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Note

THERMAL BEHAVIOUR OF SAMARIUM NITRATE AND OXIDE

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Samarium(III) oxide was found to have 2.5 molecules of water of hydration. On heating, it dehydrates completely at temperatures above 550°C passing through an intermediate which contains 0.5 water molecules. Samarium(III) nitrate contains one molecule of water of hydration and on heating it loses NO_2, O_2 and H_2O giving Sm_2O_3. However, the X-ray powder pattern of the residue obtained on heating the oxide hydrate is different from that obtained on heating the nitrate hydrate.

Sm_2O_3 (99.9%) was obtained from M/s Indian Rare Earths. When it was used to prepare other samarium compounds, there was some difficulty regarding its composition. Its X-ray powder pattern did not match any of those reported for its cubic [1], monoclinic [2] or hexagonal [3] modifications. Hence it was investigated using TG, DTA and X-ray powder techniques.

The X-ray powder pattern of the starting material is given in Fig. 1. Patterns of various known oxides are included in the figure for comparison. The TG pattern of the material is shown in Fig. 2, with a two-step weight loss in the temperature ranges 200–300 and 450–550°C, respectively, with a flat, stable region in between. The TG residue at 1000°C appeared to be monoclinic Sm_2O_3 on cooling to room temperature. Assuming that the TG residue is the oxide and that the weight loss is due to water only, the starting material deduced is $Sm_2O_3 \cdot 2.5H_2O$. The intermediate step thus corresponds to $Sm_2O_3 \cdot 0.5H_2O$. The corresponding DTA pattern is given in Fig. 4, with two endotherms at 280–375 and 475–575°C, respectively. The thermal data are summarised in Table 1.

Utilising the above starting material, samarium nitrate was prepared by repeated evaporation of the material to dryness in concentrated nitric acid. The product was dried over NaOH pellets to remove the last traces of acid, otherwise is not easy to do at room temperature without heating. The X-ray powder pattern of the product is included in Fig. 1. There is no ASTM card for any samarium nitrate. Figure 3 shows its TG pattern while Fig. 4 its DTA pattern. TG shows two points of inflexion, one at ca. 300°C and the other at 430°C. There is no indication of any stable intermediate. Assuming

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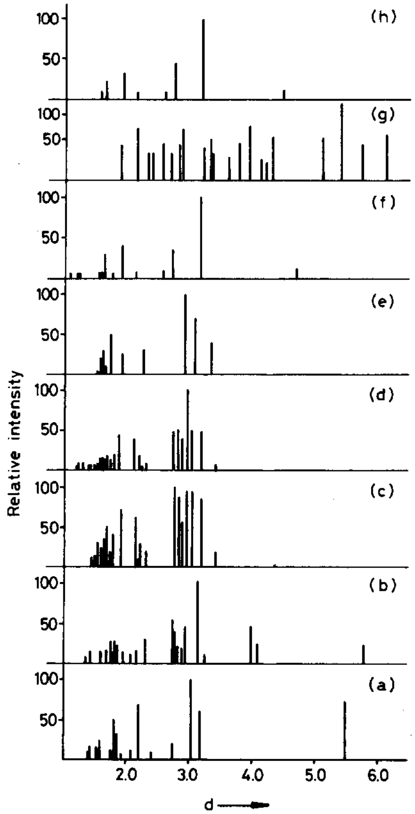

Fig. 1. X-ray powder patterns of (a) $Sm_2O_3 \cdot 2.5H_2O$, (b) $Sm_2O_3 \cdot 0.5H_2O$, (c) TG residue of (a), (d) Sm_2O_3 monoclinic, (e) Sm_2O_3 hexagonal, (f) Sm_2O_3 cubic, (g) $Sm[NO_3]_3 \cdot H_2O$ and (h) TG residue of (g).

that the residue above 650°C is the sesquioxide, the starting material in this run was deduced to be $Sm(NO_3)_3 \cdot H_2O$. The DTA curve shows four endotherms at 105, 200, 430 and 560°C. The X-ray powder pattern of the

TABLE 1

Thermal data for samarium nitrate and oxide

No.	Compound	Starting material	Product	Weight loss (%)	
				Obs.	Calc.
1	$Sm_2O_3 \cdot 2.5H_2O$	$2.5H_2O$	$0.5H_2O$	8.0	9.2
		$0.5H_2O$	$0.0H_2O$	3.5	2.3
			Total	11.5	11.5
2	$Sm(NO_3)_3 \cdot H_2O$	$Sm(NO_3)_3 \cdot H_2O$	$Sm_2O_3 \cdot H_2O$	46.5	45.8
		$Sm_2O_3 \cdot H_2O$	Sm_2O_3	4.5	5.0
			Total	51.0	50.8

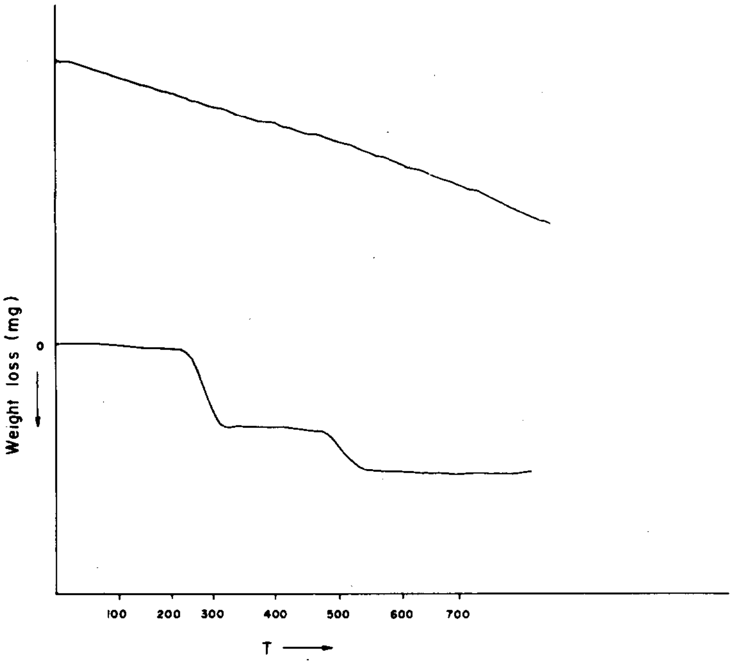

Fig. 2. TG curves of $Sm_2O_3 \cdot 2.5H_2O$.

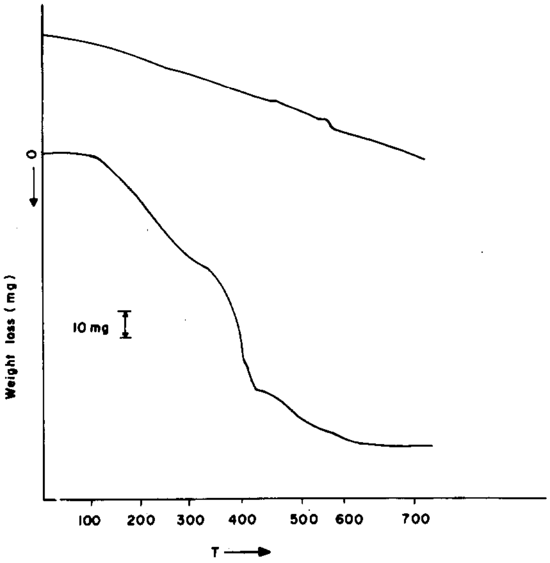

Fig. 3. TG curves of $Sm[NO_3]_3 \cdot H_2O$.

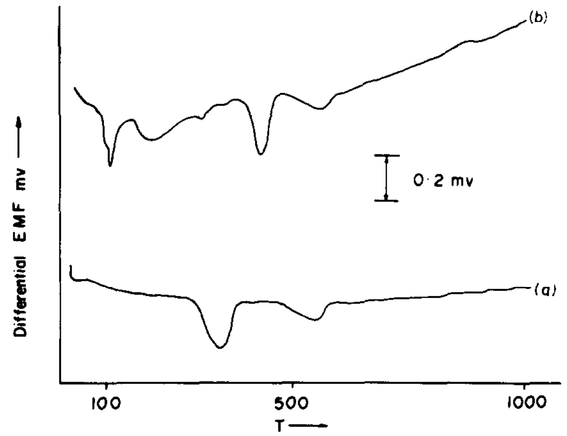

Fig. 4. DTA curves of (a) $Sm_2O_3 \cdot 2.5H_2O$ and (b) $Sm[NO_3]_3 \cdot H_2O$.

residue at 1000°C, cooled to room temperature, corresponded to that of b.c.c. Sm_2O_3, whereas in the case of samarium oxide hydrate the residue above 650°C is monoclinic Sm_2O_3. In the case of nitrate, NO_2 and oxygen are lost first followed by the loss of water of hydration. Table 1 summarises the results. The overall decomposition is as follows:

$$2Sm[NO_3]_3 \cdot H_2O \ldots Sm_2O_3 + 6NO_2 + 1.5O_2 + 2H_2O$$

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