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Note

Studies on selenates
I. Thermal decomposition of lanthanum selenate pentahydrate

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It has been reported[1] that the decomposition of lanthanum selenate pentahydrate proceeds through the formation of selenite to sesquioxide. However, it is probably by the limitations of the thermogravimetric techniques utilised that the mechanism of decomposition is not completely explained. This paper is devoted to the systematic investigation of all the intermediate decomposition stages of lanthanum selenate pentahydrate not observed previously.

EXPERIMENTAL

Lanthanum selenate pentahydrate, $La_2(SeO_4)_3 \cdot 5H_2O$, was prepared by treating an excess of lanthanum hydroxide with laboratory reagent grade selenic acid, subsequent concentration of filtered solution, followed by crystallisation in a vacuum desiccator over P_2O_5. The crystallised salt was chemically analysed on metal and selenate contents. Found: La, 35.04%; SeO_4, 54.25%; calculated for $La_2(SeO_4)_3 \cdot 5H_2O$: La, 34.80%; SeO_4, 53.81%. The decomposition of lanthanum selenate pentahydrate was investigated by simultaneous thermogravimetry (TG), differential thermal analysis (DTA) and differential thermogravimetry (DTG) techniques as described previously[2,3]. However, micro-assembly was employed in the present case.

RESULTS AND DISCUSSION

Figure 1 shows results of thermograms of lanthanum selenate pentahydrate. It is evident from the TG curve that the salt is stable up to 90°C and is dehydrated completely at 410°C in one step. The simultaneously obtained DTA curve accounts for the endothermic activity at 180°C during this dehydration. The moderate oblique of the anhydride exists up to 625°C. Beyond this temperature the decomposition of this nonhydrate begins.

Anhydrous lanthanum selenate shows interesting complex thermal effects on subsequent heating. A prominent break on the slope of the TG curve at 660°C indicates the formation of lanthanum selenite $La_2(SeO_3)_3$. The DTA peak at 650°C

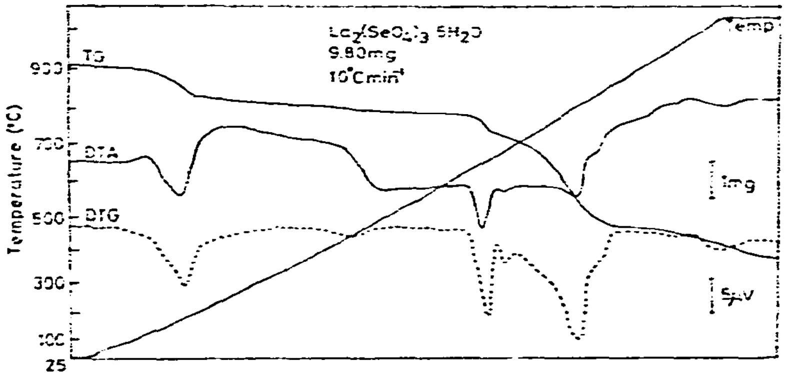
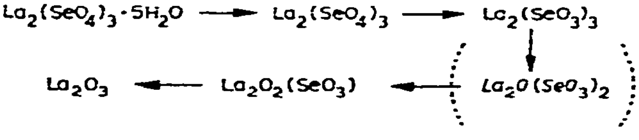


Fig. 1. Simultaneous TG–DTA–DTG of $La_2(SeO_4)_3 \cdot 5H_2O$.

accounts for the endothermic effect during the above reduction. Above this temperature, subsequent decomposition of the selenite results into a loss corresponding to the formation of a basic salt lanthanum (*di*)oxyselenite, $La_2O_2(SeO_3)$. From the TG curve, it appears that the decomposition of lanthanum selenite to (*di*)oxyselenite is only a one-stage process. However, a careful survey of the DTG curve reveals that two successive weight changes occur as exhibited from two distinct peaks at 740 and 810°C. The first weight change is an indication of a possible formation of lanthanum (*mono*)oxyselenite, $La_2O(SeO_3)_2$ corresponding to the sublimation of one molecule of selenium dioxide. This (*mono*)oxyselenite being very unstable undergoes further weight loss due to sublimation of a subsequent molecule of selenium dioxide, forming lanthanum (*di*)oxyselenite. Besides, two distinct peaks in the DTA curve at 740 and 800°C account for these successive decomposition stages.

Further rise of the temperature up to 1050°C converts lanthanum (*di*)oxyselenite into the corresponding oxide. The peak at 1010°C in the DTA curve is associated with this decomposition.

The following mechanism can thus be proposed for the decomposition of lanthanum selenate pentahydrate.



The agreement between the experimental weight changes obtained from the thermogravimetric results reported in Table 1, and the weight changes in proposed mechanism is excellent, thus supporting the above mechanism.

The proposed mechanism does not involve the formation of oxyselenate as observed by Giolito and Giesbrecht[4] in the thermogravimetric study of lanthanum selenate decahydrate. Contrary to this the formation of oxyselenite observed in the present case is more probable, since the existence of a salt as selenate at a high

TABLE I

THERMOANALYTICAL RESULTS OF LANTHANUM SELENATE PENTAHYDRATE

Dehydration/decomposition transition	*Temp. (°C)*		*Percentage loss*	
	TG	*DTA*	*Calc.*	*Exp.*
$La_2(SeO_4)_3 \cdot 5H_2O \rightarrow La_2(SeO_4)_3$	410	180	11.30	11.23
$La_2(SeO_4)_3 \rightarrow La_2(SeO_3)_3$	660	650	17.32	18.80
$La_2(SeO_3)_3 \rightarrow La_2O(SeO_3)_2$	760	740	31.25	29.08
$La_2O(SeO_3)_2 \rightarrow La_2O_2(SeO_3)$	855	800	45.17	45.41
$La_2O_2(SeO_3) \rightarrow La_2O_3$	1050	1000	59.10	58.62

temperature seems doubtful. A similar type of mechanistic scheme is proposed by Hayashi et al.[5] in the decomposition of scandium selenate pentahydrate, where selenate decomposes to selenite and subsequently to scandium oxyselenite, $Sc_2O_2(SeO_3)$.

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