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STUDIES ON SELENATES. VII. THERMAL DECOMPOSITION OF DOUBLE SELENATE HYDRATES OF HOLMIUM AND YTTERBIUM WITH CAESIUM *

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ABSTRACT

Thermoanalytical techniques have been used to study the decomposition of isostructural double selenate hydrates of holmium and ytterbium with caesium. Based on these results, the mechanism of dehydration-decomposition has been proposed. Some of the intermediate products were characterized by X-ray analysis.

INTRODUCTION

In a comprehensive study, the thermoanalytical work was carried out in this laboratory to understand the dehydration-decomposition of normal and double rare earth selenates [1—5]. The present paper, which is an extension of the previous work, deals with the study of the thermal behaviour of double selenate hydrates of holmium and ytterbium with caesium.

EXPERIMENTAL

The double selenates in the present investigation were prepared by evaporation, at ambient temperature, of an aqueous solution containing stoichiometric amounts of caesium selenate and holmium or ytterbium selenate octahydrate. The compositions of the resulting double selenates were determined by chemical analysis. Holmium and ytterbium contents were determined by complexometry. Selenate was estimated after eluting the aqueous salt solution through a cation exchanger followed by simple acid—base titration of the effluent. Water of crystallization was determined from the TG curves. Caesium contents were obtained by difference. 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) using a Mettler thermoanalyzer TA-2000 system in a flow of dry nitrogen. A heating rate of 10°C min^{-1} was employed.

The X-ray diffractograms were scanned on a standard Philips diffractometer Model No. PW 1009/30 NRD 1023, using nickel filtered $\text{Cu}K_\alpha$ radiation (mean $\lambda = 1.5418$ Å).

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* For Part VI, see ref. 5.

TABLE 1

Analytical results

Compound	Ln%		SeO_4%		H_2O%		Cs%	
	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd. [a]
$CsHo(SeO_4)_2 \cdot 3\ H_2O$	25.86	25.97	44.83	45.25	8.48	8.80	20.83	19.98
$CsYb(SeO_4)_2 \cdot 3\ H_2O$	26.79	26.63	44.27	44.76	8.37	8.90	20.57	19.71

[a] By difference.

TABLE 2

Thermoanalytical results for $CsLn(SeO_4)_2 \cdot 3\ H_2O$

Ln = Ho				Ln = Yb				Interpretation
DTA temp. (°C)	TG temp. range (°C)	% Loss		DTA temp. (°C)	TG temp. range (°C)	% Loss		
		Calcd.	Obsd.			Calcd.	Obsd.	
85	55—100	5.65	5.70	85	55—100	5.58	5.39	$CsLn(SeO_4)_2 \cdot 3\ H_2O \rightarrow CsLn(SeO_4)_2 \cdot H_2O$
185	160—350	8.48	8.80	205	160—350	8.37	8.90	$CsLn(SeO_4)_2 \cdot H_2O \rightarrow CsLn(SeO_4)_2$
				575				Crystalline phase transition
690				712				$CsLn(SeO_4)_2 \rightarrow$
712	600—750	29.64	30.11	725	600—750	29.26	31.10	$Cs_2SeO_4 + [Ln_2O(SeO_3)_2] \rightarrow Ln_2O_2(SeO_3)$
880	800—950	38.34	39.05	815	775—900	37.85	39.81	$Cs_2SeO_4 + Ln_2O_2(SeO_3) \rightarrow$ $Cs_2SeO_4 + Ln_2O_3$
960				950				Melting of Cs_2SeO_4

RESULTS AND DISCUSSION

The thermoanalytical curves of isostructural $CsHo(SeO_4)_2 \cdot 3\ H_2O$ and $CsYb(SeO_4)_2 \cdot 3\ H_2O$ are reproduced in Figs. 1 and 2, respectively.

The compounds under study dehydrate in two stages, passing through thermally stable (100—160°C) monohydrates. The dehydration starts at 55°C and is complete at 350°C, as seen from the TG curves. Table 2 includes the DTA and TG temperatures, along with the observed and calculated weight losses for these and subsequent stages.

For structural characterization, the monohydrates and the anhydrous double selenates were obtained by heating the trihydrates isothermally at 100 and 400°C, respectively. The X-ray powder data recorded for these intermediates along with those for the trihydrates are given in Table 3, which clearly indicate that the monohydrates of holmium and ytterbium are isomorphous, as are the anhydrous double selenates.

The TG curves reveal that the anhydrous salts are stable over a fairly large temperature range (350—600°C). However, an endothermic peak appears at 575°C on the DTA curve of $CsYb(SeO_4)_2$ which is not associated with any weight loss on the TG curve, thus suggesting that it undergoes a crystalline phase transition prior to the commencement of decomposition. No such endothermic activity is discernible in the case of the holmium compound. This interesting phenomenon was confirmed by heating the anhydrous salts,

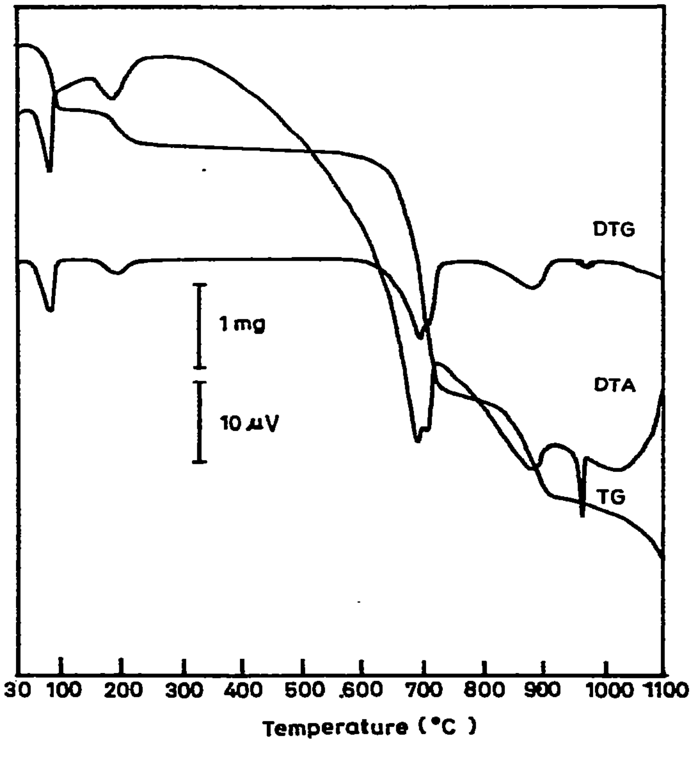

Fig. 1. Thermoanalytical curves of $CsHo(SeO_4)_2 \cdot 3\ H_2O$. Sample weight, 14.21 mg; heating rate, 10°C min^{-1}.

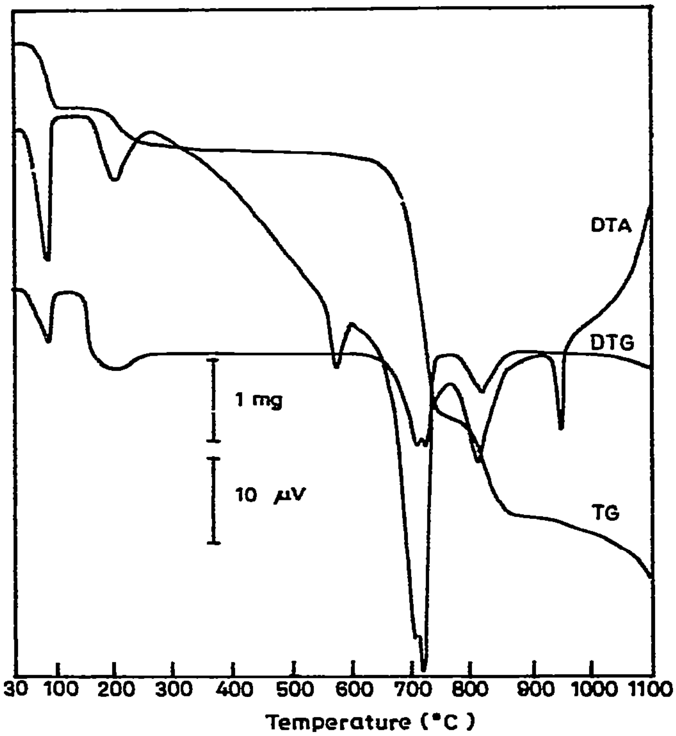

Fig. 2. Thermoanalytical curves of $CsYb(SeO_4)_2 \cdot 3\,H_2O$. Sample weight, 14.36 mg; heating rate, 10°C min^{-1}.

at intervals of 25°C, from 450 to 550°C. A new phase started to appear in the case of the ytterbium salt at 500°C and the complete transformation occurred at 525°C. The X-ray powder data for this polymorphic form of $CsYb(SeO_4)_2$ are collected in Table 3. No such structural change was observed in the case of the holmium salt.

The decomposition of the anhydrous salt proceeds through three stages, as evident from the DTA and DTG curves. The weight losses on the TG curves for the latter two stages correspond to the formation of $Ln_2O_2SeO_3$ + Cs_2SeO_4 and Ln_2O_3 + Cs_2SeO_4, respectively. However, no break on the TG curve corresponding to the first endotherm could be observed under the experimental conditions followed here. This can probably be attributed to the formation of a very unstable $Ln_2O(SeO_3)_2$.

On heating at 600°C, the anhydrous double selenates decompose to $Ln_2(SeO_4)_3$ and Cs_2SeO_4, the former concurrently decomposing into the stable dioxyselenites $Ln_2O_2(SeO_3)$. This fact is amply supported by the weight losses obtained and confirmation of the presence of Cs_2SeO_4 (whose reflexes overshadow those due to dioxyselenites) from the X-ray data given in Table 4. Isothermal heating of the compounds at 850°C yielded mixtures of Ln_2O_3 and Cs_2SeO_4, which was confirmed by X-ray analysis.

The sharp endothermic peaks at 950 and 960°C on the DTA curves of holmium and ytterbium salts, respectively, represent the melting of caesium selenate. This is in accordance with the melting point of Cs_2SeO_4 (954°C) reported by Giolito and Ionashiro [6]. The continuous weight loss corre-

TABLE 3

X-Ray powder diffraction data for $CsLn(SeO_4)_2 \cdot n\ H_2O$

$n = 3$				$n = 1$				$n = 0$					
Ln = Ho		Ln = Yb		Ln = Ho		Ln = Yb		Ln = Ho		Ln = Yb		Ln = Yb (525°C)	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
9.60	14	9.55	29	9.28	4	9.22	7	9.69	14	9.56	16	8.92	13
9.11	100	9.11	100	7.94	14	7.89	10			4.81	4	4.88	37
4.57	54	4.56	62	7.23	17	7.17	13	3.63	22	3.60	14	4.11	47
3.68	18	3.66	25			4.71	7	3.37	100	3.33	100	3.22	100
3.53	3			4.69	9	4.64	4	3.28	6			2.76	40
3.32	22	3.31	33	4.01	12	3.99	5	3.14	15	3.12	12	2.30	9
3.24	16	3.23	29	3.62	100	3.61	100	2.95	13	2.89	10	2.24	6
3.19	21	3.19	36			3.52	9	2.82	10	2.80	8	2.06	27
3.14	14	3.12	23	3.29	28	3.27	13	2.76	10	2.74	8	2.02	12
3.05	98	3.05	100			3.13	5	2.65	7	2.65	4	1.751	4
2.92	5	2.91	7	3.10	10	3.09	7	2.49	10	2.46	7	1.717	17
2.87	15	2.87	21	3.01	10	3.01	4	2.17	7			1.631	13
2.79	16	2.78	16	2.87	10	2.85	6	2.02	14	1.996	7	1.612	6
2.72	5	2.71	7	2.68	6	2.67	3	1.913	8	1.901	7	1.545	6
2.52	5	2.52	8	2.42	6	2.41	5						
2.45	2	2.44	5			2.13	2						
2.38	3												
2.24	4	2.23	10										
		2.20	5										
2.17	5	2.15	10										
2.14	3	2.13	5										
2.10	7	2.09	5										
1.974	4	1.968	7										
		1.891	5										
1.841	6	1.835	8										
1.780	5	1.774	5										

TABLE 4

X-Ray powder diffraction data for Cs_2SeO_4 + $Ln_2O_2(SeO_3)$

Ln = Ho		Ln = Yb		Cs_2SeO_4 [7]	
d(Å)	I/I_0	d(Å)	I/I_0	d(Å)	I/I_0
3.92	11	3.92	14	3.94	7
3.78	26	3.79	21	3.80	18
3.51	11	3.51	11	3.52	10
				3.44	4
3.36	100	3.35	82	3.36	100
3.24	79	3.24	96	3.25	85
3.22	97	3.22	100	3.23	65
3.11	68				
		3.01	36	2.99	8
2.80	42			2.80	8
		2.77	71		
2.70	37	2.71	36	2.72	16
				2.60	4
2.49	13	2.49	14	2.50	7
				2.47	7
				2.35	15
2.32	34	2.33	21	2.33	25
2.29	11				
2.24	11	2.24	18	2.24	4

sponding to these peaks on the TG curves is due to the evaporation of molten Cs_2SeO_4. On prolonged isothermal heating of the compounds at 1000°C the final residues contain only Ln_2O_3.

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