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Note

STUDIES ON DOUBLE SELENATES. VI. THERMAL DECOMPOSITION OF GADOLINIUM, TERBIUM, DYSPROSIUM AND ALKALI METAL DOUBLE SELENATES

I. GIOLITO *
Instituto de Química, Universidade de São Paulo, São Paulo, SP, C.P. 20780, 01498 (Brazil)

M. IONASHIRO
Instituto de Química, Universidade Estadual Paulista, Araraquara, SP (Brazil)

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Several investigations have been carried out on the preparation and thermal decomposition of gadolinium [1], terbium [1–3] and dysprosium [1,2] selenate hydrates. The preparation and thermoanalytical studies of alkali metal selenates [4], gadolinium and potassium double selenate [5], gadolinium, terbium and sodium double selenates [6] were also reported. We found no reference in the literature to the preparation and thermal decomposition of the other gadolinium, terbium, dysprosium and alkali metal double selenates.

EXPERIMENTAL

Selenic acid and gadolinium, terbium and dysprosium selenates [1], alkali metal selenates [4] and double selenates of gadolinium, terbium, dysprosium and alkali metals [7] were prepared as described previously. The lanthanide ions were determined by the usual oxalate–oxide gravimetric method, and the alakali metal ions by atomic absorption spectroscopy in a Perkin–Elmer 403 atomic absorption spectrophotometer. Selenium and water of crystallization contents were determined from the TG curves. The TG and DTA curves were obtained as described previously [4,7].

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds prepared having the formula $Ln_2(SeO_4) \cdot M_2SeO_4 \cdot nH_2O$, where Ln = Gd, Tb, Dy and M = Li, Na, K, Rb, Cs.

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* Author to whom correspondence should be addressed.

TABLE 1

Analytical and thermoanalytical (TG) results

Compound	Lanthanide (%)		Alkali metal (%)		Selenium (%)		Water (%)	
	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.
$Gd_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$	29.10	28.81	1.28	1.25	29.23	29.76	16.68	17.14
$Gd_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 13H_2O$	26.98	27.26	3.94	3.39	27.10	27.94	20.10	20.23
$Gd_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 3H_2O$	30.88	30.13	7.68	7.40	31.01	30.93	5.30	4.93
$Gd_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 12H_2O$	24.70	24.53	13.42	13.66	24.80	25.04	16.98	16.89
$Gd_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 13H_2O$	22.68	22.54	19.17	20.37 [a]	22.78	22.68	16.90	16.82
$Tb_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 14H_2O$	27.50	27.31	1.20	1.54	27.33	27.96	19.31	19.77
$Tb_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 9H_2O$	28.95	28.12	4.18	4.29	28.77	28.84	14.77	14.20
$Tb_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 6H_2O$	29.54	29.13	7.27	7.79	29.35	28.63	10.05	9.92
$Tb_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$	27.20	26.92	14.63	14.65	27.02	27.74	9.25	8.81
$Tb_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 5H_2O$	25.52	25.68	21.34	22.21 [a]	25.35	25.22	7.23	7.17
$Dy_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 18H_2O$	26.31	25.43	1.12	1.22	25.57	26.06	26.26	26.27
$Dy_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 18H_2O$	25.65	25.87	3.63	3.11	24.92	24.78	25.60	25.71
$Dy_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 18H_2O$	25.01	25.41	6.02	5.91	24.31	24.85	24.96	24.36
$Dy_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 14H_2O$	24.62	24.74	12.95	13.58	23.93	23.47	19.11	19.17
$Dy_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 14H_2O$	22.97	23.04	18.79	19.10 [a]	22.32	22.22	17.83	18.13

[a] TG curve.

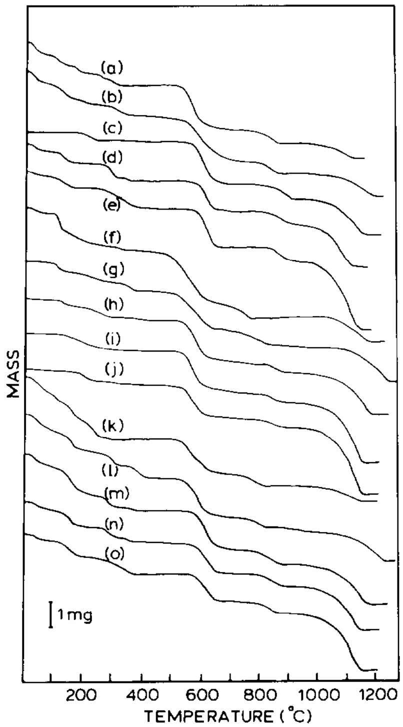

Fig. 1. TG curves of the double selenates of Gd, Tb, Dy, and alkali metal. Heating rate: 5.2° C min^{-1}. (a) $Gd_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$ (7.50 mg); (b) $Gd_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 13H_2O$ (7.32 mg); (c) $Gd_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 3H_2O$ (7.10 mg); (d) $Gd_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 12H_2O$ (7.06 mg); (e) $Gd_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 13H_2O$ (7.88 mg); (f) $Tb_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 14H_2O$ (7.28 mg); (g) $Tb_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 9H_2O$ (7.14 mg); (h) $Tb_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 6H_2O$ (7.06 mg); (i) $Tb_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$ (7.38 mg); (j) $Tb_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 5H_2O$ (7.32 mg); (k) $Dy_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 18H_2O$ (7.26 mg); (l) $Dy_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 18H_2O$ (7.70 mg); (m) $Dy_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 18H_2O$ (7.48 mg); (n) $Dy_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 14H_2O$ (7.34 mg); and (o) $Dy_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 14H_2O$ (7.32 mg).

It can be seen from the TG and DTA curves of Figs. 1 and 2, respectively, that the thermal decomposition of those double selenates still occurs in a characteristic way for each compound. All the reactions taking place during the thermal decomposition of these compounds can be summarized by the following equations

$$Ln_2(SeO_4)_3 \cdot M_2SeO_4 \cdot nH_2O \rightarrow Ln_2(SeO_4)_3 \cdot M_2SeO_4 + nH_2O \tag{1}$$

$$Ln_2(SeO_4)_3 \cdot M_2SeO_4 \rightarrow Ln_2O_2SeO_3 \cdot M_2SeO_4 + 2SeO_2 + 1.5O_2 \tag{2}$$

$$Ln_2O_2SeO_3 \cdot M_2SeO_4 \rightarrow Ln_2O_3 \cdot M_2SeO_3 + SeO_2 + 0.5O_2 \tag{3}$$

$$2Ln_2O_2SeO_3 \cdot M_2SeO_4 \rightarrow Ln_4O_7 \cdot 2M_2SeO_3 + 2SeO_2 + 0.5O_2 \tag{3'}$$

$$Ln_2O_3 \cdot M_2SeO_3 \rightarrow Ln_2O_3 + M_2O + SeO_2 \tag{4}$$

$$Ln_4O_7 \cdot 2M_2SeO_3 \rightarrow Ln_4O_7 + 2M_2O + 2SeO_2 \tag{4'}$$

$$Ln_2O_2SeO_3 \cdot M_2SeO_4 \rightarrow Ln_2O_3 \cdot M_2SeO_4 + SeO_2 \tag{5}$$

$$2Ln_2O_2SeO_3 \cdot M_2SeO_4 \rightarrow Ln_4O_7 \cdot 2M_2SeO_4 + 2SeO_2 \tag{5'}$$

$$Ln_2O_3 \cdot M_2SeO_4 \rightarrow Ln_2O_3 + M_2O + SeO_2 + 0.5O_2 \tag{6}$$

$$Ln_4O_7 \cdot 2M_2SeO_4 \rightarrow Ln_4O_7 + 2M_2O + 2SeO_2 + O_2 \tag{6'}$$

$$Ln_2O_3 \cdot M_2SeO_4 \rightarrow Ln_2O_3 + xM_2O + xSeO_2 + 0.5xO_2 + |(1-x)M_2SeO_4| \tag{7}$$

$$\begin{aligned} Ln_4O_7 \cdot 2M_2SeO_4 \rightarrow & + Ln_4O_7 + xM_2O + xSeO_2 + 0.5xO_2 \\ & + |(2-x)M_2SeO_4| \end{aligned} \tag{7'}$$

$$Ln_2O_3 \cdot M_2SeO_4 \rightarrow Ln_2O_3 + |M_2SeO_4| \tag{8}$$

In the reactions marked with ′, Ln = Tb.

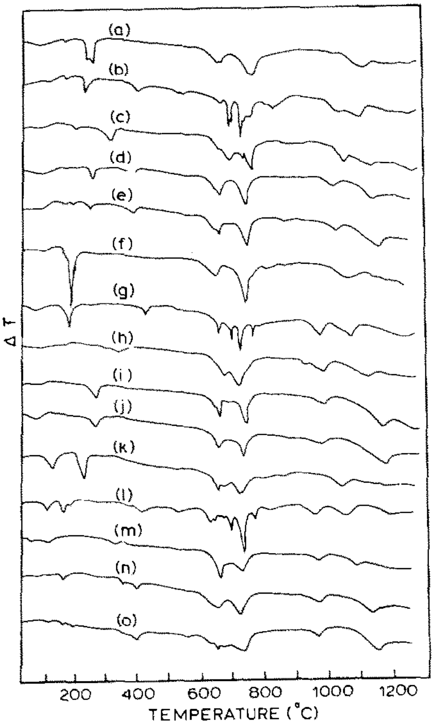

Fig. 2. DTA curves of the double selenates of Gd, Tb, Dy, and alkali metal, diluted at 20% in α-alumina. Heating rate: 9.0 °C min^{-1} (a) $Gd_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$; (b) $Gd_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 13H_2O$; (c) $Gd_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 3H_2O$; (d) $Gd_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 12H_2O$; (e) $Gd_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 13H_2O$; (f) $Tb_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 14H_2O$; (g) $Tb_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 9H_2O$; (h) $Tb_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 6H_2O$; (i) $Tb_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$; (j) $Tb_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 5H_2O$; (k) $Dy_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 18H_2O$; (l) $Dy_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 18H_2O$; (m) $Dy_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 18H_2O$; (n) $Dy_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 14H_2O$; and (o) $Dy_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 14H_2O$.

TABLE 2

Reactions and corresponding temperature ranges observed in the TG curves of the compounds $Ln_2(SeO_4)_3 \cdot M_2SeO_4 \cdot nH_2O$

Compound	Temperature range of mass loss reactions in the TG curves (° C)							
	1	2	3 (3′)	4 (4′)	5 (5′)	6 (6′)	7 (7′)	8
$Gd_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$	75–345	520–700	700–880	980–1140	–	–	–	–
$Gd_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 13H_2O$	75–380	520–730	–	–	730–890	980–1210	–	–
$Gd_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 3H_2O$	200–250	550–700	–	–	820–940	1000–1180	–	–
$Gd_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 12H_2O$	80–380	555–700	–	–	810–940	–	955–1140	–
$Gd_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 13H_2O$	80–400	550–690	–	–	810–930	–	–	955–1150
$Tb_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 14H_2O$	110–380	450–650	650–780	1020–1180	–	–	–	–
$Tb_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 9H_2O$	100–380	490–680	–	–	680–850	1050–1250	–	–
$Tb_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 6H_2O$	100–300	500–700	–	–	700–900	–	950–1190	–
$Tb_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$	110–350	520–700	–	–	700–900	–	970–1170	–
$Tb_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 5H_2O$	160–360	520–670	–	–	730–900	–	950–1165	–
$Dy_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 18H_2O$	70–330	505–670	670–830	950–1155	–	–	–	–
$Dy_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 18H_2O$	70–450	510–655	–	–	665–830	–	870–1240	–
$Dy_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 18H_2O$	70–390	550–700	–	–	740–870	–	–	950–1180
$Dy_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 14H_2O$	70–380	550–700	–	–	755–900	–	950–1150	–
$Dy_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 14H_2O$	100–370	550–660	–	–	760–870	–	900–1160	–

TABLE 3

Temperature of DTA peaks (all endothermic) corresponding to reactions and fusion of the $Ln_2(SeO_4)_3 \cdot M_2SeO_4 \cdot nH_2O$

Compound	Peak temperature in DTA curves (° C)								
	1	2	3 (3′)	4 (4′)	5 (5′)	6 (6′)	7 (7′)	8	Fusion
$Gd_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$	157, 235, 257	650, 767	1110	> 1200	–	–	–	–	650
$Gd_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 13H_2O$	157, 225, 395	661, 757, 833	–	–	1093	> 1200	–	–	723
$Gd_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 3H_2O$	194, 311	690, 760	–	–	–	1265	–	–	1137
$Gd_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 12H_2O$	161, 254, 386	659, 743	–	–	1023	–	> 1250	–	1143
$Gd_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 13H_2O$	158, 250, 386	657, 746	–	–	1023	–	–	> 1250	1160
$Tb_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 14H_2O$	179	636, 741	1060	> 1250	–	–	–	–	636
$Tb_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 9H_2O$	171, 421	653, 718	–	–	973, 1068	> 1200	–	–	693
$Tb_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 6H_2O$	336	667, 711	–	–	982	–	> 1250	–	1127
$Tb_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$	262	654, 736	–	–	982	–	> 1250	–	1167
$Tb_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 5H_2O$	264	650, 732	–	–	971	–	> 1250	–	1170
$Dy_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 18H_2O$	113, 223	671, 718	1043	> 1250	–	–	–	–	650
$Dy_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 18H_2O$	100, 160, 409	626, 727	–	–	950, 1050	–	> 1250	–	690
$Dy_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 18H_2O$	100, 328, 368	659, 728	–	–	968	–	–	> 1250	1087
$Dy_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 14H_2O$	156, 350, 395	650, 721	–	–	968	–	> 1250	–	1136
$Dy_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 14H_2O$	150, 350, 396	650, 728	–	–	964	–	> 1200	–	1150

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

Table 3 indicates the temperature of DTA peaks (all endothermic) corresponding to the reactions or fusion occurring for each compound.

As seen from the TG curves of Fig. 1, the thermal decomposition of these compounds starts with dehydration and it occurs in a characteristic way for each compound. Except for Gd–K, Tb–K, Tb–Rb, and Tb–Cs double selenates, all compounds showed a high degree of hydration. Dehydration occurs in one, two, three, or four steps, the last trace of water being eliminated up to 400 ° C, as in the case of double salts containing sodium. The mass losses observed at temperatures below 70 ° C are probably due to the presence of water because of the high hygroscopicity of these compounds at room temperature.

The TG curves of Fig. 1 also show that the subsequent thermal decomposition of the anhydrous double salts occurs in three steps. The first step corresponds to mass losses occurring between 490 and 730 ° C which are due to the intermediate formation of (di)oxyselenite of gadolinium, terbium and dysprosium. There is no evidence in the TG curves of the intermediate formation of the corresponding selenites or (mono)oxyselenite. All double selenates gave positive tests for selenite ion in the presence of selenate ion [8] after being heated at 650 ° C in a platinum crucible, indicating that the reduction of selenate ion to selenite ion and the formation of (di)oxyselenite occurs simultaneously [7].

The second step of the thermal decomposition of the anhydrous double selenates are due to the decomposition of the (di)oxyselenites, formed in the previous step, to the corresponding lanthanide oxides (Gd_2O_3, Tb_4O_7, and Dy_2O_3) and to the reduction of lithium selenate to lithium selenite [4] in the cases of Gd–Li, Tb–Li, and Dy–Li double selenates.

The last mass losses observed in the TG curves are due to the final decomposition of the alkaline selenate (selenite in the case of the three double salts containing lithium). In the case of Gd–Li, Tb–Li, and Dy–Li double selenates, the lithium selenite formed previously decomposes into lithium oxide and the final residues contain a mixture of lithium oxide and lanthanide oxide. In the double salts containing sodium partial reduction of the sodium selenate to sodium selenite probably occurs and the mixture decomposes into sodium oxide with partial evaporation occurring simultaneously.

The final mass losses of the other double selenates seem to occur without the intermediate formation of alkali metal selenites. Only Gd–K double selenate showed the theoretical residue of K_2O. In the case of Tb–K, Gd–Rb, Tb–Rb, Dy–Rb, Tb–Cs, and Dy–Cs double selenates, the final decomposition of the alkaline selenates into the corresponding oxides occurred with partial evaporation. These compounds presented final residues formed by the corresponding lanthanide oxide and 89%, 73%, 54%, 65%, 57%, and 65%, respectively, of the theoretical amount of alkali metal oxides.

The final residues of Dy–K and Gd–Cs double selenates were practically formed only by Dy_2O_3 and Gd_2O_3, indicating almost total evaporation of the alkali selenates and their oxides.

The DTA curves of Fig. 2 show endothermic peaks corresponding to all mass losses visible in the TG curves, and peaks corresponding to fusion. The temperature of each DTA peak and its probable interpretation are shown in Table 3.

CONCLUSIONS

The thermal behavior of gadolinium, terbium, dysprosium and alkali metal double selenates revealed some differences compared to the thermal behavior of the corresponding simple selenates and the double selenates already reported, specially regarding the great amount of water present, mechanism of dehydration, and the amount of alkali metal compounds undergoing volatilization. Each double selenate presents characteristic TG and DTA patterns.

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