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Note

STUDIES ON DOUBLE SELENATES. VII. THERMAL DECOMPOSITION OF HOLMIUM, ERBIUM, THULIUM AND ALKALI METAL DOUBLE SELENATES

M. IONASHIRO

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

I. GIOLITO *

Instituto de Química, Universidade de São Paulo, São Paulo, SP, C.P. 20780, 01498 (Brazil)
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The preparation and thermal decomposition of holmium, erbium and thulium selenates [1,2], alkali metal selenates [3] and holmium and cesium double selenate trihydrate [4] were already reported. There is also an old reference to the preparation of erbium and potassium double selenate octohydrate [5]. We found no reference in the literature to the preparation and thermal decomposition of the other holmium, thulium and alkali metal double selenates.

EXPERIMENTAL

Selenic acid and holmium, erbium and thulium selenates [1] alkali metal selenates [3] and double selenates of holmium, erbium, thulium and alkali metals [6] were prepared following the procedures described previously. The lanthanide ions were determined by the usual oxalate–oxide gravimetric method, and alkali metal ions by atomic absorption spectroscopy in a Perkin–Elmer 403 atomic absorption spectrophotometer. Water of crystallization and selenium contents were determined from the TG curves. The TG and DTA curves were obtained according to the procedures described previously [6].

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds prepared having the formula $Ln_2(SeO_4)_3 \cdot M_2SeO_4 \cdot nH_2O$, where Ln = Ho, Er, Tm and M = Li, Na, K, Rb, Cs.

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* Author to whom correspondence should be addressed.

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TABLE 1

Analytical and thermoanalytical TG results

Compound	Lanthanide (%)		Alkali metal (%)		Selenium (%)		Water (%)	
	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.
$Ho_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 8H_2O$	31.13	31.51	1.31	1.21	29.80	28.48	13.60	13.81
$Ho_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 6H_2O$	31.24	31.06	4.35	4.02	29.91	29.49	10.24	10.42
$Ho_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$	29.82	30.32	7.07	6.67	28.56	28.51	11.40	11.42
$Ho_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 2H_2O$	29.75	29.23	15.42	15.21	28.48	28.63	3.25	3.51
$Ho_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 4H_2O$	26.61	26.83	21.44	20.61 [a]	25.48	25.96	5.81	5.97
$Er_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 14H_2O$	28.54	28.13	1.18	1.16	26.94	27.53	21.51	21.29
$Er_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 10H_2O$	29.54	28.91	4.06	3.78	27.89	27.10	15.91	15.93
$Er_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$	31.66	30.84	7.40	7.21	29.89	30.24	6.82	7.02
$Er_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 9H_2O$	26.99	26.46	13.79	13.41	25.48	25.40	13.08	13.42
$Er_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 8H_2O$	25.41	25.13	20.19	20.03 [a]	23.99	24.04	10.95	11.00
$Tm_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$	30.61	30.12	1.26	1.45	28.62	28.09	16.31	16.71
$Tm_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 8H_2O$	30.72	30.28	4.18	4.21	28.71	28.55	13.44	13.11
$Tm_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$	30.33	30.38	7.02	6.94	28.35	28.07	11.32	11.27
$Tm_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$	28.42	28.75	14.38	13.66	26.57	26.18	9.15	9.10
$Tm_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 6H_2O$	26.32	25.71	20.71	20.71	24.61	24.07	8.42	8.29

[a] TG curve.

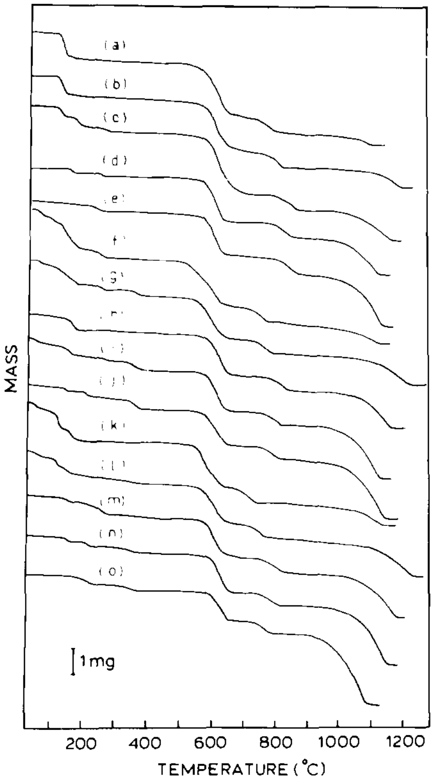

Fig. 1. TG curves of the double selenates of Ho, Er, Tm and alkali metal. Heating rate: 5.2°C min^{-1}. (a) $Ho_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 8H_2O$ (7.24 mg); (b) $Ho_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 6H_2O$ (7.20 mg); (c) $Ho_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$ (7.88 mg); (d) $Ho_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 2H_2O$ (7.12 mg); (e) $Ho_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 4H_2O$ (7.10 mg); (f) $Er_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 14H_2O$ (7.28 mg); (g) $Er_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 10H_2O$ (7.22 mg); (h) $Er_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$ (7.12 mg); (i) $Er_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 9H_2O$ (7.08 mg); (j) $Er_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 8H_2O$ (7.27 mg); (k) $Tm_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$ (7.18 mg); (l) $Tm_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 8H_2O$ (7.12 mg); (m) $Tm_2(SeO_4)_3 \cdot K_2SO_4 \cdot 7H_2O$ (7.11 mg); (n) $Tm_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$ (7.15 mg); and (o) $Tm_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 6H_2O$ (7.24 mg).

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

$$Ln_2(SeO_4)_3 \cdot M_2SeO_4 nH_2O \rightarrow Ln_2(SeO_4)_3 \cdot M_2SeO_4 + nH_2O \quad (1)$$

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

$$Ln_2O_2SeO_3 \cdot M_2SeO_4 \rightarrow Ln_2O_3 \cdot M_2SeO_4 + SeO_2 + 0.5O_2 \quad (3)$$

$$Ln_2O_3 \cdot M_2SeO_4 \rightarrow Ln_2O_3 + M_2O + SeO_2 \quad (4)$$

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

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

$$\mathrm{Ln_2O_3 \cdot M_2SeO_4 \rightarrow Ln_2O_3} + x\mathrm{M_2O} + x\mathrm{SeO_2} + 0.5\mathrm{O_2} + |(1-x)\mathrm{M_2SeO_4}| \tag{7}$$

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

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 once more it occurs in a characteris-

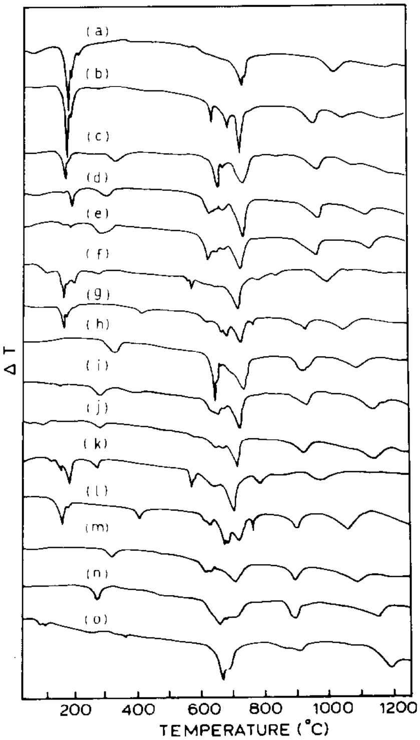

Fig. 2. DTA curves of the double selenates of Ho, Er, Tm and alkali metal, diluted at 20% in α-alumina. Heating rate: 9.0 °C min^{-1}. (a) $\mathrm{Ho_2(SeO_4)_3 \cdot Li_2(SeO_4) \cdot 8H_2O}$; (b) $\mathrm{Ho_2(SeO_4)_3 \cdot Na_2(SeO_4) \cdot 6H_2O}$; (c) $\mathrm{Ho_2(SeO_4)_3 \cdot K_2(SeO_4) \cdot 7H_2O}$; (d) $\mathrm{Ho_2(SeO_4)_3 \cdot Rb_2(SeO_4) \cdot 2H_2O}$; (e) $\mathrm{Ho_2(SeO_4)_3 \cdot Cs_2(SeO_4) \cdot 4H_2O}$; (f) $\mathrm{Er_2(SeO_4)_3 \cdot Li_2(SeO_4) \cdot 14H_2O}$; (g) $\mathrm{Er_2(SeO_4)_3 \cdot Na_2(SeO_4) \cdot 10H_2O}$; (h) $\mathrm{Er_2(SeO_4)_3 \cdot K_2(SeO_4) \cdot 4H_2O}$; (i) $\mathrm{Er_2(SeO_4)_3 \cdot Rb_2(SeO_4) \cdot 9H_2O}$; (j) $\mathrm{Er_2(SeO_4)_3 \cdot Cs_2(SeO_4) \cdot 8H_2O}$; (k) $\mathrm{Tm_2(SeO_4)_3 \cdot Li_2(SeO_4) \cdot 10H_2O}$; (l) $\mathrm{Tm_2(SeO_4)_3 \cdot Na_2(SeO_4) \cdot 8H_2O}$; (m) $\mathrm{Tm_2(SeO_4)_3 \cdot K_2(SeO_4) \cdot 7H_2O}$; (n) $\mathrm{Tm_2(SeO_4)_3 \cdot Rb_2(SeO_4) \cdot 6H_2O}$; and (o) $\mathrm{Tm_2(SeO_4)_3 \cdot Cs_2(SeO_4) \cdot 6H_2O}$.

TABLE 2

Reactions and corresponding temperature ranges observed in TG curves of the compounds $Ln_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot nH_2O$

Compound	Temperature range of mass loss reactions in the TG curves (° C)							
	1	2	3	4	5	6	7	8
$Ho_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 8H_2O$	118–184	512–684	684–800	967–1105	–	–	–	–
$Ho_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 6H_2O$	100–184	530–700	–	–	700–824	1020–1205	–	–
$Ho_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$	107–279	532–732	–	–	732–883	–	978–1167	–
$Ho_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 2H_2O$	135–264	527–650	–	–	768–860	–	955–1135	–
$Ho_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 4H_2O$	131–264	534–650	–	–	750–881	–	937–1128	–
$Er_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 14H_2O$	67–267	486–650	690–780	860–1137	–	–	–	–
$Er_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 10H_2O$	88–375	515–650	–	–	707–800	1027–1222	–	–
$Er_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$	91–173	550–677	–	–	750–850	–	1007–1166	–
$Er_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 9H_2O$	83–382	550–650	–	–	750–833	–	–	967–1137
$Er_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 8H_2O$	110–372	534–650	–	–	733–826	–	–	970–1150
$Tm_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$	84–243	512–650	650–750	900–1150	–	–	–	–
$Tm_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 8H_2O$	83–350	500–657	–	–	674–786	–	–	1000–1228
$Tm_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$	110–393	550–675	–	–	675–850	–	–	1000–1184
$Tm_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$	126–381	550–671	–	–	730–819	–	–	960–1161
$Tm_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 6H_2O$	157–377	557–657	–	–	700–793	–	–	886–1094

TABLE 3

Temperature of DTA peaks (all endothermic) corresponding to reactions and fusion of the compounds $Ln_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot nH_2O$

Compound	Peak temperature in DTA curves (° C)								
	1	2	3	4	5	6	7	8	Fusion
$Ho_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 8H_2O$	171	734, 745	1026	> 1250	–	–	–	–	–
$Ho_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 6H_2O$	169	727	–	–	961	1053, 1180	–	–	686
$Ho_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$	165, 331	675, 737	–	–	971	–	> 1250	–	1081
$Ho_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 2H_2O$	188, 300	624, 674, 736	–	–	975	–	> 1250	–	1130
$Ho_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 4H_2O$	286	625, 674, 728	–	–	968	–	> 1250	–	1137
$Er_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 14H_2O$	159, 203, 284	718	1000	> 1250	–	–	–	–	571
$Er_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 10H_2O$	161, 414	713, 775	–	–	983	1100, > 1250	–	–	733
$Er_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$	377	785	–	–	976	–	> 1250	–	1140
$Er_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 9H_2O$	150, 280, 400	708, 776	–	–	989	–	–	> 1250	1150
$Er_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 8H_2O$	280	650, 670, 717	–	–	927	–	–	> 1250	1150
$Tm_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$	117, 180, 275	645, 707, 790	980	> 1250	–	–	–	–	572
$Tm_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 8H_2O$	154, 405	629, 689, 719	–	–	904	–	–	1060, > 1250	767
$Tm_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$	320	617, 636, 709	–	–	895		–	> 1250	1093
$Tm_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$	275	662, 709	–	–	895	–	–	> 1250	1157
$Tm_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 6H_2O$	250, 363	671, 693	–	–	913	–	–	> 1250	1195

tic way for each compound. The Ho–Li, Ho–Na, Ho–Cs and Er–K double selenates dehydration occurs in one single step. In the case of the Ho–Cs double selenate trihydrate already reported [4], dehydration occurred in two steps but the part of the TG curve corresponding to the thermal decomposition of the anhydrons double salt is quite similar to the corresponding part of the TG curve of the Ho–Cs double selenate described in the present report. This difference in dehydration probably is due to the fact that these compounds were prepared by different techniques.

The Ho–Rb, Tm–Li, Tm–K, Tm–Cs double selenates undergo dehydration in two steps and Ho–K, Er–Li, Er–Na, Er–Rb, Er–Cs, Tm–Na, Tm–Rb double selenates in three steps. The mass losses observed at temperatures below 80 °C (Er–Li, Er–Na, Tm–Li, Tm–Na double selenates) probably are 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 depends upon the lanthanide and alkali metal selenate present and occurs in three steps.

The first mass losses occurring between 486 and 557 °C are due to the intermediate formation of the (di)oxyselenites of the corresponding lanthanides. There is no evidence in the TG curves of the intermediate formation of the corresponding selenites or (mono)oxyselenite. Notwithstanding all double selenates gave positive tests for selenite ion in presence of selenate ion [7] after being heated at 700 °C in platinum crucibles.

The second mass losses of the anhydrous double selenates occurring between 650 and 768 °C are due to the decomposition of the (di)oxyselenites formed previously, to the corresponding lanthanides oxides (Ho_2O_3, Er_2O_3, and Tm_2O_3) and to the reduction of lithium selenate to lithium selenite [3] in the case of Ho–Li, Er–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. In the case of the double salts containing lithium, the lithium selenite formed in the previous step decomposes into lithium oxide and the final residues contain a mixture of lithium oxide and lanthanide oxide. The sodium selenate of the double salts containing sodium probably undergoes partial reduction to sodium selenite and the mixture decomposes into sodium oxide with partial evaporation.

The alkali metal selenates of Ho–K, Ho–Rb, Ho–Cs, and Er–K double selenates decomposes into the corresponding oxides with partial evaporation. The final residues of these compounds were formed by the corresponding lanthanide oxide and 77%, 59%, 34%, and 43%, respectively, of the theoretical amount of alkali metal oxides.

The final residues of Er–Rb, Er–Cs, Tm–Na, Tm–K, Tm–Rb, and Tm–Cs double selenates were practically formed by the corresponding lanthanide oxides, which indicate almost total evaporation of the alkali selenates and their oxides.

The DTA curves of Figs. 2 show endothermic peaks in correspondence with all mass losses presented by the TG curves and peaks corresponding to fusion. The temperature of each DTA peak and its probable interpretation are shown in Table 3.

The general aspect of DTA of Ho–Cs double selenate trihydrate already reported [4] is different as compared with the DTA curve of Ho–Cs double selenate tretrahydrate described in the present report, but the peak temperatures in both DTA curves show good agreement.

CONCLUSIONS

The thermal behavior of holmium, erbium, thulium and alkali metal double selenates showed some differences compared to the thermal behavior of the corresponding simple selenates and the double selenates already reported, specially regarding the increasing amount of alkali metal compounds undergoing volatilization. Each double selenate presents characteristic TG and DTA patterns.

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