdot CaSeO_4 \cdot 16H_2O$; and o, $Y_2(SeO_4)_3 \cdot CaSeO_4 \cdot 13H_2O$.

where Ln = Nd or Sm.

$$\begin{aligned} &Ln_2(SeO_4)_3 \cdot CaSeO_4 \cdot nH_2O \xrightarrow{1} Ln_2(SeO_4)_3 \cdot CaSeO_4 \\ &\xrightarrow{3} Ln_2O_2SeO_3 \cdot CaSeO_3 \xrightarrow{4} Ln_2O_3 \cdot CaSeO_3 \xrightarrow{5} Ln_2O_3 \cdot CaO \qquad (6) \end{aligned}$$

where Ln = Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu or Y.

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

TABLE 2

Reactions and corresponding temperature ranges observed in the TG curves of the compounds Ln_2(or Y_2)$(SeO_4)_3\cdot CaSeO_4\cdot nH_2O$

Compound	Temperature range of mass loss reactions in the TG curve (°C)				
	1	2	3	4	5
$La_2(SeO_4)_3\cdot CaSeO_4\cdot 9H_2O$	80–300	540–625	625–780	900–1050	1050–1150
$Ce_2(SeO_4)_3\cdot CaSeO_4\cdot 6H_2O$	100–250	–	380–550	550– 730	870–1050
$Pr_2(SeO_4)_3\cdot CaSeO_4\cdot 8H_2O$	80–250	–	520–750	–	750–1070
$Nd_2(SeO_4)_3\cdot CaSeO_4\cdot 8H_2O$	80–250	–	520–750	–	750–1070
$Sm_2(SeO_4)_3\cdot CaSeO_4\cdot 10H_2O$	100–250	–	500–750	–	750–1070
$Eu_2(SeO_4)_3\cdot CaSeO_4\cdot 10H_2O$	100–250	–	500–750	750–1000	1000–1120
$Gd_2(SeO_4)_3\cdot CaSeO_4\cdot 12H_2O$	100–250	–	500–700	700– 900	900–1100
$Tb_2(SeO_4)_3\cdot CaSeO_4\cdot 12H_2O$	80–250	–	520–700	750– 920	920–1050
$Dy_2(SeO_4)_3\cdot CaSeO_4\cdot 9H_2O$	90–250	–	530–720	720– 900	900–1050
$Ho_2(SeO_4)_3\cdot CaSeO_4\cdot 14H_2O$	80–250	–	530–700	750– 900	900–1050
$Er_2(SeO_4)_3\cdot CaSeO_4\cdot 12H_2O$	80–250	–	550–680	750– 880	880–1050
$Tm_2(SeO_4)_3\cdot CaSeO_4\cdot 16H_2O$	60–250	–	500–680	700– 820	900–1050
$Yb_2(SeO_4)_3\cdot CaSeO_4\cdot 10H_2O$	80–250	–	550–700	700– 840	900–1050
$Lu_2(SeO_4)_3\cdot CaSeO_4\cdot 16H_2O$	60–250	–	550–700	700– 850	900–1050
$Y_2(SeO_4)_3\cdot CaSeO_4\cdot 13H_2O$	100–250	–	500–700	700– 900	900–1050

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

TABLE 3

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

Double selenates	Dehydration (Crystalline transition*)	Thermal decomposition of the anhydrous salts
La–Ca	170–220	640–680–745–860–920–980
Ce–Ca	170–220–310	505–745–840–860–950
Pr–Ca	170–220*–240	620–720–780–850–970
Nd–Ca	175–210*–255	620–725–780–970
Sm–Ca	170*–190–210*–225*	625–740–970
Eu–Ca	170*–190–225*	610–700–760–830–970–1090
Gd–Ca	185*–190–210*–225*	625–720–760–850–980–1100
Tb–Ca	185–225*	610–680–755–970–1005
Dy–Ca	60–175–210*–230	710–750–955–1030
Ho–Ca	175–190*–205*	705–735–740–1000
Er–Ca	170–180–205*–230	710–740–860–980
Tm–Ca	160–170–200*–230	650–705–855–975
Yb–Ca	110–160–175–200*	705–850–975
Lu–Ca	110–175–220	700–850–965
Y–Ca	175–180*–205*–230*	650–725–770–980–1005

The first mass losses of the TG curves of Figs. 1 and 2 show that the thermal decomposition processes start with dehydration up to 250 ° C, the last water molecules being lost most slowly. The TG curves of the Nd–Ca, Tm–Ca and Lu–Ca double selenates show evidence of the formation of unstable intermediate hydrates.

The subsequent mass losses in the TG curves are due to the thermal decomposition of the anhydrous double salts formed in the previous step, and occur in a characteristic way in the case of some compounds or groups of compounds.

The TG curve for the La–Ca double selenate shows that the thermal decomposition of the anhydrous compound occurs characteristically in four steps. The first mass loss at 540 ° C can be attributed to the decomposition of lanthanum selenate to lanthanum selenite. Then, almost simultaneously, there occurs the reduction of calcium selenate to calcium selenite, and the formation of lanthanum (di)oxyselenite. After the second mass loss, the intermediate compound $La_2O_2SeO_3 \cdot CaSeO_3$ is obtained. The two mass losses observed at the end of the TG curve are due to consecutive decomposition of the lanthanum (di)oxyselenite to La_2O_3 and of calcium selenite to CaO.

The TG curve for the Ce–Ca compound shows that the thermal decomposition of the anhydrous double selenate occurs in three steps. The first mass loss can be attributed to the thermal decomposition of cerium(III) selenate to cerium(IV) oxide; the second to the reduction of calcium selenate to calcium selenite; and the last to the thermal decomposition of calcium selenite to calcium oxide, the final residue being $CeO_2 \cdot CaO$.

The TG curves for the Pr–Ca, Nd–Ca and Sm–Ca double selenates show that the thermal decomposition of the corresponding anhydrous selenates occurs in two steps: the first is due to the thermal decomposition of the lanthanide selenates to (di)oxyselenites, accompanied by reduction of calcium selenate to calcium selenite; and the second is due to the thermal decomposition of these two intermediate compounds to the corresponding oxides, resulting in the final residue $Ln_2O_3 \cdot CaO$ ($Pr_6O_{11} \cdot CaO$ in the case of the Pr–Ca compound).

The TG curves for the remaining compounds show that the final decomposition occurs in three steps. The first is probably due to the formation of intermediate compounds of the formula $Ln_2O_2SeO_3 \cdot CaSeO_3$; the second corresponds to the formation of intermediate compounds $Ln_2O_3 \cdot CaSeO_3$; and the third is the decomposition to the corresponding oxides $Ln_2O_3 \cdot CaO$ ($Tb_4O_7 \cdot CaO$ in the case of the Tb–Ca compound) that constitute the final residue.

Each of the DTA curves of Figs. 3 and 4 shows one or more endothermic peaks corresponding to the mass losses observed in the associated TG curve, and endothermic peaks corresponding to the crystalline transitions which occur frequently during the dehydration processes. The DTA curves also show peaks which are due to the formation of intermediate compounds not detected in the TG curves. The appearance of these intermediate compounds in the DTA curves is probably due to the fact that the samples were diluted at 20% m/m in α-alumina and well packed into the inconel sample holder. Also as a result of the samples' dilution in α-alumina, the temperatures of the DTA peaks are a little higher than the temperature ranges of the mass losses observed in the TG curves. Because of this sample effect, peaks corresponding to the last mass losses observed in the TG curves were not observable up to 1150 ° C.

CONCLUSIONS

The thermal behaviour of the lanthanide, yttrium and calcium double selenate hydrates showed some differences to the thermal behaviour of the corresponding simple selenates.

The techniques used in the preparation of the compounds led to the formation of double selenate hydrates of formula Ln_2 (or Y_2)$(SeO_4)_3 \cdot CaSeO_4 \cdot nH_2O$.

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

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