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Transition Metal Iodates. V. Preparation and Characterization of the Smaller Lanthanide Iodates

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The $Ln(IO_3)_3 \cdot xH_2O$ compounds of Eu–Lu, including Y, were prepared by precipitation, thermal decomposition, and by crystallization from the gel, from ambient and boiling water, and from boiling HNO_3. Six groups of compounds were obtained and characterized by powder X-ray diffraction, DTA, TGA, and infrared spectroscopy.

Two distinct structures with $x = 0$ occur for the iodates; one occurs for Eu–Lu plus Y, and the other for Yb and Lu. Two distinct structures occur for $x = 2$; one occurs for Eu–Er plus Y, and the other for Tm–Lu. One structure with $x = 4$ occurs for Gd–Lu plus Y. An amorphous phase appears as an intermediate stage during the decomposition of the tetrahydrates. All of these phases (except the amorphous one) were prepared in single-crystal form and structural data will be reported elsewhere. Only the tetrahydrates have been previously reported; other compounds previously reported appear to have been mixtures.

A. Introduction

This work is a continuation of a study of transition metal iodates (*1–4*) that surveys compounds with possibly useful combinations of optical, magnetic, elastic, and dielectric properties. This paper deals with the smaller lanthanides from Eu–Lu (including Y), since the iodates of this group are closely related.

The literature on the existence of lathanide iodates of the type Ln $(IO_3)_3 \cdot xH_2O$ is quite contradictory and will be dealt with in Section D.

The remaining lanthanide iodates will be discussed in Part VI (*5*), and powder and single-crystal X-diffraction data in later parts of this series (*6*).

B. Experimental

Rare earth oxides used (99.9% pure from Michigan Chemicals Corp.) were dissolved in a small excess of concd HNO_3 and the iodates precipitated with a small excess of iodic acid solution. The resulting powders were washed, air dried, and used as the starting material for crystallization from boiling water or boiling nitric acid (*7*). A saturated solution of the material crystallizing from boiling water was also prepared at room temperature and permitted to evaporate either at ambient or reduced pressure. Gel growth in acetic acid–set silica gels was conducted as described previously (*3*).

All of these preparations were submitted to powder X-ray diffraction, differential thermal analysis (DTA), and thermogravimetric analysis (TGA) in N_2 at 5 and 20°/min, as previously described (*1, 3*). Additional thermal preparations were made by heating samples just past each exotherm or endotherm shown on DTA and cooling rapidly, and each preparation was examined by X rays; a total of over 100 samples were involved. Selected samples were also examined by infrared spectroscopy as previously described (*1, 3*), and for second-harmonic generation at 1.06 μm.

In all cases the generic formula $Ln(IO_3)_3 \cdot xH_2O$ was confirmed by essentially integral values of x as obtained from TGA. As

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TABLE I

PREPARATION OF THE SMALLER LANTHANIDE IODATES[a]

	Ambient temperature			Boiling point	
Ln	Precipitation[b]	Gel	Evaporation	H_2O	HNO_3
Eu	am; 2_{II}	2_{II}		2_{II}	0_I
Gd	am	$2_{II}+4$	2_{II}	2_{II}	0_I
Tb	4	4	am + 2_{II}	2_{II}	0_I
Dy	4		2_{II}	2_{II}	0_I
Y	am; 2_{II}; 4	4	2_{II}	2_{II}	0_I
Ho	4	4		2_{II}	0_I
Er	4	4		2_{II}	0_I
Tm	4			2_I	0_I
Yb	4	4		2_I	0_{II}
Lu	2_I	4	4	2_I	0_{II}

[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; "+" indicates simultaneous and ";" alternative occurrences.

[b] Excess water was frequently present.

an additional check the residual weight of Ln_2O_3 remaining above 800°C was always within the experimental error (± 2%) of that expected from the $Ln(IO_3)_3$ amount remaining at about 500°C after all water had been lost.

The notation x_N is used as an abbreviated designation for the group of compounds $Ln(IO_3)_3 \cdot xH_2O$, type N.

C. Results

All the powder X-ray diffraction patterns obtained in this series fell into 1 of 5 crystalline groups (2 being anhydrides, 2 dihydrates, and 1 the tetrahydrate) or indicated an amorphous nature showing no diffraction lines. The distribution of these 6 groups by the method of preparation is summarized in Table I, and the occurrence of crystalline compounds is given in Table II.

The DTA and TGA curves for 1 compound each of the 5 structure types, are given in Figs. 1 and 2. The observed decomposition temperatures vary with the heating rate, gas flow, sample size, and sample geometry (compiled for DTA, thin layer for TGA). The variation from one lanthanide iodate to another was sufficiently small that transition temperatures can be summarized as: $Ln(IO_3)_3 \cdot 4H_2O$ to amorphous, 80 ± 20°C; $Ln(IO_3)_3 \cdot 2H_2O$ type I or II to $Ln(IO_3)_3$ type I, 280 ± 25°C; amorphous to $Ln(IO_3)_3$ type I (exothermic), 380 ± 20°C; $Ln(IO_3)_3$ type I or II to Ln_2O_3 (cubic), 515 ± 20°C.

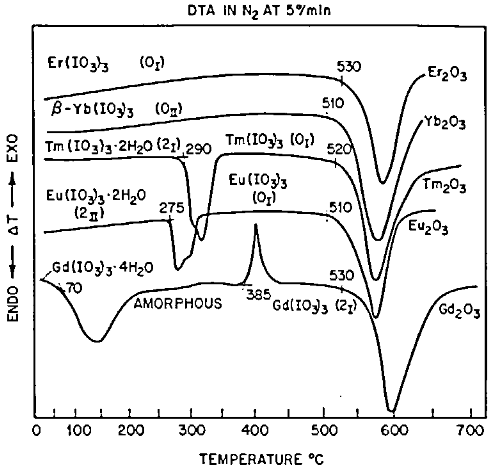

FIG. 1. DTA curves of some lanthanide iodates; in flowing N_2 at 5°/min.

Figure 3 shows the generalized decomposition scheme and the range of occurrence for the various branches. The type I dihydrate also occurs for Sm and Nd, and the type I anhydride occurs for all the lanthanides except lanthanum itself (*6*). As can be seen in

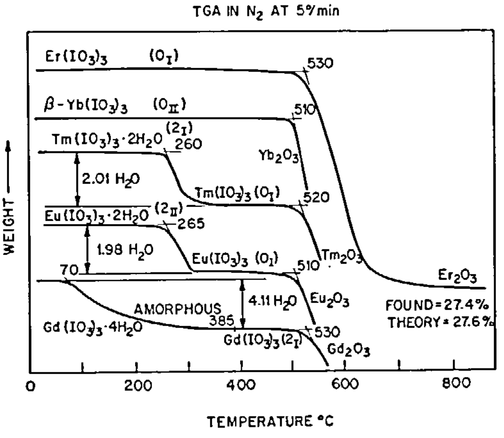

FIG. 2. TGA curves on some lanthanide iodates; in flowing N_2 at 5°/min.

TABLE II

EXISTENCE AND STRUCTURE TYPES OF THE SMALL LANTHANIDE IODATES

Tetrahydrate	Dihydrate type I	Dihydrate type II	Anhydride type I	Anhydride type II
		$Eu(IO_3)_3 \cdot 2H_2O$	$Eu(IO_3)_3$	
$Gd(IO_3)_3 \cdot 4H_2O$		$Gd(IO_3)_3 \cdot 2H_2O$	$Gd(IO_3)_3$	
$Tb(IO_3)_3 \cdot 4H_2O$		$Tb(IO_3)_3 \cdot 2H_2O$	$Tb(IO_3)_3$	
$Dy(IO_3)_3 \cdot 4H_2O$		$Dy(IO_3)_3 \cdot 2H_2O$	$Dy(IO_3)_3$	
$Y(IO_3)_3 \cdot 4H_2O$		$Y(IO_3)_3 \cdot 2H_2O$	$Y(IO_3)_3$	
$Ho(IO_3)_3 \cdot 4H_2O$		$Ho(IO_3)_3\ 2H_2O$	$Ho(IO_3)_3$	
$Er(IO_3)_3 \cdot 4H_2O$		$Er(IO_3)_3 \cdot 2H_2O$	$Er(IO_3)_3$	
$Tm(IO_3)_3 \cdot 4H_2O$	$Tm(IO_3)_3 \cdot 2H_2O$		$Tm(IO_3)_3$	
$Yb(IO_3)_3 \cdot 4H_2O$	$Yb(IO_3)_3 \cdot 2H_2O$		α-$Yb(IO_3)_3$	β-$Yb(IO_3)_3$
$Lu(IO_3)_3 \cdot 4H_2O$	$Lu(IO_3)_3 \cdot 2H_2O$		α-$Lu(IO_3)_3$	β-$Lu(IO_3)_3$

Figs. 1 and 2 for Gd, the possibly metastable amorphous phase has a variable water content. Well above the temperature at which all the water has been lost there is a sharp exothermic transition to the type I anhydride phase. The large heat emission presumably derives from the energy of ordering from the amorphous to the crystalline phase. All the other transitions were endothermic.

Iodine evolution occurs at the decomposition at about 515°C, and in Fig. 2 are given the found and calculated oxide residue values for $Er(IO_3)_3$. Such values were determined for each compound from TGA, and similarly satisfactory results in all instances serve in lieu of chemical analysis. In each case the identity of the residue was identified to be the cubic Ln_2O_3 by powder X-ray diffraction.

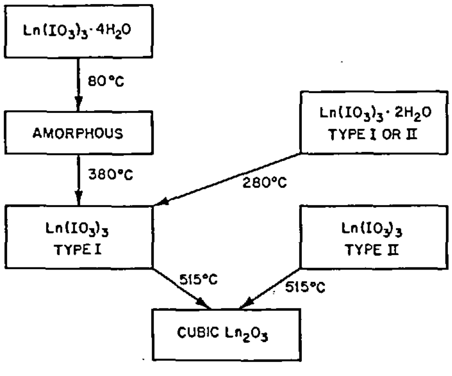

FIG. 3. Decomposition scheme of the smaller lanthanide iodates. Tetrahydrate branch: Gd–Lu; Type I—Dihydrate branch: Sm–Er; Type II—Dihydrate branch: Tm–Lu; Type II—Anhydride branch: Yb–Lu; Amorphous for Eu–Lu.

Doubled peaks were observed in some, but not all, of the water loss exotherms of the hydrated iodates as seen for Tm and Eu in Fig. 1. In several instances samples were heated at slow rates to temperatures intermediate between the 2 components of the peak and cooled rapidly, but in every case only the high-temperature (decomposed) product was observed in powder X-ray diffraction. The peak splittings could be due to fleeting intermediate modifications of the higher temperature phases which were not quenched under the conditions used.

The type of hydrate obtained on precipitation varied considerably. As shown in Table I, in the case of yttrium where several precipitations were performed, 3 forms could be obtained, presumably on minor variations in the precipitation conditions or the presence of nuclei. In addition variable and quite large amounts of water (e.g., $x \times 19.1$ for Y) were observed if washing and drying were not repeated until reproducibility was achievable. Except for the pink Er and the greenish Tm, all the other iodates were colorless or close to it.

In Figs. 4 and 5 two optical absorption spectra for each of the 5 structure types are presented for the region from 4000 to 100 cm^{-1}. The lanthanide features in the visible and ultraviolet

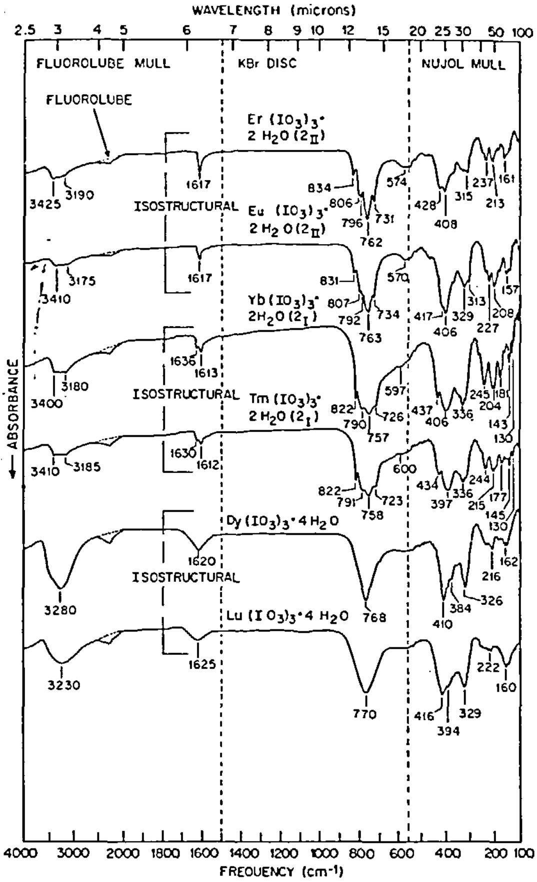

FIG. 4. Absorbance curves of some hydrated lanthanide iodates in the 100- to 4000-cm^{-1} region.

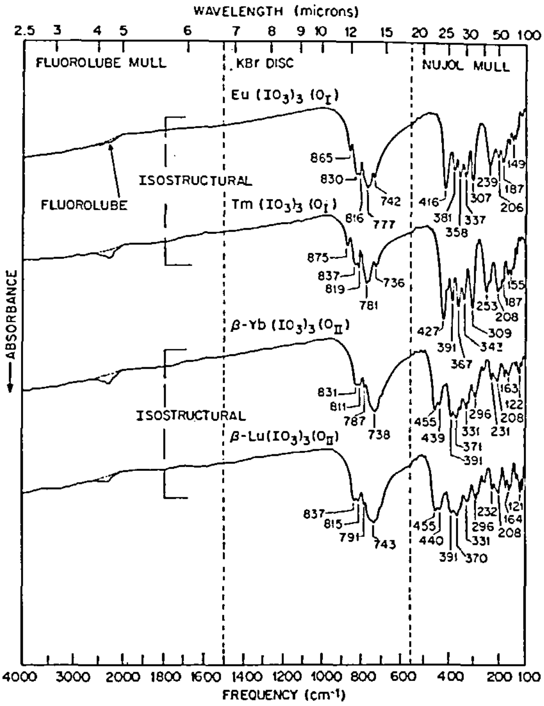

FIG. 5. Absorbance curves of some anhydrous lanthanide iodates in the 100- to 4000-cm^{-1} region.

regions of the spectrum are little affected by the chemical environment and were not examined. A comparison of the curves of Figs. 4 and 5 indicates that the 5 structure types give quite distinct spectra and that this technique is suitable for characterization as an alternative to powder X-ray diffraction.

The OH features (bands near 3300 and 1600 cm^{-1}) were shown only by the hydrous compounds of Fig. 4, as expected, and the occurrence of the 1600-cm^{-1} bands due to the H–O–H bonding mode is indicative of H_2O as distinct from –OH. Hydrogen bonding is weak, being comparable to that observed in the 3*d* iodate hydrates (*1*) but much weaker than in the copper compounds (*3*).

Several specimens of each group were checked for second-harmonic generation at 1.06 μm using microcrystalline quartz as a reference standard. Positive indication of nonlinear optical characteristics, indicating the absence of a center of symmetry was obtained only in the type II anhydrides, the response being about 0.1 that of quartz.

D. Previous Studies

One recent study examined the lutetium iodates (*8*), and two others (*9*, *10*) dealt with iodates of all or most of the lanthanides. In each case simple precipitations were used and the product examined by DTA, TGA, and infrared spectra in some cases. These studies disagree one with another. Studies earlier then these three were completely lacking in any characterization other than analysis and can be ignored.

The "lutetium iodate trihydate" of Harmelin (*8*) can be clearly identified as a mixture of the di- and tetrahydrates here reported. The DTA data given (water loss at 115 and 150°C, 2 endotherms near 335°C and a strong exotherm at 400°C) are in reasonable agreement with the data on the tetrahydrate and the type I dihydrate of Figs. 1 and 2. Harmelin's infrared spectra A corresponds reasonably well with such a mixture from Fig. 4; note, for example, that the water bands reported by Harmelin as occurring at 3180, 3280, and 3410 cm^{-1} are exactly what would be expected from such a mixture. On this basis the preparation B heated just short of the exotherm is a mixture of the anhydride type I and the amorphous phase. Preparation C is then the type I anhydride, and this spectrum agrees reasonably well with our spectrum of that type ($Tm(IO_3)_3$ in Fig. 5).

The study of Yakunina, Alekseenko, and Serebrennikov (*9*) reports tetrahydrates for the iodates here discussed (Eu–Lu, plus Y). The analystical figures as well as the DTA curves given are in reasonable agreement with our data. The exotherm temperatures were somewhat lower, possibly due to their slower heating rate of 6°/min. They gave no further characterization.

Hájek and Hradilová (*10*) report the tetrahydrates of the iodates of Eu, Er, and Yb (Tm is also erroneously listed in their Table I, but not elsewhere), and the trihydrates for Gd, Dy, Ho, Tm, and Lu; both DTA and infrared data are given. For the 2 tetrahydrates the DTA curves are not in unreasonable agreement with Yakunina *et al.* (*9*) and with our work, but show split exotherms for Eu and Yb. In the case of their trihydrates a mixture of the di- and tetrahydrates might be postulated for Dy; the other trihydrates show behavior which does not fit reasonably with any of our data. Neither can we find a reasonable fit with Figs. 4 and 5 for their infrared absorption data. They also observed iodine as a decomposition product as low as 300–420°C, making it likely that free HIO_3 was present in their samples, since neither we nor others (*8*, *9*) observe iodine much below 500°C in the lanthanide iodates; iodic acid emits iodine starting at 300°C. Overall, we cannot accept the validity of this work.

All 3 reports (*8–10*) consider the decomposition

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

as occurring once iodine is emitted. We have carefully checked X-ray powder diffraction patterns on samples quenched at various stages during the decompositions between 500 and 1000°C and have found this decomposition mechanism to apply only to lanthanum iodate (*6*); for all the other lanthanides only mixtures of the anhydrous iodate and the oxide were observed.

E. Summary

We have confirmed the iodate tetrahydrates of Eu–Lu including Y as reported by Yakunina *et al.* (*8*) Other recent studies(*9*, *10*), as well as older ones, apparently involved mixtures of the various compounds here reported, probably also containing excess iodic acid and/or free water.

In addition to the tetrahydrates, 2 types of dihydrates (type I for Tm–Lu and type II for Eu–Er and 2 types of anhydrides (type I for all of the lanthanides here considered and type II for Yb and Lu) have been observed. Characterization by DTA, TGA, and infrared spectroscopy is reported; the remaining lanthanide iodates will be discussed in Part VI (*5*), and single-crystal and powder X-ray diffraction data in later parts of this series (*6*).

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