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Note

STUDIES ON SELENATES. VIII. THE THERMAL DECOMPOSITION OF DOUBLE SELENATE HYDRATES OF HOLMIUM AND YTTERBIUM WITH RUBIDIUM *

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The thermal behaviour of the double selenate hydrates of holmium and ytterbium with caesium has been studied very recently [1] and the mechanism was proposed for the dehydration-decomposition. The results were supported by structural characterisation of some of the intermediates obtained after isothermal heating of the parent compounds. In this work, which is a continuation of the above, we present the thermal investigation of double selenate hydrates of holmium and ytterbium with rubidium.

EXPERIMENTAL

The preparation of the compounds and their chemical, thermal and X-ray analysis have been carried out following the methods described previously [1]. The results of chemical analysis are summarised in Table 1. X-Ray analysis showed the monohydrates to be isomorphous.

TABLE 1

Analytical results

Compound	Ln%		ScO_4%		H_2O%		Rb%	
	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd. [a]
$RbHo(SeO_4)_2 \cdot H_2O$	29.75	29.50	51.58	52.04	3.26	3.89	15.42	14.57
$RbYb(SeO_4)_2 \cdot H_2O$	30.77	30.42	50.83	51.51	3.20	4.08	15.20	13.99

[a] By difference.

RESULTS AND DISCUSSION

The thermoanalytical curves for $RbHo(SeO_4)_2 \cdot H_2O$ and $RbYb(SeO_4)_2 \cdot H_2O$ are reproduced in Figs. 1 and 2, respectively. The monohydrates are thermally very

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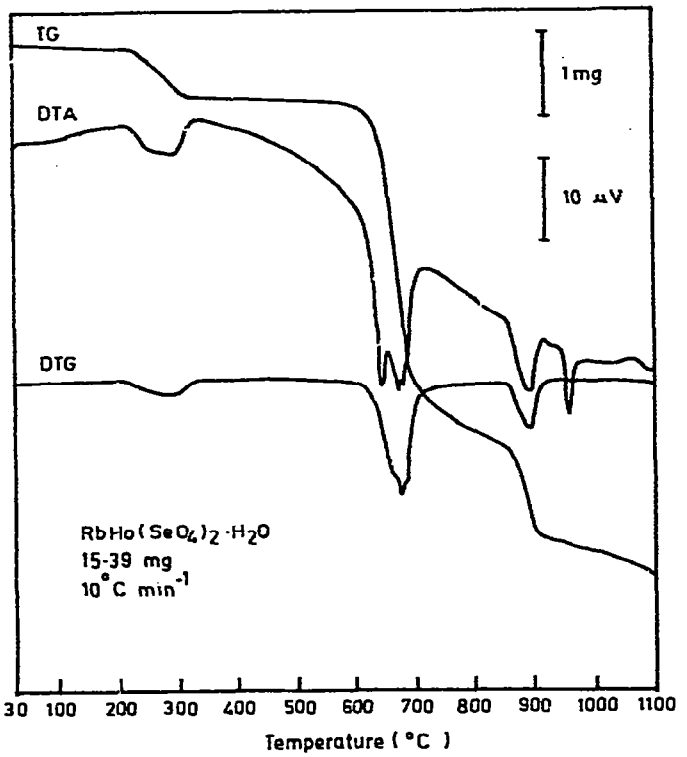

Fig. 1. Thermoanalytical curves of $RbHo(SeO_4)_2 \cdot H_2O$.

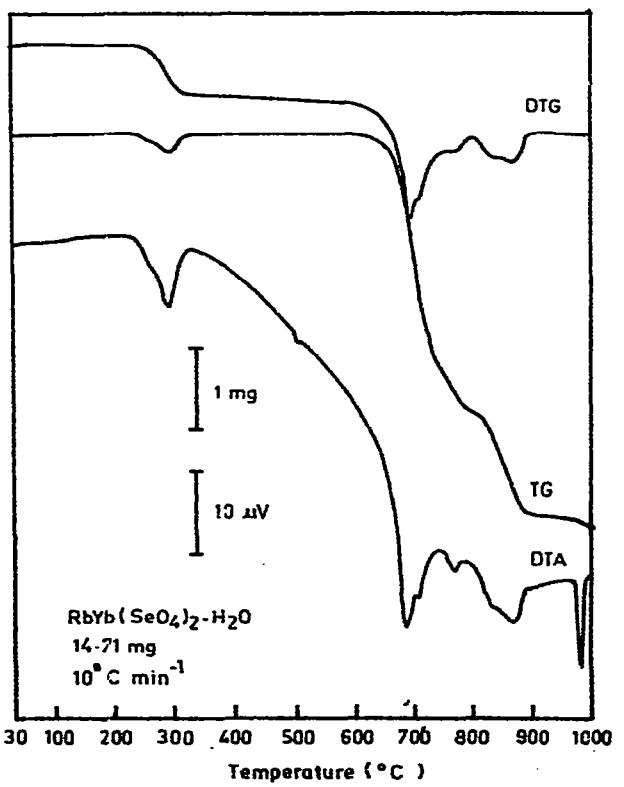

Fig. 2. Thermoanalytical curves of $RbYb(SeO_4)_2 \cdot H_2O$.

TABLE 2

X-Ray powder diffraction data for $Rb_2SeO_4 + Ln_2O_2(SeO_3)$

Ln=Ho		Ln=Yb		Rb_2SeO_4 [3]	
d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0
3.88	3			3.99	16
3.74	4			3.740	11
3.63	5	3.63	7	3.626	18
3.35	4			3.351	14
3.26	10	3.26	21	3.285	11
				3.212	100
3.20	30	3.20	38	3.202	100
3.12	100	3.11	59	3.113	92
				3.088	60
		3.06	100		
				2.902	7
				2.849	9
		2.75	10		
2.71	21			2.704	13
				2.676	16
		2.66	36		
2.59	4	2.61	16	2.584	25
				2.543	3
				2.454	4
2.38	5	2.38	9	2.383	20
				2.366	13
				2.251	8
				2.239	14
2.23	9	2.23	12	2.225	30

stable. The dehydration commences only at 215 and 235°C for the holmium and ytterbium compounds, respectively, and the process continues up to 400°C, as is evident from the TG curves. The corresponding endothermic peak is broad and unsymmetric in both cases.

The anhydrous double salts are thermally stable up to 600°C, as indicated by the fairly horizontal plateau on the TG curve. However, a very weak endothermic peak appears at 500°C on the DTA curve of $RbYb(SeO_4)_2$ which could be ascribed to a phase transformation, as it is not associated with any weight change. The DTA curve of $RbHo(SeO_4)_2$ does not show any such endothermic activity.

The major weight loss on the TG curves up to 750 and 775°C for the holmium and ytterbium compounds, respectively, corresponds to the decomposition yielding dioxyselenite, $Ln_2O_2(SeO_3)$ and Rb_2SeO_4. The corresponding DTA and DTG curves reveal that the decomposition takes place via the formation of two intermediates which could possibly be $Ln_2(SeO_3)_3$ and $Ln_2O(SeO_3)_2$, though the breaks due to their formation are not clearly visible on the TG curves. It may be recalled here that the decomposition to $Ln_2O_2(SeO_3)$ takes place through the formation of only one

TABLE 3

Thermoanalytical results for $RbLn(ScO_4)_2 \cdot H_2O$

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.	
215–330	212–400	3.25	3.90	235–330	235–400	3.20	4.08	$RbLn(ScO_4)_2 \cdot H_2O \rightarrow RbLn(ScO_4)_2$
				500				Crystalline phase transition
647				688				$RbLn(ScO_4)_2 \rightarrow Rb_2ScO_4 + [Ln_2(ScO_3)_3]$
675				705				$\downarrow$ $[Ln_2O(ScO_3)_2]$
682	600–750	27.60	28.27	770	600–775	27.20	29.20	$\downarrow$ $Ln_2O_2(ScO_3)$
895	875–950	37.62	38.66	870	825–900	37.08	38.48	$Rb_2ScO_4 + Ln_2O_2(ScO_3) \rightarrow Rb_2ScO_4 + Ln_2O_3$
965				985				Melting of Rb_2ScO_4

intermediate, $Ln_2O(SeO_3)_2$ in the case of the corresponding caesium double selenates, under similar conditions [1].

The anhydrous rubidium holmium selenate obtained on isothermal heating of the monohydrate at 400°C possessed a distinctly different structure. The corresponding ytterbium salt, however, is found to be hygroscopic in nature and is reconverted to the monohydrate. Further, the products obtained isothermally at 650°C on X-ray analysis revealed the presence of Rb_2SeO_4, as is evident from Table 2 which lists the *d*-spacings for the mixtures along with those for Rb_2SeO_4. It may thus be concluded that the anhydrous double selenates decompose into the components $Ln_2(SeO_4)_3$ and Rb_2SeO_4 before decomposition of the former begins.

The final decomposition to holmium or ytterbium oxide takes place at 950°C, as is apparent from the TG curves, rubidium selenate remaining undecomposed, and the corresponding DTA peaks appear at 895 and 870°C, respectively. The presence of $Ln_2O_3 + Rb_2SeO_4$ was confirmed by X-ray analysis of the products heated at 850°C.

The sharp endothermic peaks at 965 and 985°C (in fair agreement with the reported value of 972°C [2]) on the DTA curves of holmium and ytterbium salts, respectively, correspond to the melting of rubidium selenate. The continuous weight loss on the TG curve beyond this is attributable to the evaporation of molten Rb_2SeO_4. On prolonged heating of the compounds at 1000°C the final residues contain only Ln_2O_3.

The thermoanalytical data, consisting of the DTA and TG temperatures along with the observed and calculated weight losses, are presented inTable 3.

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REFERENCES

1 M.A. Nabar and V.R. Ajgaonkar, Thermochim. Acta, 47 (1981) 309.
2 I. Giolito and M. Ionashiro, Thermochim. Acta, 38 (1980) 341.
3 ASTM File No. 24-966.