Transition Metal Iodates. VI. Preparation and Characterization of the Larger Lanthanide Iodates

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In the continuation of this work, the $Ln^{III}(IO_3)_3 \cdot xH_2O$ type N compounds (abbreviated x_N) of La through Sm were prepared by precipitation, thermal decomposition, and by crystallization from the gel, from ambient and boiling water, and from boiling HNO_3. A total of 36 different compounds with $6 \geqslant x \geqslant 0$ were obtained occurring in 12 structural types including one amorphous; in addition $La_5(IO_6)_3$ and four isostructural double salts of the type $Ln(IO_3)_3 \cdot HIO_3$ were obtained.

Characterization techniques used included powder X-ray diffraction, differential thermal analysis, thermogravimetric analysis, second harmonic generation, and infrared spectroscopy.

Out of the total of 16 crystalline iodate structures occurring for all the lanthanides, single crystals were obtainable in 11, comprising a total of 54 compounds.

Including all the lanthanides (plus Y, less Pm), the x_N groups of isostructural compounds, with the number of compounds in parentheses, were the following: $6(1), 5_I(4), 5_{II}(2), 4(9)$, amorphous with $5 \geqslant x \geqslant 0$ (15), $2_I(3), 2_{II}(9), 1(4), \frac{1}{2}(2), O_I(14), O_{II}(2), O_{III}(4), O_{IV}(3), O_V(4)$, and $O_{VI}(1)$.

A. Introduction

The lanthanide iodates of type $Ln^{III}(IO_3)_3 \cdot xH_2O$ fall into three groups. The nine smaller lanthanides, Eu through Lu, plus Y show considerable similarity in the existence of compounds, structure, and thermal decomposition behavior as described in the fifth paper (*1*) in this series (hereafter referred to as V). The lanthanum iodates are sufficiently distinct to be considered separately in Section C, and the four closely related remaining lanthanide iodates of Ce through Sm will be discussed in Section D. Each of the five lanthanide iodates of this paper has eight or nine phases, and no assurance can be given that additional compounds may not be obtainable by additional preparation techniques or conditions. The rather contradictory literature on these compounds will be dealt with in Section G. Cerium also forms tetravalent iodates, but these were not investigated.

Experimental conditions are as reported in V; precipitations were performed under acid (HIO_3) and neutral (KIO_3) conditions as in Table I. As before, the notation x_N is used as an abbreviated designation for the isostructural group of compounds $Ln^{III}(IO_3)_3 \cdot xH_2O$, Type N. The abbreviation "ds" is used for the double salt of type $Ln(IO_3)_3 \cdot HIO_3$ and "am" for amorphous phases. The water content and the lanthanide oxide content of each compound was obtained from thermogravimetric analysis; results were usually well within the experimental error ($\pm 2\%$). Chemical analysis was used occasionally for a confirmatory check as is illustrated in Table II; in each case it confirmed the TGA result.

A total of 14 groups of isostructural crystalline compounds of the type $Ln^{III}(IO_3)_3 \cdot xH_2O$ with $6 \geqslant x \geqslant 0$, containing a total of 62 compounds were studied in V and here. There are also 15 amorphous compounds, four double salts, and the compound $La_5(IO_6)_3$, to form a total of 82 compounds, most of which are described for the first time. Single crystal growth proved possible for 11 of the 16 crystalline isostructural groups comprising 54 compounds.

TABLE I

PREPARATION OF THE LARGER LANTHANIDE IODATES[a]

| Ln | Ambient temperature | | | Boiling point | |
	Precipitation[b]	Gel	Evaporation	H_2O	HNO_3
La	am; 6	$6 + 5_{II}$	am; 5_{II}	$\frac{1}{2}$	ds
Ce	am; 5_I	5_I	am; 5_I	$1 + \frac{1}{2}$	[c]
Pr	am; 5_I	$5_I + 5_{II}$	am; 5_{II}	1	ds
Nd	am; 5_I; $5_I + ds$	$5_I + 2_{II}$	am; 5_I	1	ds
Sm	am; 2_{II}; 5_I	2_{II}	am	1	$ds + O_I$

[a] The designation x_N indicates $Ln(IO_3)_3 \cdot xH_2O$, Type N; am is an amorphous phase containing a variable amount of water; ds is the double salt $Ln(IO_3)_3 \cdot HIO_3$; + indicates simultaneous and ; alternative occurrences.

[b] Excess water was frequently present.

[c] These conditions produced $Ce(IO_3)_4$.

TABLE II

ANALYSIS OF $Nd(IO_3)_3 \cdot H_2O$

	% found	% theory
By chemical analysis:		
Iodine ($Na_2S_2O_3$ titration)	55.22	55.42
Neodymium (EDTA titration)	21.00	21.00
By thermogravimetric analysis:		
Water loss	2.49, 2.54, 2.66, 2.71, 2.88	2.62
Nd_2O_3	24.5, 24.6, 24.9	24.49

B. Results

For a convenient overview, all the lanthanide iodates found in this study, including those reported in V, are summarized in Fig. 1. Promethium is omitted; yttrium is included in the usual position according to ionic radius. Arrows indicate thermal decomposition paths in an inert atmosphere as determined by differential thermal analysis (DTA) and thermogravimetric analysis (TGA) data in conjunction with powder X-ray diffraction of the intermediate products. All phases except O_{III} were found to be stable in ambient air. This stability does not, however, guarantee equilibrium phases; the exotherms seen in some DTA's indicate that several of the phases may well be metastable.

The various preparation techniques used and the products obtained are summarized in Table I. Apparently quite minor variations in precipitation conditions could cause different compounds to nucleate from solution; in the case of Nd either the amorphous form, the Type I pentahydrate (5_I), or a mixture of this with the double salt ds (from strongly acid solution) could be precipitated. Attempts to nucleate precipitating solutions so as to extend the range of structure types, e.g., to obtain 5_{II} for Ce and Nd by adding small amounts of the $Pr5_{II}$ salt to the precipitating Ce or Nd and iodate solutions just before mixing, were not successful except in the case of Sm, where seeding with about 0.1% of Nd 5_I gave Sm 5_I. Powder and single crystal X-ray diffraction data on these compounds will be reported in a later part of this series (2).

The separation into three groups is well shown by the amorphous forms which occur for each lanthanide and have a composition
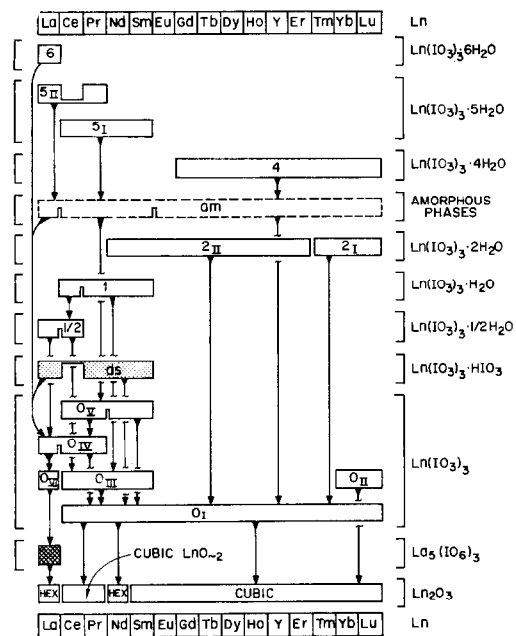
FIG. 1. Occurrence of the lanthanide iodates; the abbreviation x_N is used for $Ln(IO_3)_3 \cdot xH_2O$, Type N. Rectangles indicate groups of isostructural compounds and arrows decomposition paths on heating in N_2. A notch in the lower line of a rectangle indicates the boundary when compounds within a group decompose in different ways.

FIG. 2. The DTA curves of lanthanum iodates run at 5°C/min in nitrogen.

C. The Lanthanum Iodates

We have examined a total of eight lanthanum iodate compounds: the 6, 5_{II}, am, $\frac{1}{2}$, O_{IV}, and O_{VI} compounds in the $La(IO_3)_3 \cdot xH_2O$ series; the $La(IO_3)_3 \cdot HIO_3$ double salt; and $La_5(IO_6)_3$. Preparation conditions are given in Table I, and the thermal analysis curves (except for the double salt considered in Section E) in Figs. 2 and 3.

A correlation of the DTA deflections of Fig. 2 with the weight losses of Fig. 3 and the powder X-ray diffraction patterns after each

$Ln(IO_3)_3 \cdot xH_2O$, $5 \geqslant x \geqslant 0$. These decompose on heating into O_{IV} for La, O_V for Ce through Sm, and O_I for Eu through Lu plus Y. Again, the hemihydrates $Ln(IO_3)_3 \cdot \frac{1}{2}H_2O$, occurring for both La and Ce, decompose to different anhydrides as do the anhydrides O_{IV}.

As noted in the third paper of this series (3) with bellingerite, small amounts of free iodic acid would cause shifts in transition temperatures; as noted in V, DTA transition peaks were sometimes unaccountably doubled. Transition temperatures are also affected by the heating rate (ususally 20 and 5°/min; 2°/min was used to check questionable features), size of sample, etc., and generally should be taken as ±10°C; decompositions, being more heating rate dependent, ±25°C.

Some 306 samples, 241 powder X-ray diffraction patterns, and over 400 DTA and TGA determinations were required to clarify these complex $4f$ iodate systems.
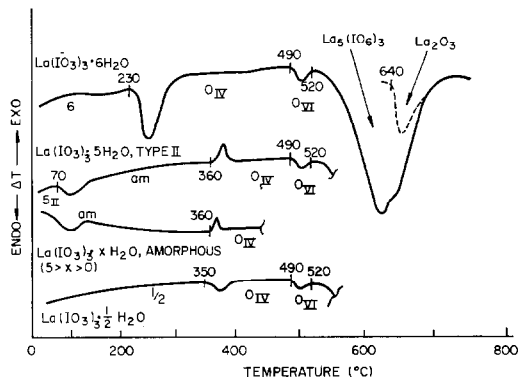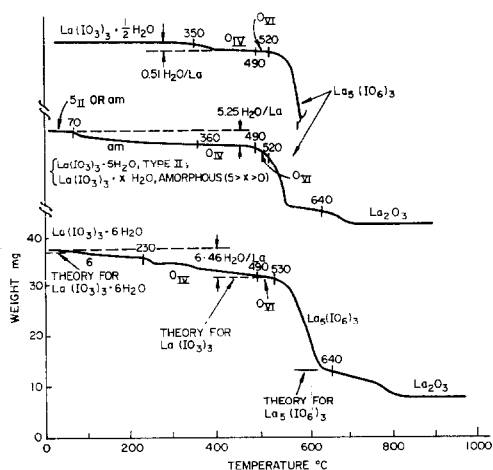

FIG. 3. The TGA curves of lanthanum iodates run at 5°C/min in nitrogen (the theory weights for compounds are calculated from the weight of La_2O_3 remaining at 950°C).
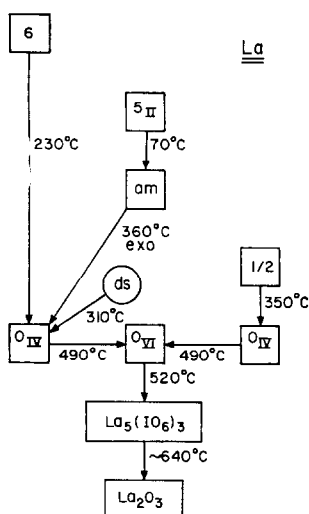
FIG. 4. Decomposition scheme of the lanthanum iodates (temperatures ±20°C).

FIG. 5. Composite decomposition scheme of the iodates of trivalent Ce, Pr, Nd, and Sm (temperatures ±20°C).

transition produced the composition assignments of Figs. 2 and 3. The decomposition for the lanthanum iodates is summarized in Fig. 4.

The 6 hydrate composition must be considered to be a tentative designation. The water content was variable, and since water was lost at a temperature as low as 70°C, drying to constant weight was difficult. In the case of the amorphous form, Fig. 3 shows that the water was lost rather slowly over a broad temperature range, and amorphous X-ray diffraction powder patterns, completely lacking any lines, were obtained for $5 \leqslant x \leqslant 0$. This phase may well be a metastable form, since as seen in Fig. 2, the final transition to the anhydride is exothermic.

At the heating rates used, the decomposition of $La(IO_3)_3$ Type VI was barely complete when the resulting $La_5(IO_6)_3$ periodate compound itself began to decompose as seen in Figs. 2 and 3. At slower heating rates this decomposition

$$10\ La(IO_3)_3 \rightarrow 2\ La_5(IO_6)_3 + 12\ I_2 + 27\ O_2$$

which had been previously reported (4, 5), became quantitative and was used to prepare this compound for characterization.

Four of the lanthanum iodates were grown as crystals: the 6 and 5_{II} hydrates crystallized simultaneously from the acetic acid set gel
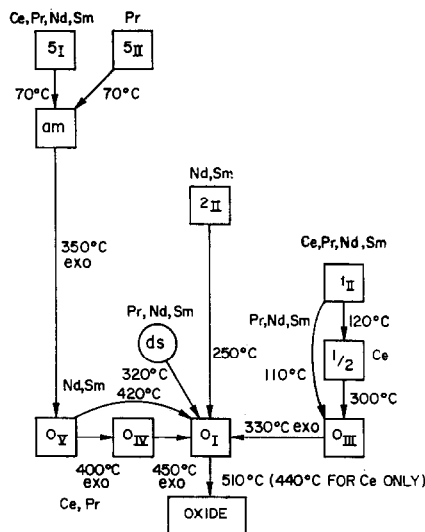
as described in Paper III (6) of this series; the hemihydrate $\frac{1}{2}$ crystallized from boiling water and the double salt ds from boiling HNO_3 solution. The remaining four compounds could be made only by thermal decomposition and crystal growth was therefore not possible.

D. The Iodates of Trivalent Ce, Pr, Nd, and Sm

These lanthanides were found to have seven or eight x_N iodates each, and all but Ce
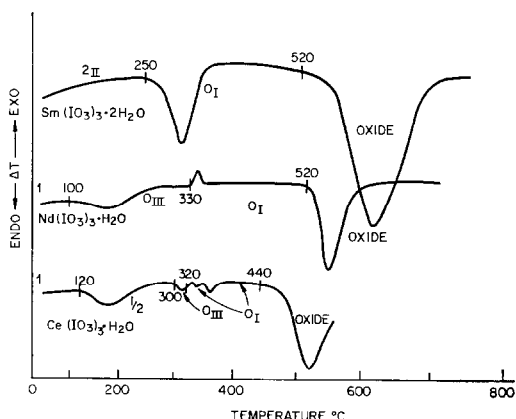

FIG. 6. The DTA curves of the Ce through Sm iodates with $x = 1$ and 2, run at 5°C/min in nitrogen.

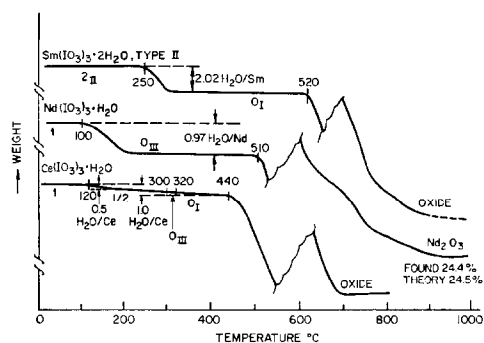FIG. 7. The TGA curves of the Ce through Sm iodates with $x = 1$ and 2, run at 5°C/min in nitrogen.

FIG. 9. The TGA curves of the Ce through Sm iodates with $x = 5$, run at 5°C/min in nitrogen. Dashed lines with numbers indicate weights for $x = 5$, 2, and 0. calculated from the weight of oxide remaining.

also yield a double salt (discussed in Section E). The $Ln_5(IO_6)_3$ compounds, previously reported to occur with all the lanthanides (4, 5), were not found to occur with any except lanthanum itself; the examination by powder X-ray diffraction of many preparations at temperatures between the formation and decomposition of the final anhydrous iodate O_I showed only mixtures of this compound and the oxide.

The occurrence of compounds and their decomposition scheme is shown in Figs. 1 and 5. These results are based on the DTA and TGA results such as those of Figs. 6–9, as well as on powder X-ray diffraction data. Preparation conditions are given in Table I.

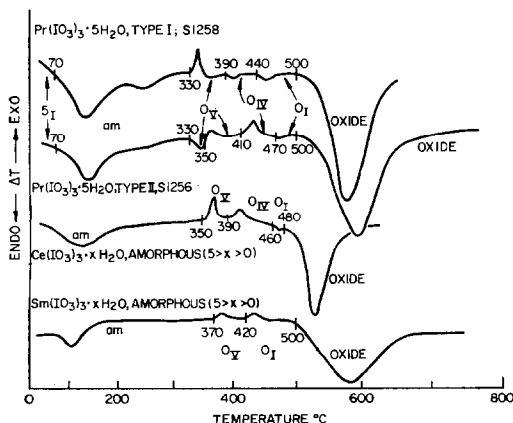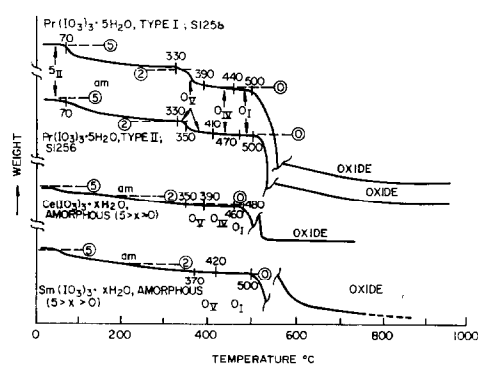The compounds in each of the groups of Fig. 1 gave essentially the same diffraction

patterns; in two cases, however, the same patterns were apparently given by different water content compositions. The 1 hydrates of Pr, Nd, and Sm appeared to give the same diffraction pattern and optical absorption spectra as the O_{III} anhydride formed from 1 by heating. A single crystal of $Nd(IO_3)_3 \cdot H_2O$ was heated to convert it to the O_{III} compound and immediately coated with a water-impermeable cement. A Gandolfi X-ray diffraction pattern had an appearance distinctly different from the 1 hydrate. Exposure to ambient conditions resulted in rapid moisture absorption and reversion from O_{III} to 1. In addition, the Ce hemihydrate $\frac{1}{2}$ powder X-ray diffraction pattern also appeared to be essentially indistinguishable from the 1 pattern. The possibility thus exists that in the 1 $\frac{1}{2}$ hydrate of Ce, the water is able to leave and reenter the structure reversibly with very little if any structural rearrangement or alternatively, that the two structures are very closely related. The fact that the same crystallizing conditions reproducibly yielded only the $\frac{1}{2}$ hydrate for La and a mixture of crystals of $Ce(IO_3)_3 \cdot H_2O$ and differently colored microcrystalline aggregates of $Ce(IO_3)_3 \cdot \frac{1}{2}H_2O$ for Ce as shown in Table I strengthens the assignment of these compounds as distinct phases and not merely a single phase of variable water content, even though all three give identical appearing powder patterns (2).

In the Ce 1 decomposition curve several endo -and exotherms occur just above 300°C

FIG. 8. The DTA curves of the Ce through Sm iodates with $x = 5$, run at 5°C/min in nitrogen.

(Fig. 6), but no recognizable changes in the powder X-ray diffraction patterns could be identified other than the $\frac{1}{2}$ to O_{III} to O_I changes. Some variability was observed in the 5_I and 5_{II} decompositions. In every case there was an exotherm after the (probably metastable) amorphous phase, but the exact details varied although the same decomposition products did appear. The curves for two Pr 5_I preparations of Figs. 8 and 9 illustrate this type of behavior. Two types of decomposition paths were observed in the 5_{II} compounds; those of Ce and Pr were essentially the same as that for Ce amorphous, and those of Nd and Sm the same as that for Sm amorphous, shown in Figs. 8 and 9. Here also there was occasional variation in the decomposition behavior, but again not in the phases obtained (analogous to the Pr 5_I compounds).

Crystals were grown in the following cases. Gel growth from acetic acid set gels (6) gave 5_I crystals for Ce and Nd, 5_I and 5_{II} crystals for Pr, and 2_{II} crystals for Sm; growth from boiling (7) water solution gave 1 crystals for Ce, Pr, Nd, and Sm; growth from boiling (7) HNO_3 solution gave the double salt ds for Pr and Nd.

An attempt at crystal growth of cerium iodate from boiling HNO_3 gave the anhydrous tetravalent compound $Ce(IO_3)_4$ due to oxidation from Ce^{3+} to Ce^{4+} by the HNO_3. DTA and TGA analysis of this compound showed that it decomposed at 420°C to O_I

$$2\ Ce(IO_3)_4 \rightarrow 2\ Ce(IO_3)_4 + I_2 + 3\ O_2.$$
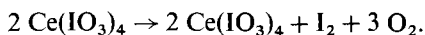
The trivalent anhydride O_I then decomposed as usual to the oxide at 440°C. This tetravalent $Ce(IO_3)_4$ has been previously reported (8), and its structure determined (9), as well as the X-ray powder diffraction pattern published (10). The structure of a monohydrate $Ce(IO_3)_4 \cdot H_2O$ has also been reported (11). The tetravalent compounds were not further investigated in this study.

E. The Double Salts

An isostructural group of double salts of the type $Ln^{III}(IO_3)_3 \cdot HIO_3$ is formed by La, Pr, Nd, and Sm. In all cases except Sm, crystals could be obtained by the slow evaporation
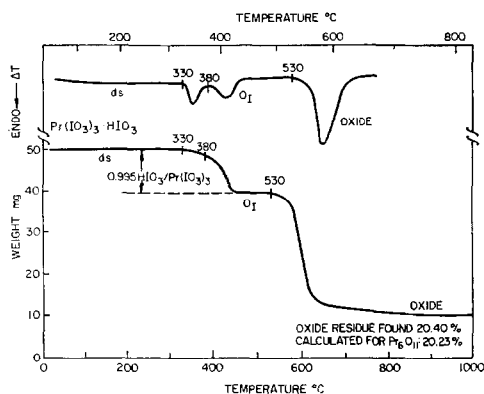

FIG. 10. The DTA and TGA curves of the $Pr(IO_3)_3 \cdot HIO_3$ double salt, run at 20°C/min in nitrogen.

of a boiling solution (7) in concentrated nitric acid.

In early experiments, previously formed $Ln(IO_3)_3$ was dissolved in HNO_3 and evaporated to about 10% of the original volume. Detailed analysis showed the resultant double salts to be off-stoichiometric, ranging from 0.82 to 0.92 HIO_3 per $Ln(IO_3)_3$ for La, Pr, and Nd. In the case of Sm a mixture of 94% O_I anhydride and 6% $Sm(IO_3)_3 \cdot HIO_3$ formed. In the case of Ce only the tetravalent $Ce(IO_3)_4$ formed as described above.

Stoichiometric double salts were obtained by adding the necessary amount of HIO_3 to the nitric acid solution, when the grown crystals proved to be stoichiometric within the experimental error of analysis as shown in Fig. 10 for $Pr(IO_3)_3 \cdot HIO_3$. On one occasion, a sample of a damp paste of incompletely washed Pr pentahydrate 5_I containing some free HIO_3 and HNO_3 also yielded 1 mm crystals of the stoichiometric double salt over a one-year period.

The decomposition to the anhydride (O_{IV} for the ds of La and O_I for the ds of Pr, Nd, and Sm) always occurred as a double endotherm (e.g., Fig. 11). Attempts to isolate an intermediate product, even at slow heating rates of 2°/min, merely resulted in mixtures of the double salt and the anhydride. Again, it was tempting to identify the second peak with the decomposition of I_2O_5 produced from the liberated HIO_3 (this decompo-
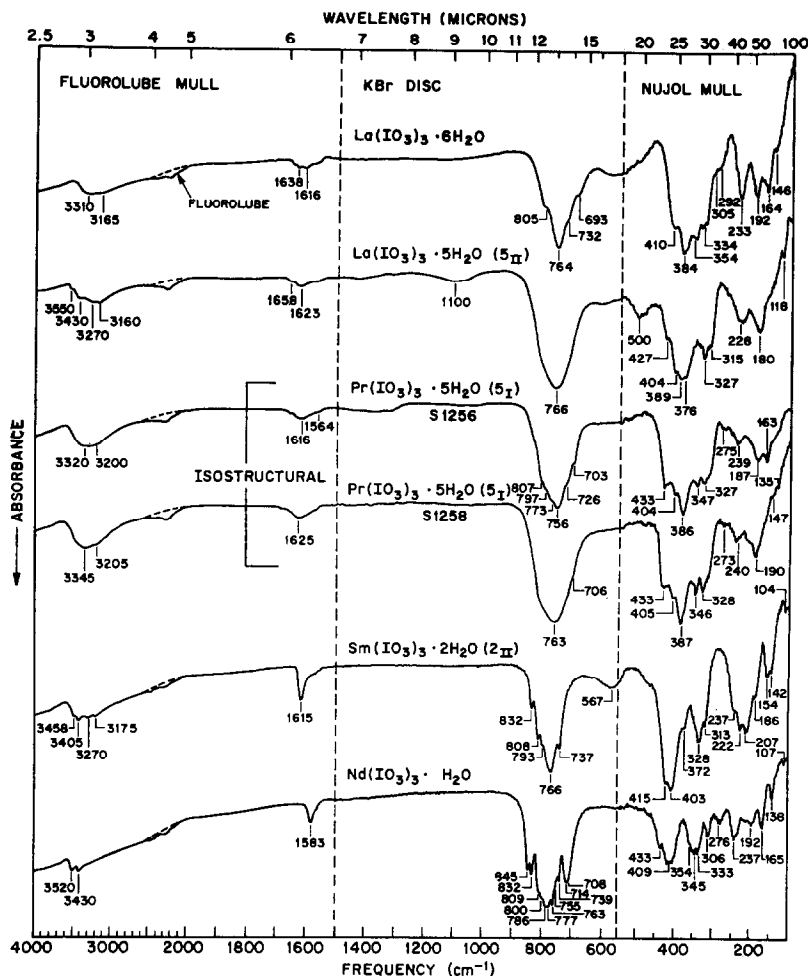
FIG. 11. Absorbance curves of some hydrated lanthanide iodates in the 100–4000 cm⁻¹ region.

sition does indeed occur at 380°C under these experimental DTA conditions with HIO_3), but free iodine was noted as soon as the decomposition began at 330°C. We have been unable to assign a cause for this double peak; there is always the possibility of a structural transformation with a partially overlapping decomposition.

No diffraction lines due to any anhydrous iodate were seen in the off-stoichiometric salts, making it likely that there is in fact a range of compositions $Ln(IO_3) \cdot (1 - y)HIO_3$ possible, with $0 \leqslant y \leqslant 0.18$. A single crystal X-ray diffraction study would be necessary to confirm this.

F. Optical Properties

Second harmonic generation at 1.06 μm was used as an indicator for the lack of a center of symmetry as well as for indicating optical nonlinear device potential. One or more samples of each isostructural group were checked and the following gave positive results (in the 0.1–10 x quartz range): 6, 1, and ½; in Paper V the anhydride O_{II} was erroneously reported to be active. Further detail will be given elsewhere (2).

Colors were the usual expected for the lanthanides: colorless for the La, Ce, and Sm iodates, green for the Pr, and lilac for the
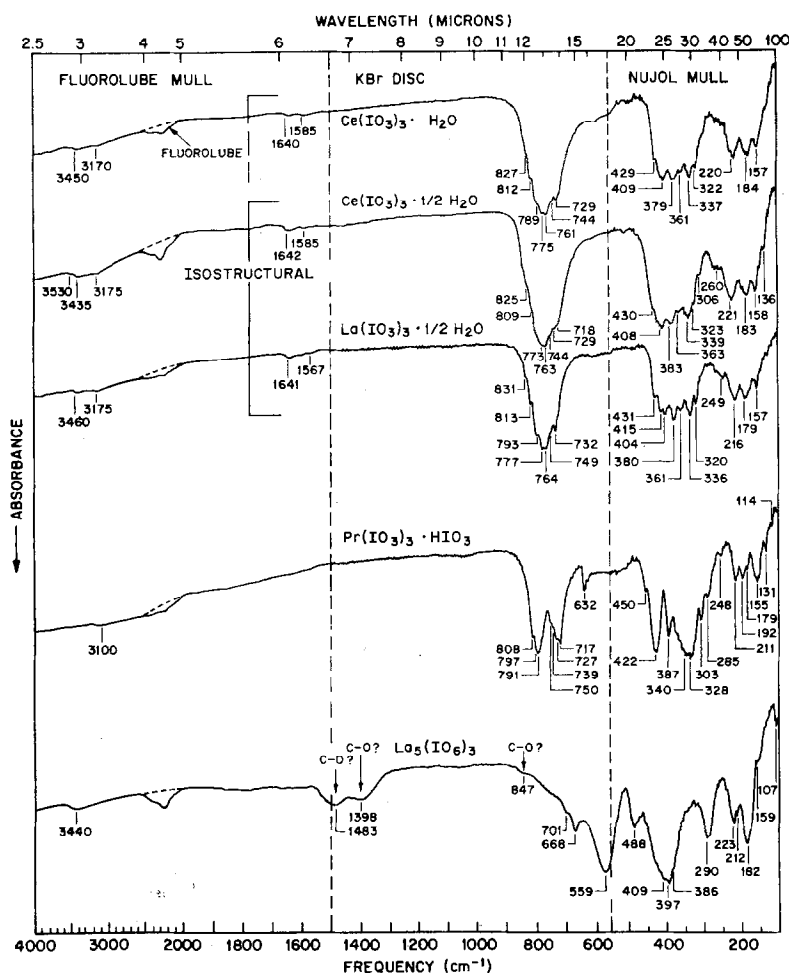
FIG. 12. Absorbance curves of some hydrated lanthanide iodates, the Pr double salt, and La$_5$(IO$_6$)$_3$ in the 100–4000 cm^{-1} region.

Nd iodates. Spot checks for refractive indexes showed values in the 1.8–2 region, similar to those we found in the 3d (3) and copper (6) iodates.

Infrared absorption spectra in the 4000–100 cm^{-1} region were run as described previously (3). They contain the same types of features (3) and are shown in Figs. 11–14. Two pairs of distinct structure types, the 1$_{II}$–$\frac{1}{2}$ and 1–0$_{III}$ sets of spectra appeared to be identical as discussed in Section D (the spectrum for 0$_{III}$ was not obtained; this type of compound absorbs moisture rapidly and then gives the same spectrum as the 1 of Fig. 11). Apart from this, each structure type gave a spectrum that

was recognizable and distinct from all our previous iodate spectra (1, 3, 6), proving almost as good a characterization technique as powder X-ray diffraction. Note the detailed agreement between the La and Ce $\frac{1}{2}$ hydrates in Fig. 12, the La and Pr O$_{IV}$ anhydrides in Fig. 13, and the Sm O$_I$ of Fig. 13 with the isostructural Eu and Tm spectra shown in Paper V. The spectrum of the Sm 2$_{II}$ hydrate (not shown) was also essentially the same as the 2$_{II}$ hydrates of Eu and Er in V. Where variability in the DTA curves was observed, as with the Pr–5$_I$ compounds of Fig. 8, the infrared spectra, just as the X-ray diffraction patterns, were nevertheless identical.
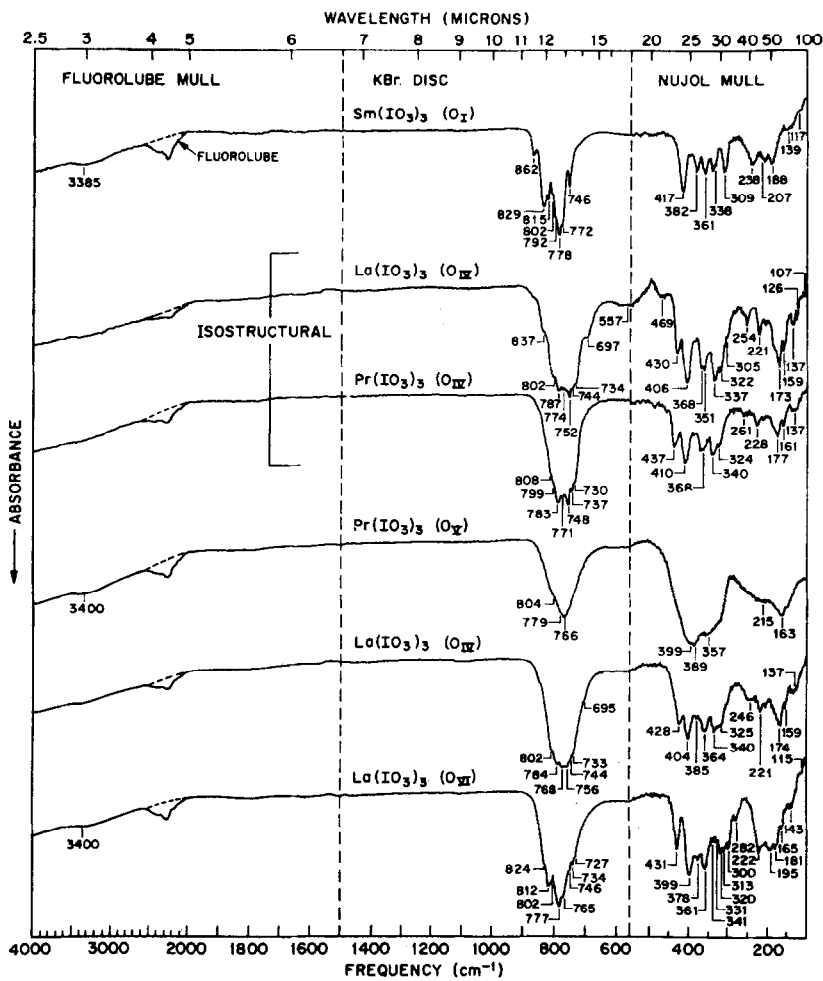
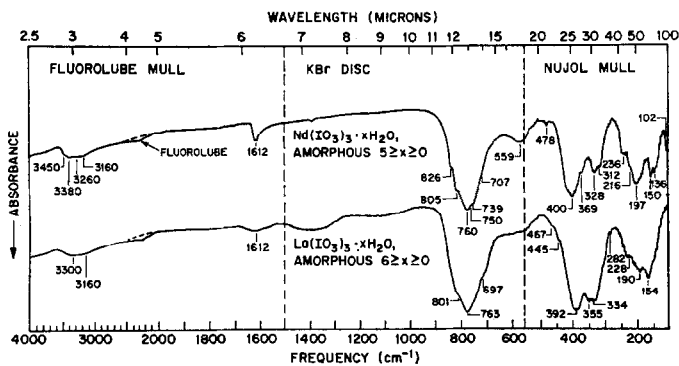FIG. 13. Absorbance curves of some anhydrous lanthanide iodates in the 100–4000 cm^{-1} region.

FIG. 14. Absorbance curves of two amorphous lanthanide iodate hydrates in the 100–4000 cm^{-1} region.

As expected, the OH features (bands near 3300 cm^{-1} and 1600 cm^{-1}) were observed in every hydrated and none of the anhydrous compounds, and the presence of the 1600 cm^{-1} bands due to the H–O–H bending mode indicates H_2O as distinct from –OH in all the hydrates. Hydrogen bonding again is weak as noted in Paper V.

The spectrum of the $La_5(IO_6)_3$ compound with iodine in the 7+ state instead of the usual 5+ lacks the usual prominent 750 cm^{-1} group of bands (originating in vibrations involving metal, iodine, and oxygen atoms) seen in the other iodates. Almost definitely the usual pyrimidal IO_6 iodate grouping is not involved in the structure of this compound. The three weak bands at 1498, 1402, and 845 cm^{-1} are undoubtedly carbonate absorbed from the atmosphere; compare for example, the almost identical bands seen in the carbonate contaminated lanthanide oxides (Nos. 360, 361, 362, and 364) reported by Nyquist and Kagel (11); the same bands are seen in the carbonate produced by heating europium oxalate to 500–600°C (12). Similarly, the weak band at 3440 is undoubtedly adsorbed moisture. A check of the spectrum of HIO$_3$ (13) showed that it was not present in the free form in this spectrum, nor were bands attributable to La$_2$O$_3$ (14) present.

The double salts, e.g., the Pr(IO$_3$)$_3$·HIO$_3$ shown in Fig. 12, also do not contain absorptions corresponding to free HIO$_3$. Here the usual prominent group of bands near 800 cm^{-1} is split into two at 791 cm^{-1} and 717 cm^{-1}, probably attributable to iodate ions in two significantly differing environments.

The spectra of the amorphous phases of La and Nd prepared by heating the 6 and 5$_{II}$ hydrates, respectively, are shown in Fig. 14. These spectra are different from all the others and may be useful for identifying these phases which appear amorphous to X-rays.

G. Previous Studies

Ignoring early reports in which no characterization of any significance were given, there are four recent studies, showing no consistency in those regions where they overlap. They all used essentially the same precipitation pro-

cedure as we did. Scherer (15) studied promethium iodate and obtained a hydrate Pm (IO$_3$)$_3$·xH$_2$O with variable water content $2 \leqslant x \leqslant 9$, isostructural with similar compounds of Pr, Nd, and Sm. His powder X-ray diffraction results are identical with our 1 compounds for Ce, Pr, Nd, and Sm, and we therefore believe that he was in fact dealing with Pm (IO$_3$)$_3$·H$_2$O which also contained excess water. Bosch-Reig et al. (16) report a 3 Pr(IO$_3$)$_3$·10 H$_2$O, i.e., 3 ⅓ H$_2$O per Pr; DTA showed this to lose water near 100°C to give an anhydride and to decompose near 500°C. In the absence of any other specific characterization we can neither confirm nor explain this result.

Yakunina et al. (4) reported a trihydrate for Ce and Pr, a tetrahydrate for Nd and Sm, and a pentahydrate for La. The DTA curve of their La(IO$_3$)$_3$·5 H$_2$O is not inconsistent with our La 5$_{II}$ compound. Their Ce, Nd, and Sm DTA curves most closely resemble our corresponding amorphous phase compounds which include the tri- and tetrahydrates in their composition ranges. Their Pr(IO$_3$)$_3$·3 H$_2$O shows some features of our 5$_I$ and is in all probability a mixture. They report a periodate Ln$_5$(IO$_6$)$_3$ composition for all the lanthanides, said to form on heating to 500°C, but despite careful examination, we have found no evidence for this composition except in the case of lanthanum itself; for all the other lanthanides we find only the oxide above this temperature. Yakunina et al. (4) gave no characterization other than DTA.

Hájek and Hradilová (5) gave both DTA and infrared absorption data (the latter only tabulated) for the 2½ hydrate of La, the hexahydrate of Nd, and the trihydrate of Sm. The data given for the La and Sm salts is roughly consistent with the amorphous phases, the water content also being within the amorphous range. In the case of Nd more water is present than in any of our Nd iodates (free water?) and a rough fit could be made with either the amorphous or the Type 1 pentahydrate. In no case is their data of enough precision for a clear-cut identification.

Many solubility studies exist in the literature for lanthanide iodates, including one on the precipitation process for La (17), but the

nature of the solid phase in equilibrium with the saturated solution was not examined in any of these studies.

In summary, of previous studies on compounds of the type here discussed, only the $La(IO_3)_3 \cdot 5\ H_2O$ (5_{II}) and the $La_5(IO_6)_3$ of Yakunina et al. (4) have been confirmed in the present study and found to have the same composition as originally reported. The "promethium iodate hydrate" of Scherer (15) was isostructural with our 1 iodates and the formula $Pm(IO_3)_3 \cdot H_2O$ is accordingly indicated.

H. Summary

In the study reported here and in V a total of 77 different lanthanide iodates of the type $Ln^{III}(IO_3)_3 \cdot xH_2O$ with $6 \geqslant x \geqslant 0$ were obtained, falling into 15 structural types including one amorphous. In addition $La_5(IO_6)_3$ and four isostructural salts of the type $Ln(IO_3)_3 \cdot HIO_3$ were also obtained. With the exception of two of the lanthanum compounds, the other 80 compounds have been obtained and characterized for the first time. Most previous reports appear to have dealt with the amorphous phase of variable water content, which occurs for each of the lanthanides.

Single crystals were grown for 11 of the 17 crystalline isostructural groups of compounds and crystallographic work will be reported in Part VII of this series (2).

Note added in proof. Most of these compounds, particularly the precipitated ones, give of small amounts of iodine on heating due to the presence of traces of free HIO_3. Only in the case of the La "6" compound were copious amounts of iodine liberated at the 230°C decomposition. It appears that this compound is in fact of the type $La(IO_3)_3 \cdot x\ H_2O \cdot y\ HIO_3$ with x near 2–1/2 and y near 0.25. Several 18 months gel-growth runs have produced enough crystals of millimeter size for precise compositional determination which are now under way.

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