STUDIES ON SELENATES. V. THERMAL DECOMPOSITION OF DOUBLE SELENATE HYDRATES OF SAMARIUM WITH SODIUM, POTASSIUM AND AMMONIUM *

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ABSTRACT

Thermoanalytical techniques have been used to study the decomposition of double selenate hydrates of samarium with sodium, potassium and ammonium. Interpreting the results obtained, the mechanisms of decomposition have been proposed. The decompositions of non-hydrates of alkali-metal salts exhibit close similarity.

INTRODUCTION

In a comprehensive study, thermoanalytical work was initiated to understand the dehydration—decomposition of normal rare-earth selenate hydrates [1,2]. Based on the critical evaluation of the results obtained the reaction mechanisms were proposed. As a natural extension of this work the thermal behaviour of the double monovalent-rare-earth selenate hydrates was also studied [3]. The present paper reports the dehydration—decomposition of crystallohydrates of double selenates of samarium with sodium, potassium and ammonium.

EXPERIMENTAL

The double selenates in this investigation were synthesised by treating mixtures of the respective metal carbonates with the stoichiometric amount of selenic acid and subsequently concentrating the filtered solution, followed by crystallisation in air. The synthesised selenates were analysed on metal and selenate. Samarium contents were determined by complexometry. Alkali-metal contents were determined by flame photometry, and direct titration method was used for ammonia determination. Selenate was estimated after eluting the aqueous salt solution through a cation exchanger fol-

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* For Part IV, see M.A. Nabar and S.V. Paralkar, J. Appl. Crystallogr., 12 (1979) 245.

TABLE 1

Analytical results

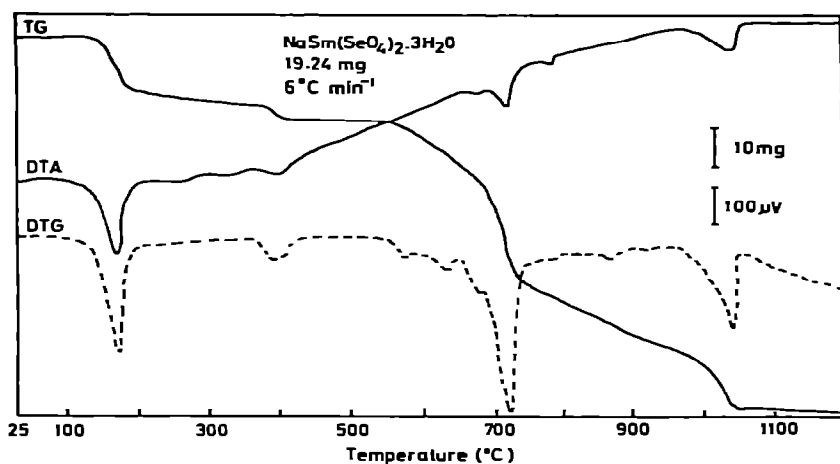| Compound	Monovalent cation (%)		Samarium (%)		Selenate (%)	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
$NaSm(SeO_4)_2 \cdot 3 H_2O$	4.479	4.459	29.29	29.11	55.70	54.73
$KSm(SeO_4)_2 \cdot 4 H_2O$	7.142	7.150	27.46	27.66	52.23	52.23
$NH_4(SeO_4)_2 \cdot 4 H_2O$	3.547	3.555	28.57	28.70	54.31	54.20

Fig. 1. Thermal dehydration—decomposition of $NaSm(SeO_4)_2 \cdot 3H_2O$.
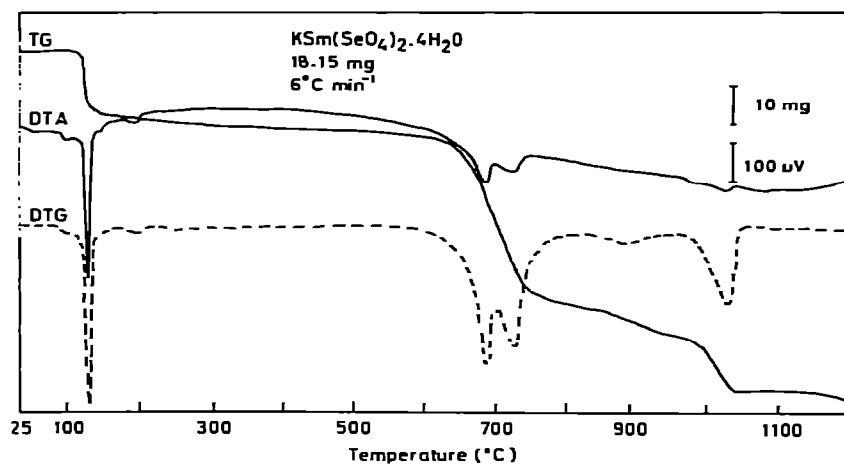

Fig. 2. Thermal dehydration—decomposition of $KSm(SeO_4)_2 \cdot 4H_2O$.
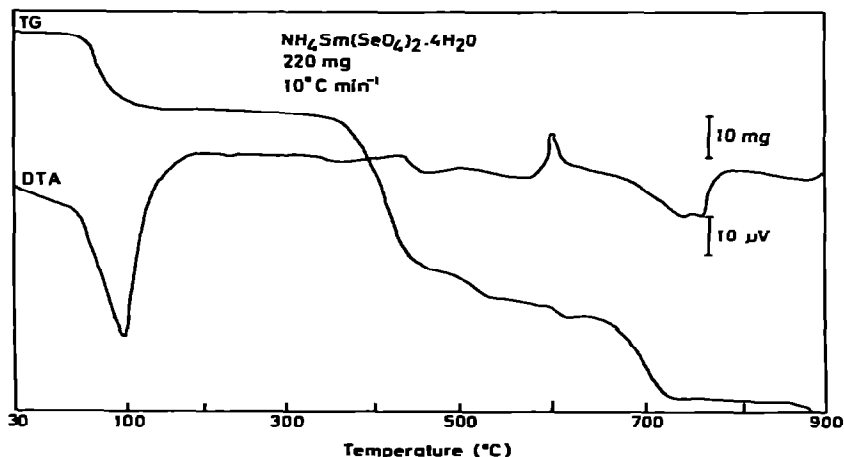
Fig. 3. Thermal dehydration—decomposition of NH₄Sm(SeO₄)₂ · 4H₂O.

lowed by simple acid—base titration of the effluent electrolyte. Table 1 summarises the analytical results.

The course of decomposition of double selenates was investigated by thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG) as described previously [4]. Figures 1—3 represent the thermoanalytical curves of $NaSm(SeO_4)_2 \cdot 3\ H_2O$, $KSm(SeO_4)_2 \cdot 4\ H_2O$

TABLE 2

Thermoanalytical data for $NaSm(SeO_4)_2 \cdot 3\ H_2O$

Dehydration/decomposition	Temp. (°C)		% loss	
	TG	DTA	Calc.	Obs.
$2\ NaSm(SeO_4)_2 \cdot 3\ H_2O \rightarrow 2\ NaSm(SeO_4)_2 \cdot 0.5\ H_2O$	325	170	7.77	8.91
$2\ NaSm(SeO_4)_2 \cdot 0.5\ H_2O \rightarrow 2\ NaSm(SeO_4)_2$	440	385	10.35	11.30
		670		
$2\ NaSm(SeO_4)_2 \rightarrow Sm_2O_2(SeO_4) \cdot Na_2SeO_4$	740	710	34.50	34.60
$Sm_2O_2(SeO_4) \cdot Na_2SeO_4 \rightarrow Sm_2O_2(SeO_3) \cdot Na_2SeO_3$	875	860	38.42	38.85
$Sm_2O_2(SeO_3) \cdot Na_2SeO_3 \rightarrow Sm_2O_3 + Na_2SeO_3$	1200	1025	49.23	49.90

TABLE 3

Thermoanalytical data for $KSm(SeO_4)_2 \cdot 4\ H_2O$

Dehydration/decomposition	Temp. (°C)		% loss	
	TG	DTA	Calc.	Obsd.
$2\ KSm(SeO_4)_2 \cdot 4\ H_2O \rightarrow 2\ KSm(SeO_4)_2$	500	130	13.16	12.94
$2\ KSm(SeO_4)_2 \rightarrow Sm_2O_2(SeO_3) \cdot K_2SeO_4$	835	680	37.81	36.90
		725		
$Sm_2O_2(SeO_3) \cdot K_2SeO_4 \rightarrow Sm_2O_2(SeO_3) \cdot K_2SeO_3$	940	870	39.27	39.12
$Sm_2O_2(SeO_3) \cdot K_2SeO_3 \rightarrow Sm_2O_3 + K_2SeO_3$	1200	1025	49.41	48.49

TABLE 4

Thermoanalytical data for $NH_4Sm(SeO_4)_2 \cdot 4 H_2O$

Dehydration/decomposition	Temp. (°C)		% loss	
	TG	DTA	Calc.	Obs.
$2 NH_4Sm(SeO_4)_2 \cdot 4 H_2O \rightarrow 2 NH_4Sm(SeO_4)_2$	340	100	13.61	13.81
$2 NH_4Sm(SeO_4)_2 \rightarrow Sm_2(SeO_4)_3$	500	470	30.68	30.96
$Sm_2(SeO_4)_3 \rightarrow Sm_2(SeO_3)_3$	630	605 *	35.26	34.31
$Sm_2(SeO_3)_3 \rightarrow Sm_2O(SeO_3)_2$	780	740	45.76	49.09
		780		

* Exothermic.

and $NH_4Sm(SeO_4)_2 \cdot 4 H_2O$. Tables 2—4 give the thermoanalytical results of the above selenates.

RESULTS AND DISCUSSION

Sodium samarium selenate trihydrate, $NaSm(SeO_4)_2 \cdot 3 H_2O$

The thermoanalytical curves of sodium samarium selenate trihydrate indicate that the salt is stable up to 120°C and its anhydride is produced through two dehydration stages in the temperature range 120—440°C. The trihydrate loses the major part of its water of crystallisation up to 325°C, forming a hemihydrate. A sharp symmetrical endothermic peak associated with this partial dehydration appears at 170°C. Just above 325°C, the hemihydrate loses its stability and the remaining water begins to separate. The anhydride of the double selenate is formed at 440°C, with a weak broad endothermic peak at 385°C in the DTA curve.

An oblique of anhydrous sodium samarium selenate persists up to 550°C, beyond which the decomposition of the anhydride begins. A prominent stage at 740°C as a result of a major weight loss corresponds to the formation of samarium (di)oxyselenate-sodium selenate, $Sm_2O_2(SeO_4) \cdot Na_2SeO_4$. It is apparent from the TG curve that the decomposition of the anhydride up to this stage is accomplished in a single step. However, observation confined to a slight break on the slope of the TG curve clearly indicates that this transformation has its origin through transient intermediate formation of samarium (mono)oxyselenite-sodium selenate, $Sm_2O(SeO_4) \cdot Na_2SeO_4$. Endothermic activities associated with these successive decompositions are represented by two weak peaks at 670 and 710°C in the DTA curve.

The product $Sm_2O_2(SeO_4) \cdot Na_2SeO_4$ formed at 740°C seems to be very susceptible to temperature and consequently undergoes reduction at 875°C forming samarium (di)oxyselenite-sodium selenite, $Sm_2O_2(SeO_3) \cdot Na_2SeO_3$. This reaction is associated with an endothermic effect giving a DTA peak at 860°C. A short oblique in the TG curve representing the existence of $Sm_2O_2(SeO_3) \cdot Na_2SeO_3$ persists over a short range and final decomposition

into samarium oxide and sodium selenite occurs at 1200°C. An unsymmetrical peak at 1025°C accounts for the endothermic change taking place during the final stage of decomposition.

Potassium samarium selenate tetrahydrate, $KSm(SeO_4)_2 \cdot 4 H_2O$

The thermoanalytical curves (Fig. 2) of potassium samarium selenate tetrahydrate are quite simple and show total dehydration of the salt in one step. The compound loses its stability just above 50°C and is dehydrated at 500°C. The simultaneously obtained DTA curve with peak maximum at 130°C accounts for the endothermic activity occurring during the dehydration.

The horizontal of potassium samarium selenate persists up to 590°C, exhibiting thermal stability of the anhydride over a considerable temperature range. Beyond this temperature the anhydride begins to decompose and is reduced to samarium (di)oxyselenite-potassium selenate, $Sm_2O_2(SeO_3) \cdot K_2SeO_4$, at 835°C. This major weight loss involves an intermediate change as evident from a slight break on the slope of the TG curve as well as a DTG peak at 680°C. This weight change may be due to the formation of imperfectly reduced unstable intermediate, samarium (mono)oxyselenite-potassium selenate, $Sm_2O(SeO_3) \cdot K_2SeO_4$, which subsequently undergoes total reduction at 835°C. The two endothermic effects with peak maxima at 680 and 730°C mark the two stages discussed above. It may be recalled that during the thermal decomposition of anhydride in the previous case, sodium selenate exhibited greater thermal stability with the result that decomposition progressed through the formation of oxyselenate, in contrast to oxyselenite as observed in the present case.

The product $Sm_2O_2(SeO_3) \cdot K_2SeO_4$ appears to be very susceptible to temperature rise and starts losing weight gradually immediately after its formation. Further elevation in temperature up to 940°C leads to the reduction of potassium selenate and formation of samarium (di)oxyselenite-potassium selenite, $Sm_2O_2(SeO_3) \cdot K_2SeO_3$. A minor endothermic effect during this decomposition is presented by a weak DTA peak at 870°C. Temperature rise above 940°C effects the decomposition of $Sm_2O_2(SeO_3) \cdot K_2SeO_3$ with a sharp weight loss up to 1200°C. The loss at this stage accounts for the complete decomposition of the above product to a mixture of samarium sesquioxide and potassium selenite. An unsymmetrical endothermic peak at 1025°C accounts for the final decomposition.

Ammonium samarium selenate tetrahydrate, $NH_4Sm(SeO_4)_2 \cdot 4 H_2O$

The thermoanalytical curves (in which DTG is not given) obtained for ammonium samarium selenate tetrahydrate evidently show (Fig. 3) that the salt loses its stability just above room temperature and is dehydrated at 340°C in a single step. A sharp symmetrical DTA peak with maximum at 100°C confirms the one-step dehydration.

The double selenate anhydride begins to decompose just above 340°C and ammonium selenate starts to come off. At 500°C, with sublimation of

ammonium selenate, samarium selenate anhydride is formed. The anhydride loses its stability soon after its formation and is reduced to samarium selenite at 630°C. The heat change accompanying this reduction is exothermic which is an unusual phenomenon observed during the decomposition of double selenates. The maximum of the exothermic peak appears at 605°C.

Further elevation in temperature effects the decomposition of samarium selenite to the corresponding (mono)oxyselenite. However, this stage being highly unstable, its exact region of existence on the TG curve is difficult to locate. As a result, the observed weight loss for this stage is slightly higher than the predicted weight loss. The peaks in the DTA curve corresponding to this decomposition appear at 740 and 780°C. Complete decomposition of the salt could not be achieved since a low temperature range furnace was employed during this decomposition.

It may be mentioned here that the thermal analysis reported for ammonium samarium sulphate octahydrate, $Sm_2(SO_4)_3 \cdot (NH_4)_2SO_4 \cdot 8 H_2O$, by Erämetsä and Niinistö [5] follows similar decomposition stages as in the present case, although the temperatures observed here for different stages of decomposition are a little lower as expected.

CONCLUDING REMARKS

The present thermal investigation on double selenate hydrates of samarium with sodium, potassium and ammonium has revealed interesting dehydration—decomposition mechanisms. It is seen that although double salts of sodium and potassium have single or two-staged deaquations, subsequent decomposition products are analogous. The decomposition temperatures of various stages in the potassium salt are higher than those for corresponding stages in the sodium salt. However, the decomposition trend observed for the ammonium salt is altogether different.

ACKNOWLEDGEMENTS

REFERENCES

1 M.A. Nabar and S.V. Paralkar, Thermochim. Acta, 15 (1976) 390.
2 M.A. Nabar and S.V. Paralkar, Thermochim. Acta, 17 (1976) 239.
3 S.V. Paralkar, Ph.D. Thesis, University of Bombay, 1978.
4 M.A. Nabar and S.V. Paralkar, Thermochim. Acta, 11 (1975) 187.
5 O. Erämetsä and L. Niinistö, Suom. Kemistil. B, 44 (1971) 207.