THERMAL DECOMPOSITION OF LIGHTER LANTHANIDE SELENATE HYDRATES AND THEIR SOLID SOLUTIONS

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Abstract

The thermal dehydration-decomposition of $Ln_2(SeO_4)_3 \cdot nH_2O$ (where $n=12$ for $Ln=$ Pr, Nd and $n=8$ for $Ln=$ Sm) and $Pr_xLn_{2-x}(SeO_4)_3 \cdot nH_2O$ (where $n=12$ for $x=1.0$ and $Ln=$ Nd; $n=8$ for $x=0.2$ and 1.0 in case of $Ln=$ Sm) have been reported.

Introduction

Many reports have appeared in the literature on rare earth selenates in the last two decades. It has been well established that the selenates of rare earths beyond neodymium crystallise as octahydrates [1–5], the only exception being the report by Giolito and Giesbrecht [6] in which some heptahydrates were reported. The stable hydrates for lanthanum, praseodymium and neodymium reported uptil now, are however pentahydrates [2, 5, 7, 8] excepting the report on the structural and thermoanalytical investigation of a highly hydrated lanthanum selenate, $La_2(SeO_4)_3 \cdot 12H_2O$ [9], which was prepared by crystallisation at a low temperature (4–12°C).

The present communication, which is a part of the investigations of solid solutions of lighter rare earth selenates, deals with the thermal dehydration–decomposition of praseodymium, neodymium, samarium selenate hydrates and of some representative solid solutions of praseodymium-neodymium and praseodymium–samarium selenates.

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Experimental

Praseodymium, neodymium and samarium selenates were prepared by the reaction of the respective carbonate with dilute selenic acid (~2 *M*) solution. the resultant solutions containing some unreacted carbonate were filtered and allowed to evaporate at 27°C in a water thermostat. The solid solutions were prepared by dissolving the individual selenates, taken in appropriate ratios, in water followed by evaporation at 27°C.

The compositions of the compounds were fixed by chemical analysis. The rare earth contents were determined complexometrically and selenate contents gravimetrically as lead selenate from 30% ethanolic solutions. The water contents were ascertained from the TG curves and in some cases by isothermal heating at 400°C. The results of chemical analysis are given in Table 1.

The compounds were characterised by scanning the X-ray powder diffractograms on Philips PW 1820 diffractometer using CuK$_\alpha$ radiation (λ=1.5406 Å) operated at 40 kV and 30 mA.

The DTA, TG curves for the praseodymium, neodymium and praseodymium–neodymium (1:1) selenates were obtained on Shimadzu thermal analyser DT 30 in nitrogen atmosphere. The DTA, TG, DTG curves for samarium selenate, praseodymium–samarium (1.0:1.0) selenate and praseodymium-samarium (0.2:1.8) selenate were obtained on a DuPont 9900 instrument in nitrogen atmosphere. The heating rate of 10 deg·min^{-1} was employed.

The infrared spectra of the parent compounds and the intermediates (in representative cases) obtained by isothermal heating at 650°C were scanned in the range 4000–400 cm^{-1} on a Shimadzu FTIR-4200 spectrophotometer using KBr disc technique.

Results and discussion

The chemical analysis data (Table 1) show that praseodymium selenate (I), neodymium selenate (III) and their solid solution having Pr:Nd mole ratio 1.0:1.0 crystallise as dodecahydrates. The degree of hydration of the selenates of lighter rare earths is very sensitive to the atmospheric conditions at the time of crystallisation, and apart from the temperature, relative humidity probably plays an important role. The samarium selenate (IV) expectedly crystallises as an octahydrate and so do the solid solutions of praseodymium and samarium selenates with mole ratios of Pr:Sm=0.2:1.8 (V) and Pr:Sm=1.0:1.0 (VI). The dodecahydrates were found to be unstable under the normal storage conditions and slowly effloresce at ambient temperature. The octahydrates are, however, more stable.

The line diagrams (*d*/Å *vs.I/I$_o$*) of the X-ray powder diffractograms for the dodecahydrates and for the octahydrates are shown in Fig. 1. The selenates with

Table 1 Results of chemical analysis

Compounds	% Ln^{3+}		% SeO_4^{2-}		% H_2O	
	calcd.	found	calcd.	found	calcd.	found
$Pr_2(SeO_4)_3 \cdot 12H_2O$	30.41	30.40	46.28	45.61	23.31	23.99*
$Pr_{1.0}Nd_{1.0}(SeO_4)_3 \cdot 12H_2O$	30.66	30.54°	46.12	45.82	23.22	23.96+
$Nd_2(SeO_4)_3 \cdot 12H_2O$	30.91	30.85	45.95	45.56	23.14	24.12+
$Pr_{0.2}Sm_{1.8}(SeO_4)_3 \cdot 8H_2O$	34.28	34.52°	49.20	49.67	16.52	16.45
$Pr_{1.0}Sm_{1.0}(SeO_4)_3 \cdot 8H_2O$	33.71	34.02°	49.63	49.25	16.66	16.84+
$Sm_2(SeO_4)_3 \cdot 8H_2O$	34.43	34.27	49.09	49.84	16.48	17.13

* by difference, + by isothermal heating at 400°C, ° total Ln %

the same number of water molecules of crystallisation are thus seen to be iso-morphous.
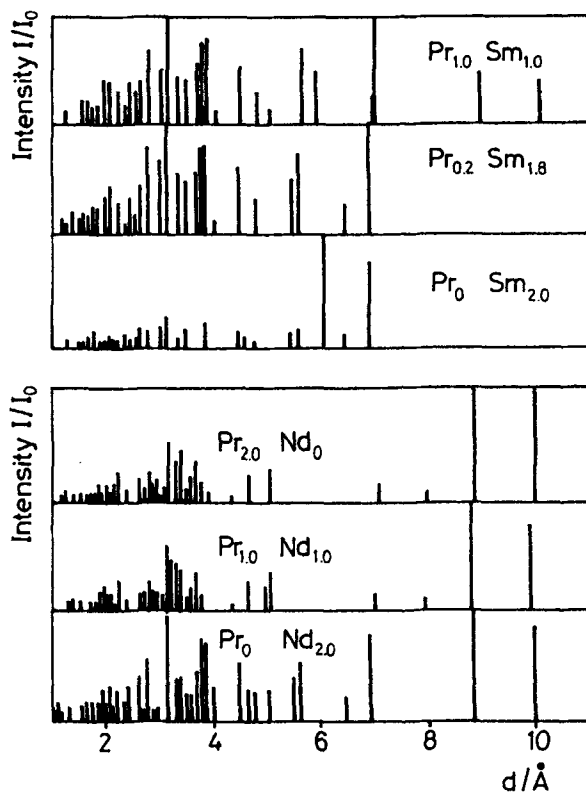

Fig. 1 Line diagrams of the XRD patterns of the selenates $Pr_xLn_{(2-x)}(SeO_4)_3 \cdot nH_2O$ where $n=12$ for $Ln \equiv Nd$ and $n=8$ for $Ln \equiv Sm$

The decomposition pattern is similar for the compounds I, II and III. The DTA and TG curves for III (representative of the dodecahydrates) are repro-duced in Fig. 2. The thermoanalytical results for I, II and III are summarised in Table 2. The dehydration of these compounds is a multistage process as per the DTA curves. However, only one break is discernible on the corresponding TG curves after the commencement of dehydration at 40°C, and this can be at-tributed to the formation of an octahydrate intermediate in case of I and II, and to a nonahydrate in case of III. The octahydrate intermediate was also reported by Karvinen and Niinistö [9] for $La_2(SeO_4)_3 \cdot 12H_2O$. After the initial relatively rapid weight loss up to 200°C, the remaining water which is perhaps strongly coordinated to the lanthanide ion is lost gradually up to ~500°C. The observed weight loss for I at this stage is 21% compared to 23.3% expected for the com-

plete dehydration of the dodecahydrate and probably corresponds to the loss of eleven water molecules. The observed weight losses up to 500°C for II and III are 23.0 and 23.4 per cent respectively, as expected.
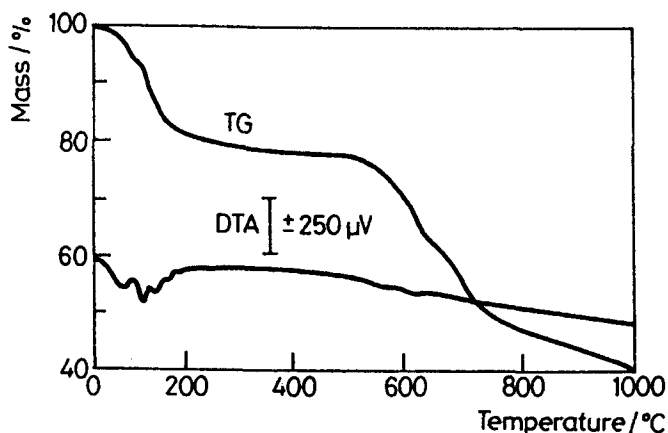

Fig. 2 DTA –TG curves of $Nd_2(SeO_4)_3 \cdot 12H_2O$ (sample weight=15.5 mg)

The decomposition of the anhydrous compound commences at ~550°C in each case. The major weight loss up to ~780°C corresponds to the formation of dioxyselenite, $Ln_2O_2(SeO_3)$ and occurs in two stages, the break in the TG curve

Table 2 Thermoanalytical results for $Ln_2(SeO_4)_3 \cdot 12H_2O$

DTA temp./°C	TG temp. range/ °C	% Loss		Interpretation
		calcd.	obsd.	
$(Ln_2 \equiv Pr_2)$				$Pr_2 (SeO_4)_3 \cdot 12H_2O$
				↓
65	40–80	7.77	8.2	$Pr_2 (SeO_4)_3 \cdot 8H_2O$
				↓
130 160 200	80–500	21.38	21.0	$Pr_2 (SeO_4)_3 \cdot H_2O$ (?)
				↓
610	550–680	37.02	36.0	$Pr_2O (SeO_4)_2$
				↓
740	680–780	52.44	52.5	$Pr_2O_2(SeO_3)$
				↓
–	780–1000	64.42	62.8	Pr_2O_3 (incomplete)

Table 2 Continued

DTA	TG	% Loss		Interpretation
temp./°C	temp. range/ °C	calcd.	obsd.	
$(Ln_2 \equiv Pr_{1.0}Nd_{1.0})$				$Pr_{1.0}Nd_{1.0} (SeO_4)_3 \cdot 12H_2O$
				$\downarrow$
75	40–90	7.75	8.0	$Pr_{1.0}Nd_{1.0} (SeO_4)_3 \cdot 8H_2O$
				$\downarrow$
115 ⎫ 160 ⎭	90–500	23.24	23.3	$Pr_{1.0}Nd_{1.0} (SeO_4)_3$
				$\downarrow$
605	550–670	36.84	36.5	$Pr_{1.0}Nd_{1.0}O(SeO_4)_2$
				$\downarrow$
740	670–790	52.26	52.5	$Pr_{1.0}Nd_{1.0}O_2(SeO_3)$
				$\downarrow$
–	790–1000	64.18	60.4	$Pr_{1.0}Nd_{1.0}O_3$ (incomplete)
$(Ln_2 \equiv Nd_2)$				$Nd_2 (SeO_4)_3 \cdot 12H_2O$
				$\downarrow$
65	40–85	5.79	6.0	$Nd_2 (SeO_4)_3 \cdot 9H_2O$
				$\downarrow$
110 ⎫ 130 ⎬ 200 ⎭	85–500	23.16	23.0	$Nd_2(SeO_4)_3$
				$\downarrow$
560	550–650	36.76	37.0	$Nd_2O(SeO_4)_2$
				$\downarrow$
625	650–770	52.07	52.0	$Nd_2O_2(SeO_3)$
				$\downarrow$
–	770–1000	63.95	60.8	Nd_2O_3 (incomplete)

being attributable to the formation of a monooxyselenate, $Ln_2O(SeO_4)_2$ intermediate. There is, however, no evidence for the formation of the dioxyselenate, $Ln_2O_2(SeO_4)$ perhaps due to its very unstable nature. The final decomposition to oxide does not go to completion up to 1000°C and the weight losses at this temperature indicate partial decomposition of the dioxyselenite to oxide. The

DTA curves of the compounds show two very weak endothermic peaks corresponding to the first two stages.
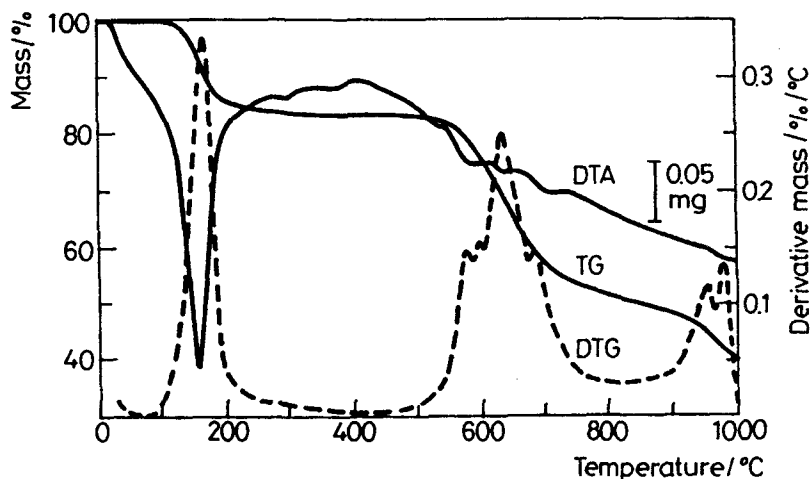

Fig. 3 DTA–TG–DTG curves of $Sm_2(SeO_4)_3 \cdot 8H_2O$ (sample weight: DTA 9.550 mg; TG 10.640 mg)

The DTA, TG, DTG curves of $Sm_2(SeO_4)_3 \cdot 8H_2O$ (IV), as a representative of the octahydrates, are reproduced in Fig. 3. The thermoanalytical data for the compounds IV, V and VI are collected in Table 3. The compounds IV and V undergo a single stage dehydration leading to anhydrous selenates, while VI shows a three stage dehydration passing through hepta- and hexahydrate intermediates. The DTA curve of samarium selenate exhibits two weak endothermic activities at 280 and 380°C which are not associated with any weight loss, and may be due to crystalline phase transitions.

The decomposition of the anhydrous compounds is a multistage process and three to four weak endothermic peaks have appeared on the DTA curves in the temperature range 500–750°C. However, no clear breaks are depicted on the TG curves. The DTG curves show a major peak at ~635°C with shoulders on either side suggesting overlapping stages. The major weight losses up to ~800°C for all these compounds correspond to the formation of $Ln_2O_2(SeO_3)$. The final decomposition to oxide is complete only in case of samarium compound, IV. In case of V and VI, the weight losses up to 1000°C correspond to partial decomposition of the dioxyselenite.

The infrared spectra of $Nd_2(SeO_4)_3 \cdot 12H_2O$, $Sm_2(SeO_4)_3 \cdot 8H_2O$ and their decomposition products obtained by heating the parent compounds isothermally at 650°C are shown in the range 1000–500 cm^{-1} in Fig. 4 for comparison. The bands due to selenate ions are absent in the spectra of the heated products which

Table 3 Thermoanalytical results for $Ln_2(SeO_4)_3 \cdot 8H_2O$

DTA temp./°C	TG temp. range /°C	% Loss		Interpretation
		calcd.	obsd.	
$(Ln_2 \equiv Sm_2)$				$Sm_2 (SeO_4)_3 \cdot 8H_2O$
				$\downarrow$
161	85– 500	16.49	17.13	$Sm_2(SeO_4)_3$
				$\downarrow$
280	–	–	–	Crystalline phase
380				transitions (?)
				$\downarrow$
548				
595	550– 800	47.38	48.00	$Sm_2O_2(SeO_3)$
640				
720				
				$\downarrow$
–	800–1000	60.08	59.36	Sm_2O_3
$(Ln_2 \equiv Pr_{0.2}Sm_{1.8})$				$Pr_{0.2}Sm_{1.8} (SeO_4)_3 \cdot 8H_2O$
				$\downarrow$
153	87– 500	16.53	16.45	$Pr_{0.2}Sm_{1.8}(SeO_4)_3$
				$\downarrow$
552				
639	550– 800	47.49	47.00	$Pr_{0.2}Sm_{1.8}O_2(SeO_3)$
696				
				$\downarrow$
966	800–1000	60.21	57.57	$Pr_{0.2}Sm_{1.8}O_3$ (incomplete)
$(Ln_2 \equiv Pr_{1.0}Sm_{1.0})$				$Pr_{1.0}Sm_{1.0} (SeO_4)_3 \cdot 8H_2O$
				$\downarrow$
42	40– 67	2.08	1.55	$Pr_{1.0}Sm_{1.0} (SeO_4)_3 \cdot 7H_2O$
				$\downarrow$
95	67– 104	4.17	3.52	$Pr_{1.0}Sm_{1.0} (SeO_4)_3 \cdot 6H_2O$

Table 3 Continued

DTA	TG	% Loss		Interpretation
temp./°C	temp. range /°C	calcd.	obsd.	
145	104–500	16.67	17.53	$Pr_{1.0}Sm_{1.0}(SeO_4)_3$
				$\downarrow$
589 623 642 724	550–800	47.90	48.0	$Pr_{1.0}Sm_{1.0}O_2(SeO_3)$
				$\downarrow$
–	800–1000	60.74	57.74	$Pr_{1.0}Sm_{1.0}O_3$ (incomplete)
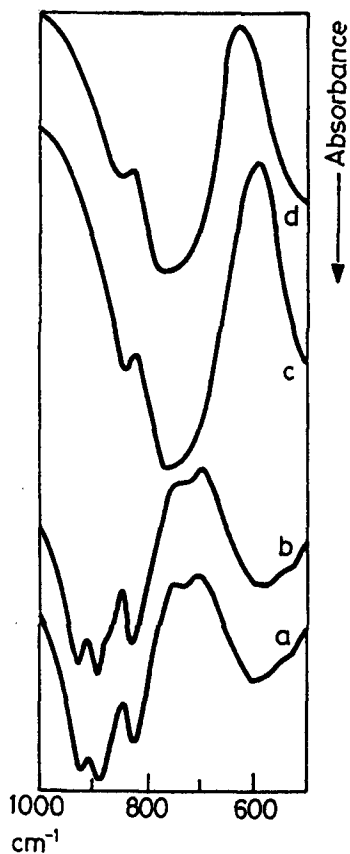
Fig. 4 Infrared absorption spectra of (a): $Nd_2(SeO_4)_3 \cdot 12H_2O$, (b): $Sm_2(SeO_4)_3 \cdot 8H_2O$, (c):$Nd_2(SeO_4)_3 \cdot 12H_2O$ heated at 650°C, (d):$Sm_2(SeO_4)_3 \cdot 8H_2O$ heated at 650°C

show characteristic bands of the selenite ions. The weight losses obtained at 650°C correspond closely to the decomposition to $Ln_2O_2(SeO_3)$.

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Zusammenfassung — Die thermische Dehydratation-Zersetzung von $Ln_2(SeO_4)_3 \cdot nH_2O$ (mit $n=12$ für $Ln=$Pr, Nd und $n=8$ für $Ln=$Sm) und $Pr_xLn_{2-x}(SeO_4)_3 \cdot nH_2O$ (mit $n=12$ für $x=1.0$ und $Ln=$Nd; $n=8$ für $x=0.2$ und 1.0 im Falle von $Ln=$Sm) wurde beschrieben.