Note

STUDIES ON DOUBLE SELENATES. V. THERMAL DECOMPOSITION OF EUROPIUM AND ALKALI METAL DOUBLE SELENATES

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There is no reference in the literature to the preparation and thermal decomposition of the double selenates of europium and alkali metals.

EXPERIMENTAL

Selenic acid and europium selenate [1] alkali metal selenates [2] and double selenates of europium and alkali metals [3] were prepared as described previously. Europium ion was determined by the usual oxalate–oxide gravimetric method and the alkali metal ions by atomic absorption 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 as described previously [3].

Similarly to the lanthanum ion [3], it was possible to prepare the double selenate of europium and lithium by spontaneous evaporation of the mother liquor. As reported elsewhere, it was not possible to isolate the Ce–Li [4], Pr–Li [5], Nd–Li and Sm–Li [6] double selenates.

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds prepared having the formula $Eu_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O$ where $Me = Li, Na, K, Rb, Cs$.

It can be seen from the TG and DTA curves of Figs. 1 and 2, respectively,

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TABLE 1

Analytical and thermoanalytical (TG) results

Compound	Europium (%)		Alkali metal (%)		Selenium (%)		Water (%)	
	Theor.	Exptl.	Theor.	Exptl.	Theor.	Exptl.	Theor.	Exptl.
$Eu_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 5 H_2O$	31.79	31.43	1.45	1.70	33.04	32.60	9.42	9.13
$Eu_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 6 H_2O$	29.51	29.12	4.46	4.24	30.67	30.95	10.49	10.48
$Eu_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7 H_2O$	28.14	27.65	7.24	7.68	29.26	28.82	11.67	11.94
$Eu_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 5 H_2O$	26.74	26.55	15.04	15.76	27.79	27.73	7.92	7.62
$Eu_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 2 H_2O$	25.81	25.13	22.57		26.82	26.51	3.06	2.78
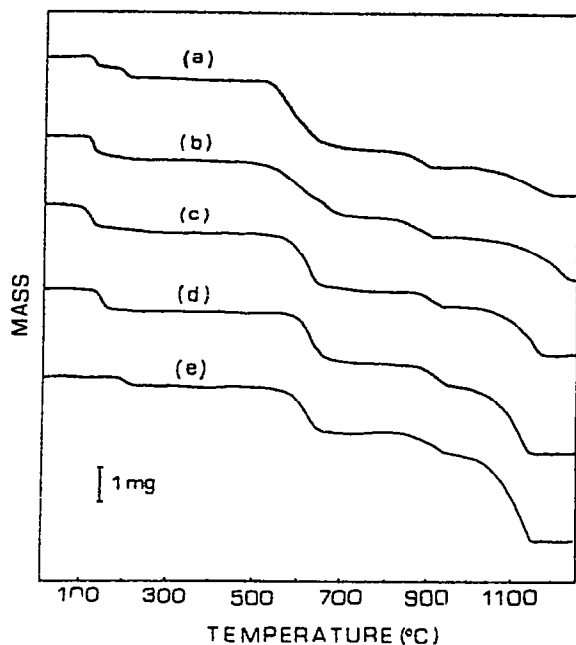
Fig. 1. TG curves of the double selenates of europium and alkali metal. Heating rate: 5 2°C min⁻¹. (a) $Eu_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 5 H_2O$ (7.12 mg); (b) $Eu_2(SeO_4)_3 Na_2SeO_4 \cdot 6 H_2O$ (7.16 mg); (c) $Eu_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7 H_2O$ (7 12 mg); (d) $Eu_2(SeO_4)_3 \cdot Rb_2SeO_4$ 5 H_2O (7 22 mg), and (e) $Eu_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 2 H_2O$ (7 20 mg).
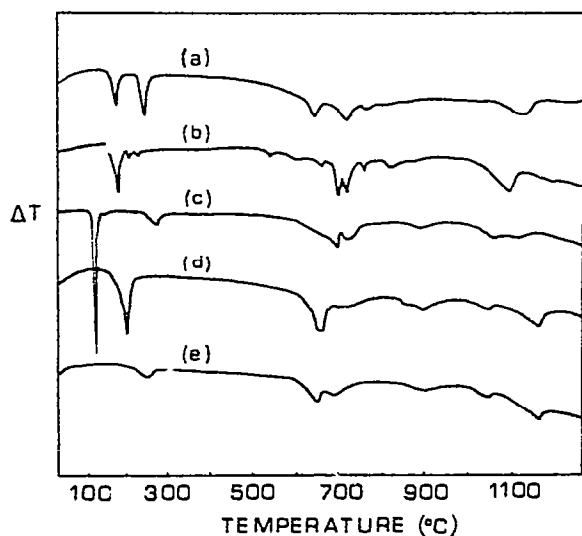

Fig. 2. DTA curves of double selenates or europium and alkali metal, diluted at 20% in α-alumina. Heating rate: 9.0°C. min⁻¹. (a) $Eu_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 5 H_2O$; (b) $Eu_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 6 H_2O$; (c) $Eu_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7 H_2O$; (d) $Eu_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 5 H_2O$; and (e) $Eu_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 2 H_2O$.

that once again the thermal decomposition of the double selenates 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
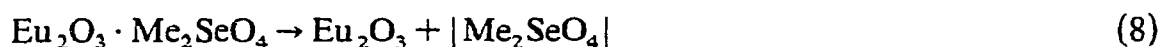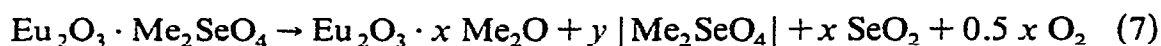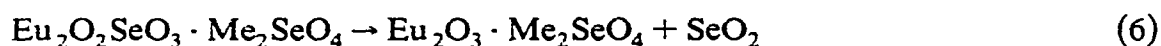
$$Eu_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n \ H_2O \rightarrow Eu_2(SeO_4)_3 \cdot Me_2SeO_4 + n \ H_2O \qquad (1)$$

$$Eu_2(SeO_4)_3 \cdot Me_2SeO_4 \rightarrow Eu_2(SeO_3)_3 \cdot Me_2SeO_4 + 1.5 \ O_2 \qquad (2)$$

$$Eu_2(SeO_3)_3 \cdot Me_2SeO_4 \rightarrow Eu_2O_2SeO_3 \cdot Me_2SeO_4 + SeO_2 \qquad (3)$$

$$Eu_2O_2SeO_3 \cdot Me_2SeO_4 \rightarrow Eu_2O_3 \cdot Me_2SeO_3 + SeO_2 + 0.5 \ O_2 \qquad (4)$$

$$Eu_2O_3 \cdot SeO_3 \cdot Me_2SeO_3 \rightarrow Eu_2O_3 \cdot Me_2O + SeO_2 + 1.5 \ O_2 \qquad (5)$$

$$Eu_2O_2SeO_3 \cdot Me_2SeO_4 \rightarrow Eu_2O_3 \cdot Me_2SeO_4 + SeO_2 \qquad (6)$$

$$Eu_2O_3 \cdot Me_2SeO_4 \rightarrow Eu_2O_3 \cdot x \ Me_2O + y \ |Me_2SeO_4| + x \ SeO_2 + 0.5 \ x \ O_2 \quad (7)$$

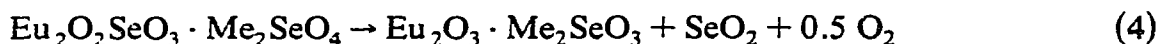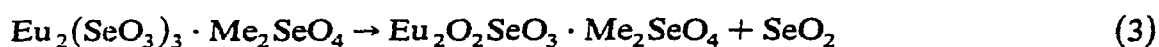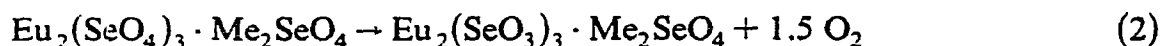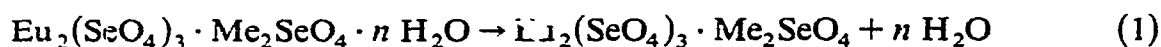$$Eu_2O_3 \cdot Me_2SeO_4 \rightarrow Eu_2O_3 + |Me_2SeO_4| \qquad (8)$$

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

Table 3 indicates the temperature of DTA peaks (all endothermic) in correspondence with the reactions, fusion or transitions occurring for each compound.

As is 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. The Eu–Li double selenate pentahydrate undergoes dehydration in two distinct steps: losing two water molecules in the first step between 114 and 130°C and three in the second between 167 and 217°C. In the case of Eu–Na double selenate hexahydrate the loss of four water molecules occurs through a rapid process between 114 and 210°C. The Eu–K double selenate heptahydrate forms the monohydrate through a rapid process between 90 and 143°C and the remaining molecule of water is slowly lost between 143 and 210°C. Finally Eu–Rb double selenate pentahydrate and Eu–Cs double selenate dihydrate undergo dehydration in one single step between 114 and 175°C and 178 and 218°C, respectively.

The TG curves of Fig. 1 also show that the subsequent thermal decomposition of the anhydrous double salts occurs in three steps. The first corresponds to the mass losses occurring between 494 and 707°C which are due to the formation of the intermediate compound: $Eu_2O_2SeO_3 \cdot Me_2SeO_4$. The different slope of that part of the TG curves of Eu–Li and Eu–Na double selenates suggests that there is probably the intermediate formation of very unstable compounds containing the (mono) oxyselenite of europium $[Eu_2O(SeO_3)_2]$ already reported in the case of other single selenates of lanthanides [7,8]. Although the TG curves do not show any evidence of the formation of europium selenite, samples of these compounds heated up to

TABLE 2

Reactions and corresponding temperature ranges observed in the TG curves of the compounds $Eu_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\,H_2O$

Compound	Temperature range of mass-loss reactions in the TG curves (°C)							
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
$Eu_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 5\,H_2O$	114–130; 167–217	505–684		810–914	1000–1184			
$Eu_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 6\,H_2O$	114–210	494–707				800–910	1010–1234	
$Eu_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\,H_2O$	90–220	550–693				850–943		1035–1177
$Eu_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 5\,H_2O$	114–175	557–690				850–950		950–1146
$Eu_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 2\,H_2O$	178–218	550–668				850–942		950–1157

TABLE 3

Temperature of DTA peaks (all endothermic) in correspondence with reactions and fusion of the compounds $Eu_2(SeO_4)_3 \cdot MeSeO_4 \cdot n\,H_2O$

Compound	Peak temperature in DTA curves (°C)								Fusion	Transition
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)		
$Eu_2(SeO_4)_3 \cdot Li_2SeO_4 \cdot 5\,H_2O$	173–241	643	717–746	1137	>1200				643	
$Eu_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 6\,H_2O$ 660–761	177–207–232	600	717	821		1100	>1200		700	537–
$Eu_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\,H_2O$	121–279		700	730		1068		>1200	900	
$Eu_2(SeO_4)_3 \cdot Rb_2SeO_4\;5\,H_2O$	204		664	710		1050		>1200	900	
$Eu_2(SeO_4)_3 \cdot Cs_2SeO_4 \cdot 2\,H_2O$	257		650	700		1050		>1200	900	

550°C in platinum crucibles give a positive test for selenite ion in the presence of selenate ion [9].

The second step of the thermal decomposition corresponds to the mass losses between 800 and 950°C and are due to further decomposition of the intermediate compound formed in the previous step to $Eu_2O_3 \cdot Me_2SeO_4$, except in the case of the intermediate compound of Eu–Li which decomposes to $Eu_2O_3 \cdot Li_2SeO_3$. The lower stability of these intermediate compounds of Eu–Li and Eu–Na is probably related to the fact that these double salts undergo fusion around 700°C.

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 lithium compound) present. Lithium selenite starts decomposition above 1000°C and the residue at 1184°C contains Eu_2O_3 and Li_2O. In the case of sodium selenate, above 1010°C partial reduction of Se(VI) to Se(IV) and evaporation probably occur [2]. At 1234°C the residue contains Eu_2O_3 and 57.6% of the theoretical amount of Na_2O. The final mass losses of the other double selenates (Eu–K, Eu–Rb and Eu–Cs) are due to the total evaporation of the alkaline selenate present so that the final residues contain only Eu_2O_3.

The DTA curves of Fig. 2 show one or more peaks in correspondence to each mass loss observed in the TG curves and peaks corresponding to fusion and crystalline transitions. The temperature of each DTA peak and its probable interpretation are shown in Table 3.

CONCLUSION

The thermal behaviour of europium and alkali metal double selenates show some differences as compared with the thermal behaviour of the corresponding simple selenates, especially with regard to the mechanism of dehydration and the amount of alkaline metal undergoing volatilization. Each double selenate presents characteristic TG and DTA patterns.

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