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THERMAL DECOMPOSITION OF LANTHANUM SELENATE PENTAHYDRATE IN AIR AND NITROGEN

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Thermogravimetric studies, supported by IR and X-ray diffraction measurements, were carried out for $La_2(SeO_4)_3 \cdot 5H_2O$ in order to establish its decomposition scheme under various experimental conditions. Several analytical methods were tested for the simultaneous determination of Se(IV) and Se(VI) in the quenched samples. TG weight losses and analyses of the solid intermediates indicated that after dehydration $La_2(SeO_4)_3$ decomposes in nitrogen mainly to oxyselenite(IV) compounds *via* the normal selenite(IV) but in air the oxyselenate $La_2O_2SeO_4$ was detected as one of the intermediates. The final product of the thermal degradation is La_2O_3. TG curves of $La_2(SeO_4)_3 \cdot 5H_2O$ were also compared with those obtained for the isostructural neodymium compound.

Whereas the thermal decomposition scheme for rare earth sulfate hydrates is well established [1–3], the reports concerning corresponding selenate hydrates are contradictory especially regarding the reaction mechanism and intermediates at higher temperatures.

Giolito and Giesbrecht [4] were probably the first investigators who applied thermogravimetric methods to the study of rare earth selenate hydrates, including the decahydrate of lanthanum selenate. The decomposition curves appeared complex and, besides the anhydrous selenate, the $La_2O_2SeO_4$ phase was considered as a possible intermediate. More recently, Nabar and Paralkar [5] have investigated the decomposition of $La(SeO_4)_3 \cdot 5H_2O$ up to 1050° and concluded that the anhydrous selenate decomposes first to selenite and then to dioxyselenite $La_2O_2SeO_3$ *via* an unstable intermediate $La_2O(SeO_3)_2$; the final product at over 1000° is La_2O_3. Hajek et al. [6] have also suggested only Se(IV) compounds when an anhydrous rare earth selenate decomposes. On the other hand, Hayashi Tetsu et al. [7] found by analyzing the thermal decomposition products of $Sc_2(SeO_4)_3 \cdot 5H_2O$ at various temperatures that both Se(IV) and Se(VI) were present. The presence of Se(VI) was attributed to incomplete decomposition of the starting material,

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however, and the decomposition mechanism suggested was based on $Sc_2(SeO_3)_3$ and $Sc_2O_2SeO_3$ only.

Thermogravimetric data are also available for $La_2(SeO_4)_3 \cdot 12H_2O$ [8], and recently the structural chemistry and thermal properties of rare earth selenates have been reviewed in detail [9].

The aim of the present study was to study, using a combination of chemical and thermogravimetric analyses, the thermal decomposition mechanism of rare earth selenate hydrates. $La_2(SeO_4)_3 \cdot 5H_2O$ was used as a model compound and studied under various experimental conditions. The results were compared with those obtained for the isostructural neodymium compound.

Experimental

Materials. $La_2(SeO_4)_3 \cdot 5H_2O$ was prepared as a crystalline precipitate by evaporating a solution of La_2O_3 (99.9%, Kemira Oy, Finland) dissolved in 3 mol dm^{-3} selenic acid [10] on a water bath. $Nd_2(SeO_4)_3 \cdot 5H_2O$ was crystallized in a similar way. The identity of the compounds was checked by X-ray diffraction.

Thermoanalytical measurements. TG curves in dynamic air or nitrogen atmosphere (0.1 dm^3 min^{-1}) were recorded in the temperature range 50–1025° by using a Perkin–Elmer TGS_2 Thermobalance coupled with a System 7/4 Controller and TADS Data Station. In order to study the effect of various experimental parameters on the decomposition mechanism of $La_2(SeO_4)_3 \cdot 5H_2O$, either sample weight (4.5–40 mg) was varied while heating rate was constant at 5 deg min^{-1}, or heating rate was varied (2–20 deg min^{-1}) and sample weight was kept constant (4.5 mg). Standard platinum crucibles were employed in all experiments (diam. 5.8 mm, height 1.8 mm). For comparison, some experiments were carried out with a Mettler TA-1 and MOM Q-Derivatograph instruments capable for simultaneous recording of TG, DTG and DTA curves and with a Perkin–Elmer DTA-1700 high-temperature DTA apparatus.

X-ray diffraction and IR measurements. X-ray powder diffraction diagrams were recorded at 25° on a Philips diffractometer using Ni-filtered CuK_α radiation (λ = 1.54178 Å). The diagrams were calibrated with NaCl.

The IR spectra of the quenched samples were recorded in the region 4000–300 cm^{-1} on a Perkin–Elmer 521 using the KBr technique.

Chemical analyses. For the separation of Se(IV) and Se(VI) species in the quenched samples, an anion exchange method employing DEAE cellulose columns [11] was found more satisfactory than the extraction method based on the formation of a Se–DDTC complex [12]. For the determination of Se(IV), iodometric titration was used [13] and the same method was found most accurate also for Se(VI), which had to be first reduced by hydrochloric acid [14]. In a test series based on Na_2SeO_3 and Na_2SeO_4 [15], it was established that the separation-determination method chosen was capable of quantitatively determining 0.5 mg of Se(IV) or Se(VI), thus making possible the use of small sample size in the TG experiments. When the amounts of Se(IV) and Se(VI) in the test samples were 2.00 mg each, five determinations gave mean values 2.00 ± 0.04 and 1.88 ± 0.11 mg, respectively.

In experiments aimed at clarifying the decomposition mechanism, samples for chemical analyses were prepared in the TG apparatus starting with 40 mg of $La_2(SeO_4)_3 \cdot 5H_2O$; the sample size was large enough for satisfactory accuracy. The samples were heated in air or N_2 up to the desired temperature using a heating rate of 5 deg min^{-1} and then quenched with a maximum cooling rate attainable (320 deg min^{-1}) to room temperature.

Results and discussion

Thermogravimetric data. The dehydration of $La_2(SeO_4)_3 \cdot 5H_2O$ in air starts around 80° and is completed by 300°. As seen from Figs 1 and 2, the changes in heating rate and sample weight effect somewhat the dehydration temperatures but the two-step mechanism remains the same in all experiments. The first step corresponds to a loss of 4 moles of water leading to the formation of a monohydrate; the average weight loss in the seven experiments, depicted in Figs 1 and 2, is 8.6% while the calculated weight loss is 9.0%. The monohydrate phase was not detected in a previous study obviously due to a different experimental set-up [5]; the decomposition temperatures agree well with the present study, however.

The anhydrous selenate is surprisingly stable over a wide temperature range but above 600° a fast decomposition takes place (Figs 1 and 2). This decomposition, which according to XRD data eventually leads to oxide as final product above 1200°, proceeds through intermediate plateaus none of which is distinct, however. The reaction temperatures and mechanism seem to be strongly dependent on experimental conditions, small sample size and slow heating rate leading to greater weight losses as expected.

Decomposition mechanism. After the dehydration steps $La_2(SeO_4)_3 \cdot 5H_2O \xrightarrow{-4H_2O} La_2(SeO_4)_3 \cdot H_2O \xrightarrow{-H_2O} La_2(SeO_4)_3$, it seems not to be possible to describe the decomposition with a simple equation as the plateaus are not clear and furthermore they do not correspond to any of the intermediate compounds for which theoretical weight losses have been calculated in Figs 1 and 2. It seems plausible, however, to assume that the more stable Se(IV) [16],

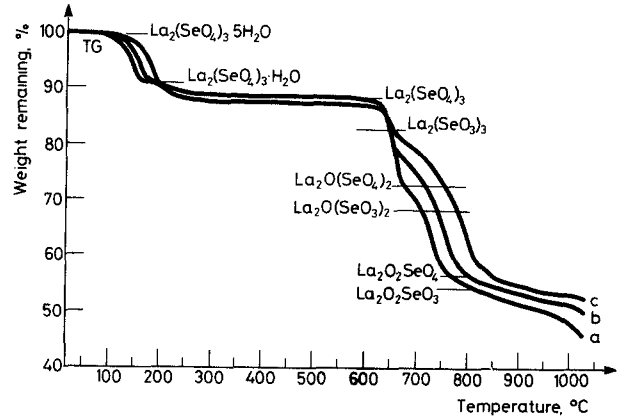

Fig. 1 TG curves of $La_2(SeO_4)_3 \cdot 5H_2O$ recorded in air at a heating rate of 5 deg min^{-1} using different sample weights: $a=4.4$ mg, $b=13.9$ mg and $c=41.1$ mg

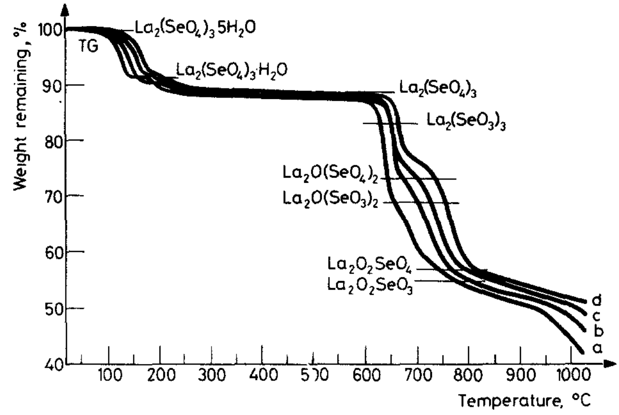

Fig. 2 TG curves of $La_2(SeO_4)_3 \cdot 5H_2O$ recorded in air using various heating rates (deg min^{-1}): $a=2$, $b=5$, $c=10$ and $d=20$. The sample weight is in all cases 4.5 mg

plays a dominant role in the decomposition of anhydrous $La_2(SeO_4)_3$ as has been suggested previously [5–7].

When the thermal degradation of $La_2(SeO_4)_3 \cdot 5H_2O$ in air and N_2 atmospheres was compared (Fig. 3), the nonisothermal TG curves showed completely similar behaviour until temperatures over 800°. Chemical analyses confirmed this (Table 1); only in higher temperatures there was an essential difference, *i.e.* Se(VI) compounds were present in samples heated in air while samples heated in nitrogen contained only Se(IV). The presence of selenium compounds in the oxidation state +IV was dominating, however, in all experiments. The significant amount of

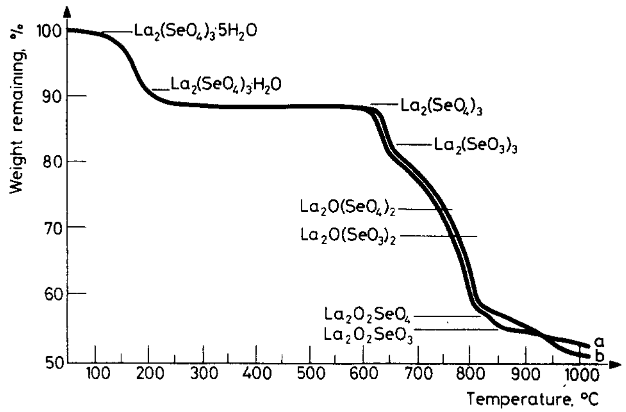

Fig. 3 TG curves for the decomposition of $La_2(SeO_4)_3 \cdot 5H_2O$ in nitrogen *(a)* and in air *(b)*. The sample weight is 39.5 mg and the heating rate is 5 deg min^{-1}

Table 1 Amounts of Se(VI) and Se(IV) in samples quenched from the TG experiments. Initial sample weight is in all cases 40.0 mg

Programmed end temperature, °C	Atmosphere	Weight loss, %	Amount of selenium, %		
			total	Se(VI)	Se(IV)
650	air	18.6	30.4	9.5	20.9
650	N_2	18.4	31.5	11.0	20.5
730	air	27.5	28.3	1.4	26.9
730	N_2	25.0	31.6	1.3	30.3
830	air	43.9	16.1	1.3	14.8
830	N_2	42.1	20.7	0	20.7
930	air	46.5	15.4	2.8	12.6
930	N_2	46.6	15.9	0	15.9
1025	air	48.6	16.6	6.8	7.8
1025	N_2	49.6	12.4	0	12.4

Se(VI) present at 650° is due to unreacted selenate which by 730° is almost totally converted to Se(IV).

Further support for the effect of atmosphere was obtained from IR and XRD experiments. When $La_2(SeO_4)_3 \cdot 5H_2O$ is heated isothermally in air at 750°, its IR spectrum contains medium to strong absorption bands around 900 cm^{-1} indicating the presence of selenate groups (ν_1 and ν_3 stretching fundamentals) [6, 17]. The corresponding Se—O stretching bands for selenite would appear in a somewhat lower wave number region [18]. The spectrum resembles also that of the hydrated rare earth selenates but differs from the spectra recorded for a sample heated in nitrogen (Fig. 4).

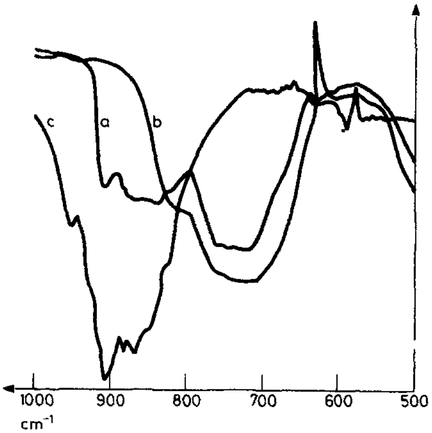

Fig. 4 A comparison of the IR spectra of two quenched samples *(a, b)* with that of $Nd_2(SeO_4)_3 \cdot 5H_2O$ *(c)*. Sample *a* has been heated isothermally at 750° in air and sample *b* in nitrogen

X-ray diffraction diagrams recorded for lanthanum selenate samples kept in air at 750° show a characteristic pattern of diffraction peaks consisting of a triple peak around 1.80 Å (1.77, 1.79 and 1.81 Å) and another one around 3.10 Å (3.06, 3.13 and 3.19 Å). This type of pattern is typical for the rare earth oxysulfates [19–22] and assuming the isostructurality of lanthanum oxyselenate with the oxysulfate, the XRD pattern thus indicates the presence of the oxyselenate phase as suggested by Giolito and Giesbrecht [4].

In this connection it is also relevant to note that very recently Leskelä and Hölsä [23], when studying the thermal stability of rare earth hydrogen selenites [24], found evidence for the presence of $La_2O_2SeO_4$ when $LaH(SeO_3)_2 \cdot 2^1/_2H_2O$ is heated in air.

It should be noted that there are several sources of error mainly due to the fact that, although same samples were used, TG runs and characterizations of the solid residues cannot be performed simultaneously. Besides possible errors in temperatures, there is the possibility that reactions continue after the end temperature has been observed. Therefore, weight change was monitored during cooling, too, and indeed a small change of 1–2% was observed when cooling was performed in air. This change, as revealed by analyses, was connected to a slight increase of Se(IV) as compared to samples cooled in nitrogen.

Conclusions

Thermal degradation of $La_2(SeO_4)_3 \cdot 5H_2O$ is initiated by a two-step dehydration process which is completed by 300°, both in air and in nitrogen. On the basis of TG, XRD IR and chemical analyses, $La_2(SeO_3)_3$, $La_2O_2SeO_3$ and in air also $La_2O_2SeO_4$ appear as intermediates when the anhydrous selenate is heated above 600°. Final thermal decomposition product is La_2O_3 at temperatures exceeding 1200°. Although no evidence for its presence was found, $La_2O(SeO_3)_2$ [5] cannot be excluded as an unstable intermediate.

The formation of $La_2O_2SeO_4$ takes apparently place by reoxidation of the selenite(IV) compounds above 750°. The reaction scheme, which includes the Se(VI) oxyselenate, appears to be a combination of those presented in the literature [4–6] and it is also in agreement with most recent results [2, 3]

The decomposition of the isostructural neodymium compound appears to proceed in a very simmlar way (Fig. 5) but in this case the decomposition intermediates were not analyzed in detail.

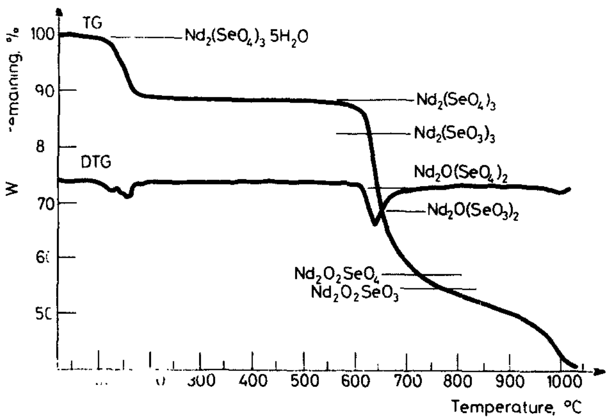

Fig. 5 TG curve of $Nd_2(SeO_4)_3 \cdot 5H_2O$ recorded in air. Sample weight is 4.6 mg and heating rate is 5 deg min^{-1}

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Zusammenfassung — Thermogravimetrische, von IR-spektroskopischen und röntgendiffraktometrischen Messungen gestützte Untersuchungen von $La_2(SeO_4)_3 \cdot 5H_2O$ wurden ausgeführt, um dessen Zersetzungsschema unter verschiedenen experimentellen Bedingungen zu ermitteln. Verschiedene analytische Methoden zur simultanen Bestimmung von Se(IV) und Se(VI) in den abgeschreckten Proben wurden getestet. TG-Gewichtsverluste und Analysen der festen Intermediärverbindungen haben ergeben, daß nach Dehydratation $La_2(SeO_4)_3$ in Stickstoff hauptsächlich über das normale Selenit(IV) zu Oxyselenit(IV)-Verbindungen abgebaut wird, während in Luft das Oxyselenat $La_2O_2SeO_4$ als eine der Intermediärverbindungen auftritt. Endprodukt der thermischen Zersetzung ist La_2O_3. Die TG-Kurven von $La_2(SeO_4)_3 \cdot 5H_2O$ wurden auch mit den für die isostrukturelle Neodymverbindung erhaltenen Kurven verglichen.

Резюме — Термогравиметрические исследования пентагидрата селената лантана, наряду с ИК спектроскопией и рентгенофазовым анализом, были проведены с целью установления схемы его разложения при различных экспериментальных условиях. Было испытано несколько аналитических методов для одновременного определения четырех- и шестивалентного селена в резко охлажденных образцах. Потеря веса в методе ТГ и анализ твердых промежуточных продуктов показали, что после дегидратации селенат лантана разлагается в атмосфере азота до оксиселенитов(IV) через стадию образования нормального селенита(IV). При разложении в атмосфере воздуха в качестве одного из промежуточных продуктов был обнаружен оксиселенат лантана $La_2O_2SeO_4$. Конечным продуктом термического разложения являлась окись лантана. Кривые ТГ пентагидрата селената лантана сопоставлены с таковыми для изоструктурного соединения неодима.