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Note

STUDIES ON DOUBLE SELENATES. VIII. THERMAL DECOMPOSITION OF YTTERBIUM, LUTETIUM, YTTRIUM AND ALKALI METAL DOUBLE SELENATES

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The preparation and thermal decomposition of ytterbium, lutetium and yttrium selenates [1,2] and alkali metal selenates [3] were already reported. There are also two old references to the preparation of yttrium and potassium double selenate di- and tetrahydrate [4] and hexahydrate, with data about its solubility in water and indication of the loss of $5H_2O$ at 185 °C [5]. More recently it was reported the preparation and thermal decomposition of ytterbium and cesium double selenate trihydrate [6]. We found no reference in the literature to the preparation and thermal decomposition of the other ytterbium, lutetium, yttrium and alkali metal double selenates.

EXPERIMENTAL

Selenic acid and ytterbium, lutetium and yttrium selenates [1] alkali metal senelates [3] and double selenates ytterbium, lutetium, yttrium, and alkali metal [7] were prepared following the procedures described previously.

The lanthanide ions were determined by the usual oxalate–oxide gravimetric method, and the 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 procedures described previously [7].

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RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds prepared having the formula $Ln_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot nH_2O$, where Ln = Yb, Lu, Y and Me = Li, Na, K, Rb, Cs.

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

$$Ln_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot nH_2O \rightarrow Ln_2(SeO_4)_3 \cdot Me_2SeO_4 + nH_2O \tag{1}$$

$$Ln_2(SeO_4)_3 \cdot Me_2SeO_4 \rightarrow Ln_2O_2SeO_3 \cdot Me_2SeO_4 + 2SeO_2 + 1.5O_2 \tag{2}$$

$$Ln_2O_2SeO_3 \cdot Me_2SeO_4 \rightarrow Ln_2O_3 \cdot Me_2SeO_3 + SeO_2 + 0.5O_2 \tag{3}$$

$$Ln_2O_3 \cdot Me_2SeO_3 \rightarrow Ln_2O_3 + Me_2O + SeO_2 \tag{4}$$

$$Ln_2O_2 \cdot SeO_3 \cdot Me_2SeO_4 \rightarrow Ln_2O_3 \cdot Me_2SeO_4 + SeO_2 \tag{5}$$

$$\begin{aligned} Ln_2O_2SeO_3 \cdot MeSeO_4 \rightarrow\ & Ln_2O_3 + xMe_2O + xSeO_2 + 0.5O_2 \\ & + |(1-x)Me_2SeO_4| \end{aligned} \tag{6}$$

$$Ln_2O_3 \cdot Me_2SeO_4 \rightarrow Ln_2O_3 + |Me_2SeO_4| \tag{7}$$

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 1

Analytical and thermoanalytical (TG) results

Compound	Lanthanide (%)		Alkali metal (%)		Selenium (%)		Water (%)	
	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.	Theor.	Expt.
$Yb_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 9H_2O$	31.64	31.45	1.27	1.43	28.88	28.32	14.81	15.28
$Yb_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 10H_2O$	30.25	29.66	4.02	4.05	27.61	27.51	15.74	15.97
$Yb_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$	32.40	31.72	1.32	7.12	29.57	29.01	6.75	6.67
$Yb_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3H_2O$	30.28	29.63	14.96	14.22	27.63	27.38	4.73	4.81
$Yb_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 3H_2O$	27.96	27.86	21.47	21.68	25.52	25.52	4.37	4.51
$Lu_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 9H_2O$	31.88	31.14	1.26	1.42	28.77	27.99	14.76	14.42
$Lu_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 7H_2O$	31.99	31.54	4.20	3.83	28.88	28.52	11.52	11.64
$Lu_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$	32.64	31.94	7.29	6.84	29.46	28.84	6.72	7.01
$Lu_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3H_2O$	30.52	29.56	14.91	14.72	27.54	27.18	4.72	4.83
$Lu_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 2H_2O$	28.60	28.41	21.72	21.81	25.81	25.84	2.95	2.96
$Y_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$	18.84	18.19	1.47	1.60	33.47	32.75	19.09	19.23
$Y_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 9H_2O$	18.56	17.98	4.80	4.60	32.98	32.67	16.93	16.92
$Y_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$	18.64	18.51	8.20	7.80	33.11	33.08	13.22	13.09
$Y_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 7H_2O$	17.28	17.38	16.62	16.96	30.70	30.72	10.51	10.53
$Y_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 6H_2O$	15.82	16.02	23.66	23.61	28.11	28.40	9.62	9.54

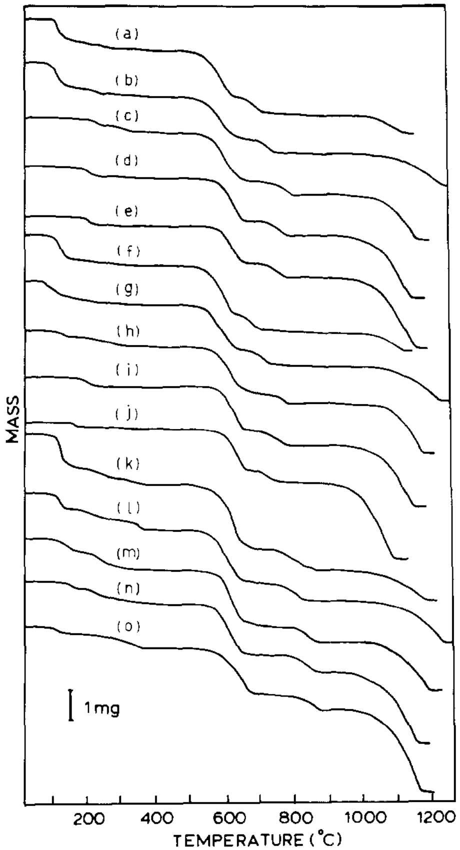

Fig. 1. TG curves of the double selenates of Yb, Lu, Y and alkali metal. Heating rate: 5.2° C min^{-1}. (a) $Yb_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 9H_2O$ (7.16 mg); (b) $Yb_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 10H_2O$ (7.20 mg); (c) $Yb_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$ (7.50 mg); (d) $Yb_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3H_2O$ (7.28 mg); (e) $Yb_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 3H_2O$ (7.20 mg); (f) $Lu_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 9H_2O$ (7.28 mg); (g) $Lu_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 7H_2O$ (7.30 mg); (h) $Lu_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$ (7.18 mg); (i) $Lu_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3H_2O$ (7.24 mg); (j) $Lu_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 2H_2O$ (7.60 mg); (k) $Y_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$ (8.32 mg); (l) $Y_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 9H_2O$ (7.24 mg); (m) $Y_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$ (7.29 mg); (n) $Y_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$ (7.36 mg); and (o) $Y_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 6H_2O$ (7.34 mg).

Table 3 gives the temperatures of DTA peaks, all endothermic, corresponding to the reactions or fusion occurring for each compound.

The TG curves of Fig. 1 show that the thermal decomposition of these compounds starts with dehydration; it occurs in a characteristic way for each double salt of the same lanthanide. Many compounds show the existence of intermediate hydrates, the last traces of water being eliminated up to 364° C. Though the Yb–Cs double selenate reported by Nabar and Ajgaonkar [6] and that reported in the present note are both trihydrate, in the first case the loss of water occurs in two steps and in the present instance

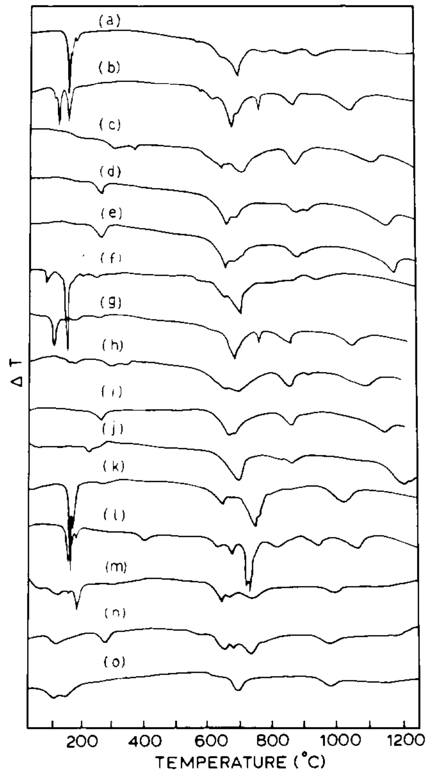

Fig. 2. DTA curves of double selenates of Yb, Lu, Y and alkali metal, diluted at 20% in α-alumina. Heating rate: 9.0 °C min^{-1}. (a) $Yb_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 9H_2O$; (b) $Yb_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 10H_2O$; (c) $Yb_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$; (d) $Yb_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3H_2O$; (e) $Yb_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 3H_2O$; (f) $Lu_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 9H_2O$; (g) $Lu_2(SeO_4)_3 \cdot Na_sSeO_4 \cdot 7H_2O$; (h) $Lu_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$; (i) $Lu_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3H_2O$; (j) $Lu_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 2H_2O$; (k) $Y_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$; (l) $Y_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 9H_2O$; (m) $Y_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$; (n) $Y_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$; and (o) $Y_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 6H_2O$.

in only one step. Probably that difference in behavior is due to differences in preparation procedures and aging time.

The TG curves of Fig. 1 also show that the subsequent thermal decomposition of the anhydrous double selenates depends upon the lanthanide and alkali metal selenate present and occurs in three steps.

The first mass losses with initial temperature between 495 and 550 °C are due to the intermediate formation of the (di)oxyselenites of the corresponding lanthanides. Once more there is no evidence of intermediate formation of selenites or (mono)oxyselenites. All double selenates gave positive tests for selenite ion in the presence of selenate ion [8] after being heated at 650 °C in platinum crucibles.

The second mass losses of the anhydrous double selenates occurring between 638 and 778 °C are due to the decomposition of the (di)oxyselenites

TABLE 2

Reactions and corresponding temperature ranges observed in TG curves of the compounds $Ln_2(SeO_4)_2 \cdot Me_2SeO_4 \cdot nH_2O$

Compound	Temperature range of mass loss reactions in the TG curves (° C)						
	1	2	3	4	5	6	7
$Yb_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 9H_2O$	87–288	500–643	643–730	1032–1141	–	–	–
$Yb_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 10H_2O$	73–232	500–657	–	–	657–755	1000–1243	–
$Yb_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$	182–331	530–680	–	–	718–814	–	1040–1190
$Yb_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3H_2O$	181–250	543–671	–	–	707–793	–	968–1164
$Yb_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 3H_2O$	171–268	550–672	–	–	713–768	–	971–1167
$Lu_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 9H_2O$	85–271	500–638	638–722	1011–1134	–	–	–
$Lu_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 7H_2O$	60–250	495–654	–	–	654–750	1050–1234	–
$Lu_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$	100–320	533–689	–	–	732–793	–	1000–1180
$Lu_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3H_2O$	175–228	550–668	–	–	700–796	–	961–1158
$Lu_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 2H_2O$	150–179	540–660	–	–	688–750	–	900–1100
$Y_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$	86–350	500–700	734–867	1000–1180	–	–	–
$Y_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 9H_2O$	106–364	533–671	–	–	720–832	1050–1241	–
$Y_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$	100–320	538–686	–	–	778–867	–	1017–1190
$Y_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$	128–350	536–664	–	–	750–871	–	967–1164
$Y_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 6H_2O$	89–357	533–700	–	–	764–877	–	975–1172

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	Fusion
$Yb_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 9H_2O$	152	650, 703	850, 950	1219	–	–	–	568
$Yb_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 10H_2O$	116, 152	618, 692, 700	–	–	878	1057, >1250	–	766
$Yb_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$	305	647, 710	–	–	884	–	>1250	1130
$Yb_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3H_2O$	269	663, 687	–	–	883	–	>1250	1162
$Yb_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 3H_2O$	269	658, 687	–	–	883	–	>1250	1183
$Lu_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 9H_2O$	150	650, 700	867, 933	>1250	–	–	–	568
$Lu_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 7H_2O$	108, 173, 259	688	–	–	863	1058, >1250	–	766
$Lu_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4H_2O$	183, 307, 354	650, 700	–	–	860	–	>1250	1100
$Lu_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3H_2O$	270	671	–	–	865	–	>1250	1150
$Lu_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 2H_2O$	223	696	–	–	862	–	>1200	1200
$Y_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 10H_2O$	165, 280	648, 750	1025	1223	–	–	–	648
$Y_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 9H_2O$	156, 400	634, 657, 825	–	–	950	1067, >1250	–	731
$Y_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7H_2O$	114, 185, 300	643, 731	–	–	988	–	>1250	–
$Y_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 6H_2O$	108, 181	657, 683, 734	–	–	977	–	>1250	–
$Y_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 6H_2O$	154, 142	693	–	–	974	–	>1250	–

formed in the preceding step to the corresponding lanthanides oxides (Yb_2O_3, Ln_2O_3, and Y_2O_3) and to the reduction of lithium selenate to lithium selenite [3] in the case of Yb–Li, Lu–Li, and Y–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 lanthanide oxide. The sodium selenate of the Yb–Na, Lu–Na and Y–Na double selenate probably undergoes partial reduction to sodium selenite and the mixture decomposes into sodium oxide with partial evaporation. The final residues of these compounds containing sodium were formed by the corresponding lanthanide oxide and 87%, 80%, and 95%, respectively, of the theoretical amount of Na_2O.

The final residues of the remaining double salts containing potassium, rubidium and cesium were practically formed by the corresponding lanthanide oxide 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 shown by the TG curves and peaks corresponding to fusion. The temperature of each DTA peak and its probable interpretation is shown in Table 3.

The following small peaks: Yb–Li, 164, 179 °C; Yb–Na, 579 °C; Yb–K, 375 °C; Lu–Li, 79, 207, 250 °C; Y–Li, 172 °C; Y–Na, 186, 723 °C, and Y–K, 156 °C probably indicate crystalline transitions.

The peak temperatures of the DTA curve of Yb–Cs double selenate trihydrate do not agree with the peak temperature of the DTA curve of the same compound already reported [6]. Neither does it show the peak at 575 °C attributed to a crystalline transition. Probably these differences are due to the differences in the preparation procedures of both compounds.

CONCLUSIONS

The thermal behavior of ytterbium, lutetium, yttrium and alkali metal double selenates showed some differences compared to the thermal behavior of the corresponding simple selenates and the other double selenates of the lanthanide series already reported, specially regarding the increasing amount of alkali metal compounds undergoing volatilization in the case of double salts of potassium, rubidium, and cesium with lanthanide elements of the end of the lanthanide series.

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