

Structural and Thermal Properties of Rare Earth Triiodide Hydrates

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The rare earth triiodide hydrates $\text{LnI}_3 \cdot n\text{H}_2\text{O}$ form hygroscopic crystals, with $n=9$ for the lighter ($\text{Ln}=\text{La}-\text{Ho}$) and $n=8$ for the heavier ($\text{Ln}=\text{Er}-\text{Lu}$ incl. Y) rare earths. Tb, Dy, Ho and Y may crystallize in either form at room temperature, depending on the ambient water pressure. The nonahydrates form orthorhombic crystals with $a=8.442(6)$, $b=10.460(8)$, $c=12.238(8)$ Å for $\text{LaI}_3 \cdot 9\text{H}_2\text{O}$ and $a=7.621(3)$, $b=9.535(4)$, $c=11.026(7)$ Å for $\text{HoI}_3 \cdot 9\text{H}_2\text{O}$. Thermal decomposition of $\text{LnI}_3 \cdot n\text{H}_2\text{O}$ was studied in the range 25–500 °C. Dehydration takes place in several steps but the stability of the intermediate hydrates is low, especially for the heavier rare earths. The anhydrous iodide is formed below 200 °C and it immediately starts to oxidize to the oxyiodide LnOI . In vacuum, the anhydrous iodide is formed at a lower temperature and its stability range is broader. The final decomposition product in air is a mixed phase of LnOI and Ln_2O_3 , the amount of the latter increasing with atomic number.

Owing probably to the very low stability against atmospheric moisture, the properties of the rare earth triiodide hydrates have not been thoroughly studied. Earlier reports have mostly dealt with their preparation and composition. In general the lighter rare earths have been found to form nonhydrated compounds,^{1–6} though some lower hydrates have been reported, too.⁷ Besides preparative and analytical data, there are some thermoanalytical data available for the nonhydrates^{1,3} and X-ray diffraction data limited to some uninterpreted powder patterns.^{3–6}

As the triiodide hydrates are possible starting materials for the synthesis of anhydrous iodides and oxyiodides, both interesting rare earth materials, we took as our goal the fuller characterization, both structurally and thermally, of the triiodide nonahydrates. The present study is also a continuation of the earlier investigations carried out in this laboratory.^{8,9}

EXPERIMENTAL

Preparation of the compounds. Rare earth triiodide hydrates $\text{LnI}_3 \cdot n\text{H}_2\text{O}$ were prepared by dissolving, at 70–80 °C, 1.5 mmol Ln_2O_3 in a diluted solution (0.3 mol/dm³) of freshly distilled HI using a 40% excess of the acid. The solution was allowed to evaporate at this temperature to a volume of a few milliliters; upon standing at room temperature crystals usually deposited within a few hours. The crystalline precipitate was filtered by suction and dried over CaCl_2 on a filter paper support which absorbed the excess acid and iodide. The transparent needle-shaped crystals showed the characteristic color of the trivalent rare earth ion. Their composition was established by determining the rare earth and iodide contents by complexometry and argentometry, respectively. The mean value of three determinations deviated from the calculated value by less than 0.5%: for instance, $\text{SmI}_3 \cdot 9\text{H}_2\text{O}$, Anal. Sm 21.70; I 54.93. Calc. Sm 21.70; I 54.97%.

The rare earth oxides used for the syntheses were generally of 99.9% purity (Kemira Oy, Oulu, Finland). Hydrogen iodide was an analytical grade reagent (E. Merck, AG, Darmstadt, Germany) purified immediately before use.¹⁰

X-Ray diffraction. The initial unit cell parameters for $\text{EuI}_3 \cdot 9\text{H}_2\text{O}$ were determined with a Syntex P₂₁ diffractometer by refining the angular settings of 25 reflections. Axial photographs were then taken

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to confirm the orthorhombic solution given by the diffractometer. These unit cell values were used to calculate from the powder patterns by least-squares methods the accurate unit cell values for all compounds in the isostructural series. The registration and measuring of the powder patterns, as well as the calculations, were performed as described earlier.¹¹ In all stages of the X-ray measurements, care was taken to exclude atmospheric moisture (use of a dry box, drying agent under the diffractometer hood, etc.).

Thermal analysis. The thermal stability of the hydrates was studied by recording the TG, DTG, and DTA curves simultaneously in a static air atmosphere with a MOM Q-Derivatograph apparatus. The sample size was 200 mg and the heating rate 2.5 °C min⁻¹. Aluminium oxide crucibles were employed and alumina was used as the reference material in DTA.

For comparison, similar runs were recorded with a Mettler Thermoanalyzer TA-1 apparatus and speeds ranging from 2 to 6 °C min⁻¹. Standard aluminium oxide crucibles (diam. 7 mm, depth 19 mm) were used. Sample size was 75 mg and the flow rate of air 95 cm³/min in dynamic atmosphere. The runs in vacuum were performed with the latter apparatus, using a pressure of 0.1–0.15 Torr and a heating rate of 2 °C min⁻¹.

RESULTS AND DISCUSSION

Chemical analyses and X-ray diffraction studies showed clearly that the lighter rare earths up to holmium form isostructural nonahydrated crystals, whereas the heavier ones including yttrium crystallize with eight molecules of water. The three last members of the first series and yttrium may crystallize at room temperature either as nonahydrates or octahydrates depending on the ambient water pressure. As all the crystals are highly hygroscopic the ambient relative humidity may not exceed 25% in any case.

The present data on the composition are in general agreement with the comprehensive study by Kwestroo and Hall.³ These authors did not, however, prepare the nonahydrated forms for holmium and yttrium; the existence of the latter compound at 0 °C has recently been reported by Yastrebova *et al.*¹² while Shevtsova *et al.*¹³ report that at 25 °C the crystalline phase has the composition YI₃.6H₂O.

The unit cell dimensions for the nonhydrate series are given in Table 1, while Table 2 gives as an example the indexed powder pattern of SmI₃.9H₂O up to sin²θ=0.2. Owing to the instability of the

Table 1. Unit cell dimensions for the rare earth triiodide nonahydrates.

Compound	a/Å	b/Å	c/Å	V/Å ³
LaI ₃ .9H ₂ O	8.442(6)	10.460(8)	12.238(8)	1080.7
PrI ₃ .9H ₂ O	8.219(6)	10.286(5)	12.017(9)	1015.9
NdI ₃ .9H ₂ O	8.151(3)	10.256(7)	11.749(9)	982.2
SmI ₃ .9H ₂ O	7.990(3)	10.003(4)	11.600(5)	927.1
EuI ₃ .9H ₂ O	7.949(5)	9.956(5)	11.493(6)	909.6
GdI ₃ .9H ₂ O	7.938(7)	9.821(10)	11.481(6)	895.1
TbI ₃ .9H ₂ O	7.738(5)	9.700(8)	11.311(10)	849.0
DyI ₃ .9H ₂ O	7.708(6)	9.569(7)	11.117(7)	820.0
HolI ₃ .9H ₂ O	7.621(3)	9.535(4)	11.026(7)	801.2

Table 2. X-Ray powder diffraction pattern of SmI₃.9H₂O (CuKα₁-radiation, λ=1.54056 Å).

h k l	d _{obs}	d _{calc}	I _{obs}
1 0 1	6.609	6.580	10
1 1 0	6.229	6.242	5
0 2 0	4.923	4.984	45
0 2 1	4.560	4.592	30
1 2 0	4.159	4.225	100
2 0 0		3.995	
1 2 1	3.987	3.982	55
0 0 3	3.907	3.868	50
2 1 1	3.535	3.534	15
1 3 0	3.078	3.077	40
1 3 1	2.979	2.974	25
0 3 2	2.881	2.890	35
2 2 2	2.743	2.748	5
3 0 0	2.647	2.663	35
2 3 1	2.496	2.499	10
3 0 2	2.421	2.420	15
2 3 2		2.341	
1 4 1	2.332	2.337	35
0 0 5	2.316	2.320	25
2 1 4	2.284	2.284	10
1 4 2	2.176	2.188	30
2 2 4	2.126	2.125	10
0 5 0		2.001	
4 0 0	1.995	1.997	10
1 0 6	1.879	1.879	5
1 1 6	1.845	1.846	5
3 2 4	1.828	1.826	25
2 5 0	1.791	1.789	15
2 5 1		1.768	
4 2 2	1.767	1.767	5
3 1 5	1.726	1.723	10

crystals the space group could not be unequivocally determined; the observed density for LaI₃.9H₂O of 4.2 g cm⁻³ gives a plausible value of 4 for the number of molecules in the cell, however.

Table 3. Stability ranges (°C) of the intermediate compounds and the analytical composition of the end-product at 500 °C in the thermal decomposition of $\text{LnI}_3 \cdot 9\text{H}_2\text{O}$ ($\text{Ln} = \text{La} - \text{Ho}$). Heating rate 2.5 °C/min.

Compound	La	Pr	Nd	Sm	Eu	Gd	Tb	Dy	Ho
$\text{LnI}_3 \cdot 9\text{H}_2\text{O}$	<50	<50	<50	<45	<45	<35	<35	<35	<35
$\text{LnI}_3 \cdot 6\text{H}_2\text{O}$	120–125	120–125	120–125	125–130	110–115	140–145	135–140	—	—
$\text{LnI}_3 \cdot 3\text{H}_2\text{O}$	140–145	150–155	140–145	160–165	125–130	165–170	160–165	—	—
LnI_3	165–170	165–170	150–155	170–175	135–140	185–190	190	180–185	190–195
$2\text{LnI}_3 \cdot \text{LnOI}$	190–200	200–205	165–170	—	—	—	—	—	—
LnOI	240–250	240–245	220–225	220–225	200–220	240–245	225–230	225–230	230–235
End product ^a	^a	^b	^c	^c	^c	^d	^d	^d	^d

^a $6\text{LaOI} \cdot \text{La}_2\text{O}_3$, ^b $5\text{PrOI} \cdot \text{Pr}_2\text{O}_3$, ^c $3\text{LnOI} \cdot \text{Ln}_2\text{O}_3$, ^d $2\text{LnOI} \cdot 3\text{Ln}_2\text{O}_3$.

The powder patterns for the octahydrate series were recorded, too, and found similar to the pattern published for $\text{NdI}_3 \cdot 8\text{H}_2\text{O}$.³ Owing to the lack of single crystal data the indexing of these patterns was not attempted.

Thermal decomposition of the nonahydrates in air starts with dehydration reactions; hexa- and trihydrates are visible as intermediates in the thermoanalytical curves before the anhydrous triiodide appears. The stability of the intermediate hydrates is low, however, and decreases with increasing atomic number: for dysprosium and holmium the intermediates could not be detected at all.

On the basis of the decomposition of the anhydrous triiodide the nonahydrates may be divided into two groups: lanthanum, praseodymium and

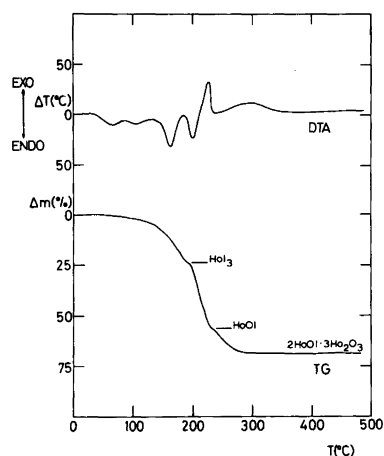


Fig. 2. Thermal decomposition of $\text{HoI}_3 \cdot 9\text{H}_2\text{O}$ in air.

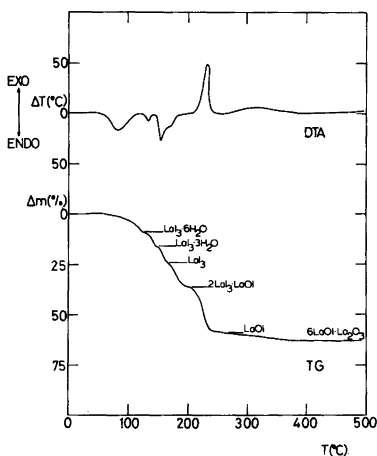


Fig. 1. Thermal decomposition of $\text{LaI}_3 \cdot 9\text{H}_2\text{O}$ in air.

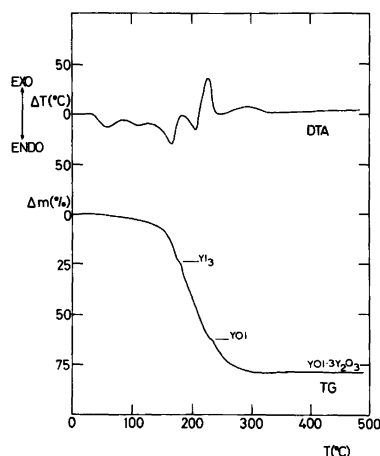


Fig. 3. Thermal decomposition of $\text{YI}_3 \cdot 8\text{H}_2\text{O}$ in air.

Table 4. Stability ranges (°C) of the intermediate compounds and the analytical composition of the end-product at 500 °C in the thermal decomposition of $\text{LnI}_3 \cdot 8\text{H}_2\text{O}$ (Ln = Y, Er–Lu). Heating rate 2.5 °C/min.

Compound	Y	Er	Tm	Yb	Lu
$\text{LnI}_3 \cdot 8\text{H}_2\text{O}$	< 45	< 50	< 50	< 45	< 45
LnI_3	180	180–185	185	165–170	185
LnOI	230–235	240–245	230–235	225	230–240
End-product	$\text{YOI} \cdot 3\text{Y}_2\text{O}_3$	$\text{ErOI} \cdot 3\text{Er}_2\text{O}_3$	$\text{TmOI} \cdot 3\text{Tm}_2\text{O}_3$	$\text{YbOI} \cdot 4\text{Yb}_2\text{O}_3$	$\text{LuOI} \cdot 4\text{Lu}_2\text{O}_3$

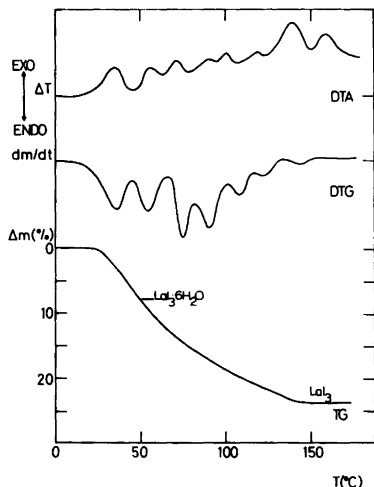


Fig. 4. Thermal decomposition of $\text{LaI}_3 \cdot 9\text{H}_2\text{O}$ in vacuum ($p < 0.1$ Torr) in a Mettler Thermoanalyzer.

neodymium decompose through an intermediate phase $2\text{LnI}_3 \cdot \text{LnOI}$, whereas the other triiodides decompose in a single exothermic step to the oxyiodide. The final decomposition product in all cases is a mixed phase of the oxyiodide and oxide: the amount of oxide increases along the series as can be seen from Table 3, which summarizes the thermo-analytical measurements in air. Note that no compound corresponding to formula $\text{Ln}_3\text{O}_4\text{I}$ ($\text{Ln}_2\text{O}_3 \cdot \text{LnOI}$) is detected among the decomposition products, in contrast to the decomposition of oxybromides where in some cases $\text{Ln}_3\text{O}_4\text{Br}$ occurs.¹⁴ To exemplify the decomposition mechanisms, the TG and DTA curves for $\text{LaI}_3 \cdot 9\text{H}_2\text{O}$ and $\text{HoI}_3 \cdot 9\text{H}_2\text{O}$ are shown in Figs. 1 and 2, respectively.

The thermal behaviour of the octahydrates shows similar trends as the last members of the nonahydrate series: the intermediate hydrates are absent in the curves and the amount of oxide in the final

decomposition product increases with the atomic number. Table 2 summarizes the TG data and as an example the DTA and TG curves for $\text{YI}_3 \cdot 8\text{H}_2\text{O}$ are given in Fig. 3.

In all cases the stability range of the anhydrous triiodide and the oxyiodide is low, extending at best only over some 5–20 degrees. As has been suggested earlier,^{3,8,9} however, the use of vacuum offers a possibility of preparing the anhydrous triiodides. The dehydration reactions then take place at considerably lower temperatures and the stability range of the triiodide extends over a rather wide temperature range (see Fig. 4). It should be noted, however, that under actual preparative conditions the decomposition of the triiodides may seriously hamper the applicability of the direct dehydration method.^{3,15}

On the other hand, the oxyiodide evidently cannot be prepared conveniently by thermal decomposition because the reaction requires an oxidizing environment where it may easily proceed further to the oxide. The presence of oxide was detected by X-ray diffraction in all samples prepared isothermally at temperatures indicated by the nonisothermal runs.

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