

## **THERMAL DECOMPOSITION OF NOVEL RARE-EARTH SELENITES**

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TG and DTA have been carried out on new anhydrous rare-earth selenites  $R_2Se_aO_{3+2a}$  ( $a = 3.5, 4$ ) in order to establish their stability. Decomposition occurs in three steps attributed to successive losses of  $SeO_2$ . The first process gives rise to other new group of selenites of composition  $R_2Se_3O_9$ , which crystallize in two different forms depending on the rare-earth element. The second process leads to isomorphous compounds  $R_2SeO_5$ . The final product of thermal degradation is  $R_2O_3$ . All products were characterized by chemical analysis and X-ray powder diffraction methods.

**Keywords:** rare-earth selenites, TG-DTA, X-ray

### **Introduction**

Almost one hundred years ago, Espil [1] prepared, for the first time, some anhydrous rare-earth selenites, but none have been well characterized subsequently, with the exception of  $Eu_2Se_5O_{13}$  [2]. Nevertheless, a large number of sodium rare-earth selenites, hydrogen-selenites and hydrated selenites have been prepared and studied [3–6].

This paper reports results of the thermal decomposition of the anhydrous rare-earth selenites  $R_2Se_aO_{3+2a}$  ( $a = 3.5, 4$ ) recently described [7], as well as the production of new rare-earth selenites,  $R_2Se_3O_9$  and  $R_2SeO_5$ . All the materials were characterized by X-ray powder diffraction and chemical analysis.

### **Experimental**

The starting anhydrous rare-earth selenites of compositions  $R_2Se_4O_{11}$  ( $R = Y, La, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu$ ) and  $R_2Se_{3.5}O_{10}$  ( $R = Pr, Nd, Sm, Eu, Tb$ ) were prepared by solid-state reactions, at 688 K for 36 h, in evacuated ( $10^{-3}$  Torr) pyrex

ampoules, between stoichiometric mixtures of analytical grade  $R_2O_3$  ( $R = Y, La, Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu$ ),  $Pr_2O_3$  or  $Tb_4O_7$  with  $SeO_2$ .

Thermogravimetric and differential thermal analyses were performed in air at ambient pressure between 298 and 1473 K. In order to compare the results, both heating rate and sample weight were kept constant at  $5 \text{ deg}\cdot\text{min}^{-1}$  and 10 mg, respectively. The experiments were carried out using a Stanton Redcroft STA-781 instrument. Standard platinum crucibles were employed in all experiments.

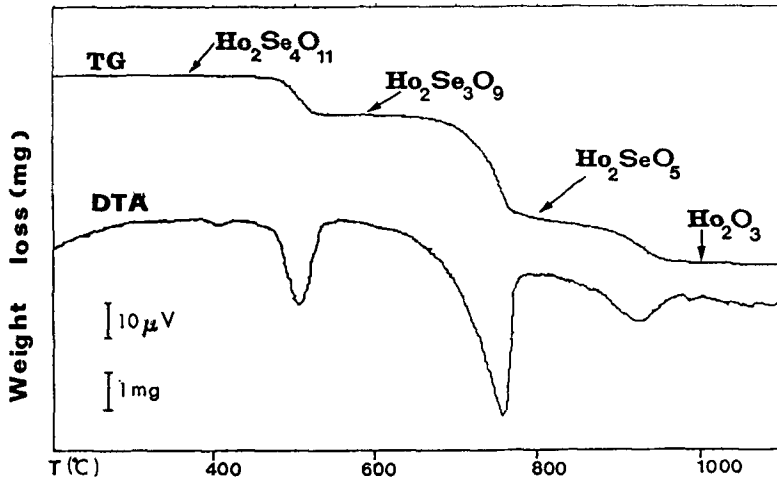


Fig. 1 TG and DTA curves of a representative  $R_2Se_4O_{11}$  compound ( $R = Ho$ )

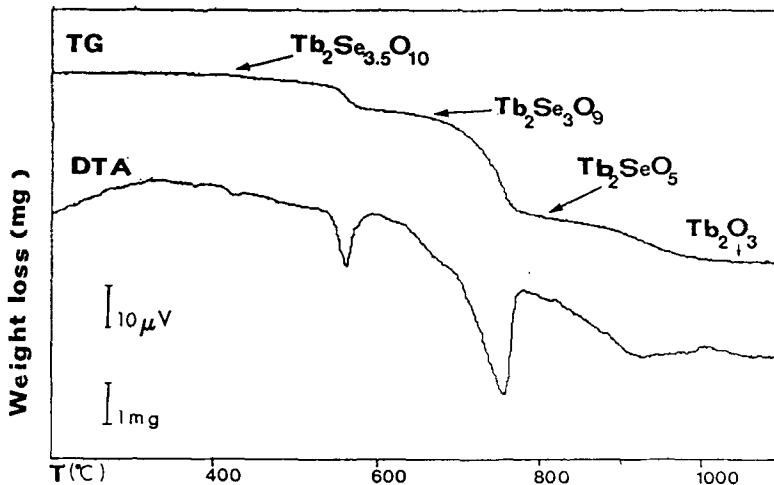


Fig. 2 TG and DTA curves of a characteristic  $R_2Se_{3.5}O_{10}$  selenite ( $R = Tb$ )

Chemical compositions of the metals were determined by emission and inductively coupled plasma spectroscopy. All products were characterized by X-ray powder diffraction, using a Siemens Kristalloflex 810 generator, a D-501 goniometer provided with  $2\theta$  compensating slit and a graphite monochromator controlled by a DACO-MP computer, and  $\text{CuK}\alpha$  radiation. Diffraction patterns of the samples were recorded between  $4-70^\circ 2\theta$  with increments of  $0.05^\circ 2\theta$  and a counting time of 4 seconds per step.

## Results and discussion

Thermal decomposition of the anhydrous rare-earth selenites  $\text{R}_2\text{Se}_4\text{O}_{11}$  and  $\text{R}_2\text{Se}_{3.5}\text{O}_{10}$  examined occurs in three steps between 673 and 1313 K, depending on the rare-earth element (Figs. 1 and 2). It is worth noting that although these materials crystallize in four different structure types, three for  $\text{R}_2\text{Se}_4\text{O}_{11}$  ( $R = \text{La}$ ;  $R = \text{Gd, Tb, Dy, Ho}$ ;  $R = \text{Y, Er, Tm, Yb, Lu}$ ) and one for  $\text{R}_2\text{Se}_{3.5}\text{O}_{10}$  ( $R = \text{Pr, Nd, Sm, Eu, Gd, Tb}$ ), their thermal behaviour is identical and consists in successive losses of  $\text{SeO}_2$  molecules.

Table 1 summarizes the decomposition processes for all the  $\text{R}_2\text{Se}_a\text{O}_{3+2a}$  selenites; calculated weight losses for each step are in good agreement with those observed. DTA curves show three endothermic peaks, in accordance with each mass loss observed in the TG curves.

The first process starts between 673 K for  $\text{La}_2\text{Se}_4\text{O}_{11}$  and 795 K for  $\text{Tb}_2\text{Se}_{3.5}\text{O}_{10}$  and is complete at 868 K for all compounds. The weight loss for this step correspond to loss of one half molecule of  $\text{SeO}_2$  for  $\text{R}_2\text{Se}_{3.5}\text{O}_{10}$ , and one  $\text{SeO}_2$  for the  $\text{R}_2\text{Se}_4\text{O}_{11}$  phases, leading to the same composition for all the compounds,  $\text{R}_2\text{Se}_3\text{O}_9$ , as confirmed by chemical analyses. X-ray diffraction patterns of  $\text{R}_2\text{Se}_3\text{O}_9$  show the existence of two different crystalline modifications, corresponding to  $R = \text{La, Pr, Nd, Sm, Eu, Tb}$  and to  $R = \text{Y, Gd, Dy, Ho, Er, Tm, Yb, Lu}$ . The Gd and Tb compounds show crystalline forms different to those expected, bearing in mind their ionic sizes.

The second process starts between 875 K for  $\text{Tm}_2\text{Se}_3\text{O}_9$  and 1073 K for  $\text{Pr}_2\text{Se}_3\text{O}_9$  (Table 1). This process corresponds to further degradation of the  $\text{R}_2\text{Se}_3\text{O}_9$  selenites, giving rise to another family of isomorphous anhydrous rare-earth selenites of composition  $\text{R}_2\text{SeO}_5$ , which are stable until about 1100 K.

The existence of the compounds  $\text{R}_2\text{Se}_3\text{O}_9$  and  $\text{R}_2\text{SeO}_5$  had been reported previously [8–10] as sub-products of the thermal decomposition of hydrated selenates, but they had not until now been characterized.

The last observed effect due to total elimination of  $\text{SeO}_2$  is not so well defined as the previous two, and corresponds to degradation of the remaining  $\text{R}_2\text{SeO}_5$  compounds. The final residues obtained after prolonged heating of these

**Table 1** Thermal analysis data obtained by TG on the decomposition of  $R_2Se_aO_{3+2a}$ . Separated lines delimit different structure modifications

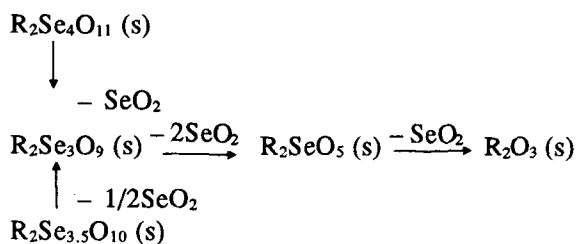
<i>a</i>	<i>R</i>	Temperature interval/ K	Weight loss/%	
			Calculated	Observed
4	La	673–810	14.4	12.6
	Gd	774–861	13.8	13.8
	Dy	729–803	13.6	13.6
	Ho	707–767	13.5	13.5
	Y	729–849	16.6	16.6
	Er	752–825	13.4	14.4
	Tm	745–832	13.4	13.4
	Yb	774–839	13.2	13.2
	Lu	759–868	13.2	13.2
	3.5	Pr	789–846	7.7
Nd		736–846	7.7	7.7
Sm		789–861	7.5	7.7
Eu		767–832	7.5	8.3
Tb		795–853	7.4	7.4
3	La	978–1125	33.7	30.0
	Pr	1073–1253	33.5	35.5
	Nd	948–1056	33.2	33.2
	Sm	930–1052	32.6	32.6
	Eu	944–1058	32.4	32.4
	Tb	958–1059	31.8	31.8
	Y	882–1077	39.7	39.7
	Gd	972–1077	31.9	31.9
	Dy	917–1058	31.4	31.4
	Ho	896–1045	31.2	31.2
	Er	958–1038	31.0	31.0
	Tm	875–1032	30.9	30.9
	Yb	888–1019	30.5	30.5
	Lu	896–1024	30.4	30.4

Table 1 (continued)

<i>a</i>	<i>R</i>	Temperature interval/ K	Weight loss/%	
			Calculated	Observed
1	Y	1128–1268	32.9	32.9
	La	1313–1457	25.4	30.6
	Pr	1268–1473	25.2	25.2
	Nd	1278–1361	24.8	24.8
	Sm	1210–1303	24.1	26.0
	Eu	1122–1301	24.0	23.0
	Gd	1191–1290	23.4	22.0
	Tb	1109–1271	23.2	23.2
	Dy	1141–1253	22.9	22.9
	Ho	1128–1278	22.7	22.7
	Er	1141–1238	22.5	22.4
	Tm	1071–1241	22.3	22.3
	Yb	1074–1204	22.0	22.0
	Lu	1096–1216	21.8	21.8

materials up to 1473 K show X-ray diffraction patterns characteristic of the corresponding rare-earth sesquioxides.

A general decomposition scheme for the anhydrous rare-earth selenites can be proposed on the basis of the present results:



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The authors thank the Consejo Superior de Investigaciones Científicas of Spain for the financial support under its 630/00/070 Program.

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**Zusammenfassung** — Mittels TG und DTA-Untersuchungen sollte die Stabilität von neuen wasserfreien Seltenerd-seleniten  $R_2Se_aO_{3+2a}$  ( $a \approx 3.5, 4$ ) bestimmt werden. Die Zersetzung verläuft in drei Schritten unter nacheinanderfolgender Abgabe von  $SeO_2$ . Der erste Prozeß verursacht eine andere Gruppe von Seleniten mit der Zusammensetzung  $R_2Se_3O_9$ , welche je nach Art des Seltenerdenmetalles in zwei verschiedenen Formen kristallisieren. Der zweite Prozeß führt zu isomorphen Verbindungen  $R_2SeO_5$ . Das Endprodukt des abschließenden Abbaues ist  $R_2O_3$ . Alle Produkte werden mittels chemischer Analyse und Debye-Scherer-Methoden beschrieben.