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Note

STUDIES ON DOUBLE SELENATES. III. THERMAL DECOMPOSITION OF PRASEODYMIUM AND ALKALI METAL DOUBLE SELENATES

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The only communication available about praseodymium and alkali metal double selenates describes the preparation of the compound $Pr_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 4\,H_2O$ [1]. No reference was found to the application of TG and DTA in the study of these double salts.

EXPERIMENTAL

Alkali metal selenates [2], selenic acid and praseodymium selenate [3] and praseodymium and alkali metal double selenates [4] were prepared as described previously. As for the double selenate of cerium(III) and lithium [5], it was not possible to prepare the double selenate of praseodymium and lithium; the isolated solid from the mother liquor by spontaneous evaporation proved only to be praseodymium selenate. Praseodymium ions were determined by the usual oxalate—oxide method and the alkali metal ions by atomic absorption spectroscopy in a Perkin-Elmer 403 atomic absorption spectrophotometer. Water of crystallization and selenium content were determined from the TG curves. The TG and DTA curves were obtained as described previously [4].

RESULTS AND DISCUSSION

Table 1 presents the analytical and thermoanalytical (TG) data of the compounds prepared having the formula $Pr_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\,H_2O$ (Me = Na, K, Rb, Cs).

The thermal decomposition of the praseodymium and alkali metal (except

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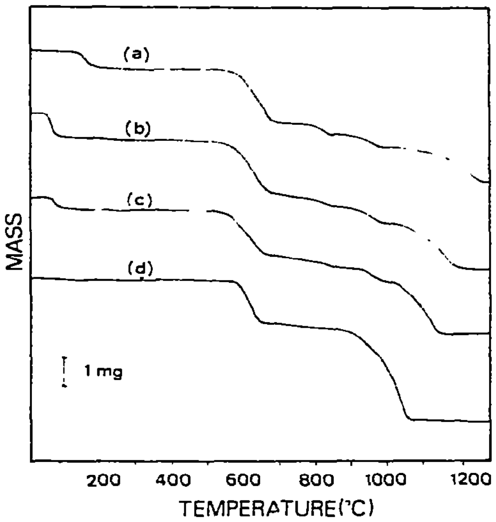
TABLE 1

Analytical and thermoanalytical (TG) results

Compound	Analytical results							
	Praseodymium (%)		Alkali metal (%)		Selenium (%)		Water (%)	
	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.	Theor.	Exp.
$Pr_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	29.01	28.53	4.73	4.10	32.51	32.43	7.41	7.49
$Pr_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\ H_2O$	26.64	26.13	7.39	7.79	29.86	31.21	11.91	11.81
$Pr_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3\ H_2O$	26.13	26.02	15.85	15.03	29.28	28.37	5.01	4.93
$Pr_2(SeO_4)_3 \cdot Cs_2SeO_4$	25.18	24.50	23.74	22.62	28.21	28.68		



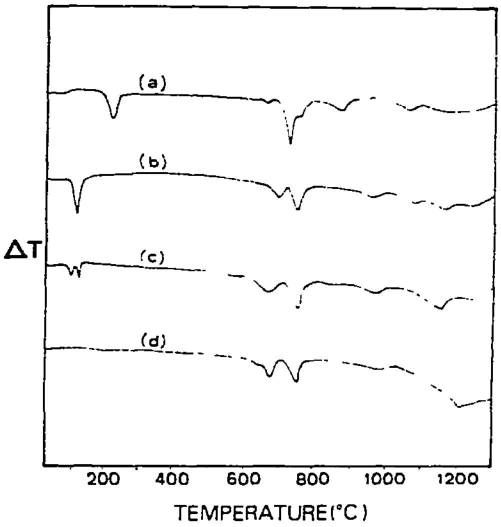


Fig. 1. TG curves of the double selenates of praseodymium and alkali metal. Heating rate: 5.2°C min^{-1}. (a) $Pr_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$ (7.34 mg); (b) $Pr_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\ H_2O$ (7.20 mg); (c) $Pr_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3\ H_2O$ (7.10 mg); and (d) $Pr_2(SeO_4)_3 \cdot Cs_2SeO_4$ (7.04 mg).

Fig. 2. DTA curves of the double selenates of praseodymium and alkali metal diluted to 20% α-alumina. Heating rate: 9°C min^{-1}. (a) $Pr_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$; (b) $Pr_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\ H_2O$; (c) $Pr_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3\ H_2O$; and (d) $Pr_2(SeO_4)_3 \cdot Cs_2SeO_4$.

lithium) double selenates occurs in a characteristic way, depending on the alkali metal, as can be seen from the TG and DTA curves of Figs. 1 and 2, respectively.

All the reactions taking place during the thermal decomposition of these compounds can be summarized by the following equations

$$Pr_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O \rightarrow Pr_2(SeO_4)_3 \cdot Me_2SeO_4 + n\ H_2O \quad (1)$$

$$Pr_2(SeO_4)_3 \cdot Me_2SeO_4 \rightarrow Pr_2(SeO_3)_3 \cdot Me_2SeO_4 + 1.5\ O_2 \quad (2)$$

$$Pr_2(SeO_3)_3 \cdot Me_2SeO_4 \rightarrow Pr_2O_2SeO_3 \cdot Me_2SeO_4 + 2\ SeO_2 \quad (3)$$

$$2\ (Pr_2O_2SeO_3 \cdot Me_2SeO_4) + 0.5\ O_2$$
$$\rightarrow Pr_2O_2SeO_3 \cdot 2\ PrO_2 \cdot 2\ Me_2SeO_4 + SeO_2 \quad (4)$$

$$3\ (Pr_2O_2SeO_3 \cdot 2\ PrO_2 \cdot 2\ Me_2SeO_4) + 0.5\ O_2$$
$$\rightarrow 2\ Pr_6O_{11} \cdot 6\ Me_2SeO_4 + 3\ SeO_2 \quad (5)$$

$$Pr_6O_{11} \cdot 3\ Me_2SeO_4 \rightarrow Pr_6O_{11} + 3\ Me_2SeO_3 + 1.5\ O_2 \quad (6)$$

$$Pr_6O_{11} \cdot 3\ Me_2SeO_3 \rightarrow Pr_6O_{11} + 3\ Me_2O + 3\ SeO_2 \quad (7)$$

$$Pr_6O_{11} \cdot 3\ Me_2SeO_4 \rightarrow Pr_6O_{11} + |3\ Me_2SeO_4| \quad (8)$$

TABLE 2

Reactions and corresponding temperature ranges observed in the TG curves of the compounds: $Pr_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O$

Compound	Temp. range of mass loss reactions in the TG curves (°C)						
	(1)	(2) (3)	(4)	(5)	(6)	(7)	(8)
$Pr_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	143—210	535—690	720—834	870— 970	1000—1250	100—1250	
$Pr_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\ H_2O$	60—100	523—690	680—840	850— 980			1000—1184
$Pr_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3\ H_2O$	60— 85	500—690	660—850	840—1000			980—1140
$Pr_2(SeO_4)_3 \cdot Cs_2SeO_4$		550—660	650—760	760—			—1065

TABLE 3

Temperature of DTA peaks (all endothermic) corresponding to reactions and fusion of the compounds: $Pr_2(SeO_4)_3 \cdot Me_2SeO_4 \cdot n\ H_2O$

Compound	Peak temp. in DTA curves (°C)								
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	Fusion (a) or transition (b) temp.
$Pr_2(SeO_4)_3 \cdot Na_2SeO_4 \cdot 4\ H_2O$	228	669	760	876	1068	1200	1200		731 (a)
$Pr_2(SeO_4)_3 \cdot K_2SeO_4 \cdot 7\ H_2O$	115	700	757	969	1090			1165	
$Pr_2(SeO_4)_3 \cdot Rb_2SeO_4 \cdot 3\ H_2O$	103	667	757	974	1155			1155	125 (*b*)
$Pr_2(SeO_4)_3 \cdot Cs_2SeO_4$		667	757	990				1200	

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

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

The first mass losses observed in the TG curves of the compounds up to 210°C are due to dehydration. The next step in the TG curves, between 500 and 690°C, corresponds to the first decomposition of the praseodymium selenate to praseodymium (di)oxyselenite, which occurs with simultaneous reduction of selenate ion to selenite ion. Samples of praseodymium and sodium double selenate heated up to 600°C in platinum crucibles suspended inside a furnace near a thermocouple of Pt/Pt—Rh 13% connected to a pyrometer, still showed the characteristic greenish colour of Pr(III) ion and the content of selenite ion in these samples, determined iodometrically [3], was 9.8%, which corresponds to a 30% conversion of selenate to selenite. Samples of the same compound heated up to 700°C already presented a dark grey colour of Pr(IV) ion and the analysis revealed 32% selenite ion, indicating almost total reduction of Se(VI) to Se(IV).

The other two subsequent and almost identical mass losses between 780 and 980°C probably correspond to the partial decomposition of praseodymium (di)oxyselenite to PrO_2 followed by the decomposition of the remainder residue of $Pr_2O_2SeO_3$ and PrO_2 to Pr_6O_{11}. Calculations according to this supposition are in good agreement with the two experimental mass losses. In the TG curve of praseodymium and caesium double selenate, these two steps are not observed because the decomposition of the intermediate compounds occurs simultaneously with the volatilization of the caesium selenate. The last step in the TG curves of the praseodymium and alkali metal double selenates depends upon the nature of the alkali metal considered [2]. Above 1000°C the sodium selenate decomposes to sodium oxide, probably with intermediate formation of sodium selenite [2], but without evaporation; at 1275°C the residue is probably a mixture of Pr_6O_{11} and Na_2O.

The final mass losses of the other praseodymium and alkali metal double selenates (Pr--K, Pr--Rb and Pr--Cs) is due to evaporation of the corresponding alkali metal selenate which seems to occur without intermediate formation of alkali metal selenite; the final residue contains only Pr_6O_{11}.

The DTA curves of Fig. 2 show peaks corresponding to all mass losses observed in the TG curves; one peak corresponds to fusion and another corresponds to crystalline transition. The teperature of each DTA peak and its probable interpretation are summarized in Table 3.

CONCLUDING REMARKS

The thermal behaviour of praseodymium and alkali metal (except lithium) double selenates presents many variations as compared with the thermal behaviour of the corresponding simple selenates. Each double selenate exhibits characteristic TG and DTA patterns.

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