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Note

STUDIES ON DOUBLE SELENATES. IV. THERMAL DECOMPOSITION OF NEODYMIUM, SAMARIUM AND ALKALI METAL DOUBLE SELENATES

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The first communication about the double selenates of neodymium or samarium and alkali metals described the compound $Sm_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4\ H_2O$ [1]. A second communication described the preparation and solubility at 0°C of the compounds $Nd_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 2\ H_2O$, $Nd_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4\ H_2O$ and $Nd_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 4\ H_2O$ [2]. More recently, the preparation and thermal properties of the compounds $NaSm(SeO_4)_2 \cdot 3\ H_2O$, $KSm(SeO_4)_2 \cdot 4\ H_2O$ and $NH_4Sm(SeO_4)_2 \cdot 4\ H_2O$ were reported [3].

EXPERIMENTAL

Selenic acid, neodymium and samarium selenates [4], alkali metal selenates [5] and double selenates of neodymium, samarium and alkali metals [6] were prepared as described previously. The lanthanide ions were determined by the usual oxalate–oxide method and the alkali metal ions by atomic absorption 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 [6].

Similarly to double selenates of cerium(III) and lithium [7] and of praseodymium and lithium [8], it was not possible to prepare Nd–Li and Sm–Li double selenates; the crystals that were isolated from the mother liquor by spontaneous evaporation proved only to be neodymium and samarium selenates, respectively.

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds prepared having the formula $x\mathrm{Ln}_2(SeO_4)_3 \cdot y\mathrm{Me}_2SeO_4 \cdot n\ H_2O$

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TABLE 1

Analytical and thermoanalytical (TG) results

	Analytical results							
	Lanthanide (%)		Alkali metal (%)		Selenium (%)		Water (%)	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$Nd_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	29.49	29.14	4.70	4.05	32.28	32.56	7.36	6.74
$Nd_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\ H_2O$	27.10	26.91	7.35	6.64	29.67	29.72	11.84	11.81
$Nd_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot H_2O$	27.49	26.75	16.29	15.20	30.10	30.32	1.72	1.41
$3\ Nd_2(SeO_4)_3 \cdot 2\ Cs_2SeO_4 \cdot 7\ H_2O$	27.96	27.61	17.17	16.51	28.06	27.63	4.07	4.13
$Sm_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	30.36	29.97	4.64	4.14	31.88	31.71	7.27	7.14
$Sm_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 5\ H_2O$	28.89	28.37	7.51	6.94	30.34	30.36	8.65	8.38
$Sm_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 5\ H_2O$	26.54	25.90	15.08	14.24	27.86	27.65	7.95	7.68
$Sm_2(SeO_4)_3 \cdot 2\ Cs_2SeO_4 \cdot 4\ H_2O$	18.57	19.10	32.83	32.02	24.38	24.30	4.45	4.21

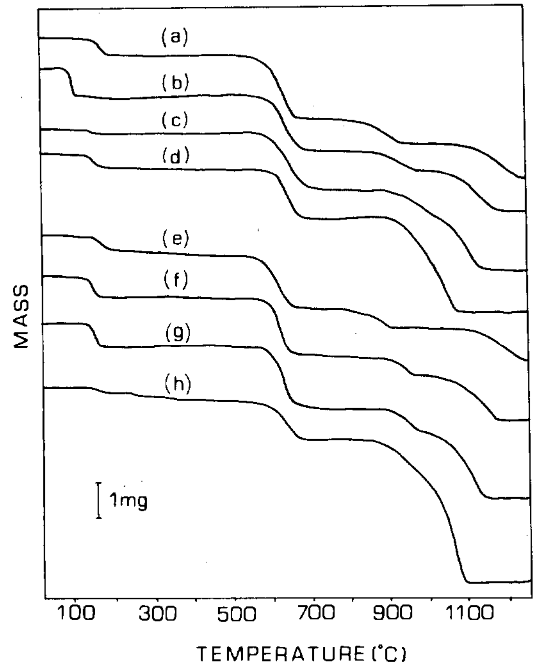

Fig. 1. TG curves of the double selenates of neodymium, samarium and alkali metal. Heating rate: 5.2°C min^{-1}. (a) $Nd_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$ (7.45 mg); (b) $Nd_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\ H_2O$ (7.20 mg); (c) $Nd_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot H_2O$ (7.08 mg); (d) $3\ Nd_2(SeO_4)_3 \cdot 2\ Cs_2SeO_4 \cdot 7\ H_2O$ (7.26 mg); (e) $Sm_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$ (7.00 mg); (f) $Sm_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 5\ H_2O$ (7.20 mg); (g) $Sm_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 5\ H_2O$ (7.20 mg); and (h) $Sm_2(SeO_4)_3 \cdot 2\ Cs_2SeO_4 \cdot 4\ H_2O$ (7.12 mg).

(Ln = Nd, Sm, and Me = Na, K, Rb, Cs). In the case of the double selenate of Nd–Na, Nd–K, Nd–Rb, Sm–Na, Sm–K and Sm–Rb, $x = y = 1$; in the case of the double selenate of Nd–Cs, $x = 3$, $y = 2$; and in the case of the double selenate of Sm–Cs, $x = 1$, $y = 2$.

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

$$x Ln_2(SeO_4)_3 \cdot y Me_2SeO_4 \cdot n\ H_2O \rightarrow x Ln_2(SeO_4)_3 \cdot y Me_2SeO_4 + n\ H_2O \quad (1)$$

$$x Ln_2(SeO_4)_3 \cdot y Me_2SeO_4 \rightarrow x Ln_2O_2SeO_3 \cdot y Me_2SeO_4 + 2\ x SeO_2 + 1.5x\ O_2 \quad (2)$$

$$x Ln_2O_2SeO_3 \cdot y Me_2SeO_4 \rightarrow x Ln_2O_3 \cdot y Me_2Seo_4 + x SeO_2 \quad (3)$$

$$x Ln_2O_3 \cdot y Me_2SeO_4 \rightarrow x Ln_2O_3 + y Me_2SeO_4 \quad (4)$$

$$x Ln_2O_3 \cdot y Me_2SeO_4 \rightarrow x Ln_2O_3 + y Me_2O + y SeO_2 + 0.5y\ O_2 \quad (5)$$

Table 2 attributes to each compound the probable set of the above

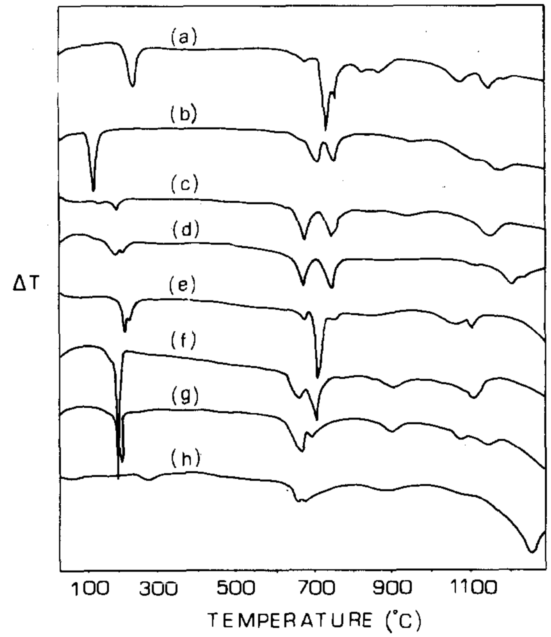

Fig. 2. DTA curves of double selenates of neodymium, samarium and alkali metal diluted at 20% in α-alumina. Heating rate: 9.0°C min^{-1}. (a) $Nd_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$; (b) $Nd_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\ H_2O$; (c) $Nd_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot H_2O$; (d) $3\ Nd_2(SeO_4)_3 \cdot 2\ Cs_2SeO_4 \cdot 7\ H_2O$; (e) $Sm_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$; (f) $Sm_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 5\ H_2O$; (g) $Sm_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 5\ H_2O$; and (h) $Sm_2(SeO_4)_3 \cdot 2\ Cs_2SeO_4 \cdot 4\ H_2O$.

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 or fusion occurring for each compound.

The first mass losses observed in the TG curves of Fig. 1 are due to dehydration, the anhydrous double salts being formed up to 250°C with two exceptions. In the case of Sm–Na double selenate, dehydration is almost complete at about 200°C but the last traces of water are slowly lost until 420°C. The mass loss at 400°C reported previously [3] was not observed. In the case of Sm–Cs double selenate the water loss is slow and progressive, resulting in the anhydrous salt at about 350°C.

The next mass loss in the TG curves, between 540 and 700°C, corresponds to the decomposition of the corresponding selenate of lanthanide to (di) oxyselenite. Although the TG curves do not show any evidence of intermediate formation of the selenite of lanthanide, samples of these compounds heated up to 700°C in platinum crucibles suspended inside a furnace near the junction of a Pt/Pt–Rh 13% thermocouple, connected to a pyrometer, give a positive test for selenite ion in the presence of selenate ion [6]. The selenite ion content in these samples, determined iodometrically [4], showed

TABLE 2

Reactions and corresponding temperature ranges observed in the TG curves of the double selenates of neodymium, samarium and alkali metal

Compound	Temp. range of mass loss reactions in the TG curves (°C)				
	(1)	(2)	(3)	(4)	(5)
$Nd_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	143–186	540–668	790– 936		1050–1237
$Nd_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\ H_2O$	81–114	540–700	850– 986	1032–1167	
$Nd_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot H_2O$	132–150	550–715	860–1133	860–1133	
$3\ Nd_2(SeO_4)_3 \cdot 2\ Cs_2SeO_4 \cdot 7\ H_2O$	117–168	568–682	875–1077	875–1077	
$Sm_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	136–200	533–680	760– 905		1075–1240
$Sm_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 5\ H_2O$	127–167	550–700	850– 964	1025–1168	
$Sm_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 5\ H_2O$	125–173	550–700	864– 970	970–1136	
$Sm_2(SeO_4)_3 \cdot 2\ Cs_2SeO_4 \cdot 4\ H_2O$	125–160, 170–218	550–675	850–1100	850–1110	

TABLE 3

Temperature of DTA peaks (all endothermic) in correspondence with reactions and fusion of the double selenates of neodymium, samarium and alkali metal

Compound	Peak temp. in DTA curves (°C)					
	(1)	(2)	(3)	(4)	(5)	Fusion
$Nd_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	229	672–750–863	1075–1143		1250	725
$Nd_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\ H_2O$	112	703–745	1100–1167	1250		950
$Nd_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot H_2O$	188	680–750	1143	1162		950
$3\ Nd_2(SeO_4)_3 \cdot 2\ Cs_2SeO_4 \cdot 7\ H_2O$	185–206	675–750	1107	1200		
$Sm_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	213–228	672–750	1058–1102		>1200	705
$Sm_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 5\ H_2O$	190	663–712	1117	>1200		905
$Sm_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 5\ H_2O$	202	672–700	1083–1150	>1200		905
$Sm_2(SeO_4)_3 \cdot 2\ Cs_2SeO_4 \cdot 4\ H_2O$	175–259	650–673		1244		900

a quantitative formation of (di) oxyselenites of neodymium and samarium.

The subsequent steps in the TG curves of these compounds, between 760 and 875°C, are due to the decomposition of the formed (di) oxyselenites of neodymium and samarium to the corresponding lanthanide oxides. In the case of Sm–Cs double selenate this decomposition occurs almost simultaneously with the evaporation of the caesium selenate present; in the case of Nd–Cs double selenate these two final steps occur simultaneously.

With respect to the other double selenates of neodymium, samarium and alkali metals, the final step in the respective TG curves depends upon the nature of the alkali metal present [5].

In the case of Nd–Na and Sm–Na double selenates the decomposition of sodium selenate to sodium oxide starts at 1050 and 1075°C, respectively, and is probably accompanied by partial and simultaneous decomposition to sodium selenite [5]; above 1250°C the residue is formed by a mixture of $Nd_2O_3 \cdot Na_2O$ and $Sm_2O_3 \cdot Na_2O$, respectively, and there was no evidence of evaporation of the sodium selenate in either case.

The final decomposition of the alkaline selenates present in the other double selenates seems to occur without quantitative reduction of Se(VI) to Se(IV), already reported in the case of Sm–K double selenate [3]. In the case of Nd–K, Nd–Rb and Sm–K double selenates the final residue was formed by the theoretical amount of the corresponding lanthanide oxide in the mixture with 43, 23 and 41% of the theoretical amount of each alkaline oxide, respectively. In the case of Nd–Cs, Sm–Rb and Sm–Cs double selenates total evaporation of the alkaline selenate present occurred, and the final residues contained only the corresponding lanthanide oxide.

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

CONCLUSION

The thermal behaviour of neodymium, samarium and alkali metal (except lithium) double selenates show some differences as compared with the thermal behaviour of the corresponding simple selenates, especially regarding the amount of alkaline metal undergoing volatilization. Each double selenate presents characteristic TG and DTA patterns.

REFERENCES

1 P.T. Clève, Bull. Soc. Chim., 43 (1883) 167.
2 J. Meyer and C. Kittelmann, Z. Anorg. Allg. Chem., 195 (1931) 121.

3 M.A. Nabar and S.V. Paralkar, Thermochim. Acta, 35 (1980) 287.
4 I. Giolito and E. Giesbrecht, Ann. Acad. Bras. Cienc., 41 (1971) 2921.
5 I. Giolito and M. Ionashiro, Thermochim. Acta, 38 (1980) 341.
6 M. Ionashiro and I. Giolito, Thermochim. Acta, 38 (1980) 258.
7 I. Giolito and M. Ionashiro, Thermochim. Acta, 46 (1981) 77.
8 I. Giolito and M. Ionashiro, Thermochim. Acta, 46 (1981) 83.