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Transition Metal Iodates. VII. Crystallographic and Nonlinear Optic Survey of the 4*f*-Iodates

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Thirteen crystallographically distinct families of 4*f*-iodates, including hydrates, have been investigated. The anhydrous Type I family, extending from Ce to Lu, crystallizes in the monoclinic system, space group $P2_1/a$: The lattice constants of $Gd(IO_3)_3$, for example, are $a = 13.389 \pm 0.006$, $b = 8.500 \pm 0.002$, $c = 7.106 \pm 0.002$ Å, $\beta = 99.73 \pm 0.03°$ with four formulas per unit cell. $Yb(IO_3)_3$ and $Lu(IO_3)_3$ also crystallize in Type II with monoclinic space group $P2_1/c$ and lattice constants for $Yb(IO_3)_3$ of $a = 8.685 \pm 0.005$, $b = 6.066 \pm 0.002$, $c = 16.687 \pm 0.009$ Å, $\beta = 115.01 \pm 0.18°$, and four formulas per unit cell. Polycrystalline samples only of the anhydrous Types III, IV, V, and VI have been prepared and typical powder patterns are given. All anhydrous 4*f*-iodates form in centrosymmetric space groups. La and Ce grow as hemihydrates in the orthorhombic space group $C222_1$, with $a = 19.26 \pm 0.01$, $b = 7.40 \pm 0.01$, $c = 6.76 \pm 0.01$ for $La(IO_3)_3\cdot\frac{1}{2}H_2O$, and both generate second harmonics more efficiently than quartz. Ce, Pr, Nd, Pm, and Sm form monohydrates, space group $P2_1$, with lattice constants for $Sm(IO_3)_3\cdot H_2O$ of $a = 10.080 \pm 0.007$, $b = 6.642 \pm 0.006$, $c = 7.250 \pm 0.008$ Å, $\beta = 112.9 \pm 0.1°$, and two formulas per unit cell. The monohydrates are also more efficient than quartz at generating second harmonics. Two dihydrated families grow: Type I from Tm to Lu and Type II from Nd to Er, both triclinic. $Lu(IO_3)_3\cdot 2H_2O$ has $a = 8.018 \pm 0.012$, $b = 9.956 \pm 0.021$, $c = 6.969 \pm 0.016$ Å, $\alpha = 99.8 \pm 0.2°$, $\beta = 93.8 \pm 0.2°$, $\gamma = 68.2 \pm 0.2°$ with two formulas in the unit cell, space group $P\bar{1}$. $Nd(IO_3)_3\cdot 2H_2O$ has $a = 7.56 \pm 0.04$, $b = 10.77 \pm 0.05$, $c = 7.34 \pm 0.02$ Å, $\alpha = 105.3 \pm 0.4°$, $\beta = 110.8 \pm 0.7°$, $\gamma = 97.9 \pm 0.6°$ with two formulas per cell and space group $P\bar{1}$. Polycrystalline Gd to $Lu(IO_3)_3\cdot 4H_2O$, and Ce to $Sm(IO_3)_3\cdot 5H_2O$ Type I form in centrosymmetric space groups; powder patterns for two tetrahydrates and the four pentahydrates are given. $La(IO_3)_3\cdot 5H_2O$ and $Pr(IO_3)_3\cdot 5H_2O$, Type II, are monoclinic, space group $P2_1/m$, with lattice constants for $Pr(IO_3)_3\cdot 5H_2O$ of $a = 6.768 \pm 0.008$, $b = 23.120 \pm 0.039$, $c = 7.107 \pm 0.007$ Å, $\beta = 112.7 \pm 0.1°$, and four formulas per unit cell.

1. Introduction

The search for new materials with an enhanced possibility of coupled magnetic, optic, and polar properties (*1*) has led previously to the preparation and characterization of the 3*d* and cupric iodates (*2*, *3*) and to a crystallographic, magnetic, and nonlinear optic survey of the properties of these crystals (*4*, *5*). The lanthanide iodates with formula $Ln(IO_3)_3\cdot xH_2O$ (Ln from Eu to Lu, including Y, and $0 \leqslant x \leqslant 4$) have now been prepared and characterized (*6*), followed by a comparable study on materials with Ln from Ce to Sm, but excluding Pm, and $0 \leqslant x \leqslant 5$ (*7*). Following the earlier convention for polymorphic iodates (*6*), a Type N iodate is designated by the notation x_N. The crystallographic and nonlinear optic properties of these new anhydrous and hydrated 4*f*-iodates have been surveyed and the results are reported in the present paper.

2. Anhydrous Type I 4*f*-Iodates from Ce to Lu

The largest family of isostructural rare-earth iodates is the anhydrous Type I, crystallizing in the monoclinic system. All

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TABLE I

CRYSTALLOGRAPHIC DATA FOR THE ANHYDROUS 4f-IODATES OF TYPE I

Rare earth	a (Å)[a]	b (Å)	c (Å)	β (°)	Volume (Å^3)	Calculated[b] density (g cm^{-3})
Ce	13.555 ± 20	8.565 ± 9	7.214 ± 12	99.68 ± 0.28	825.6	5.35
Pr	13.520 ± 8	8.557 ± 4	7.198 ± 8	99.88 ± 0.07	820.4	5.39
Nd	13.504 ± 19	8.534 ± 6	7.192 ± 8	100.05 ± 0.12	816.1	5.44
Sm	13.404 ± 5	8.509 ± 2	7.143 ± 2	99.82 ± 0.03	802.8	5.58
Eu	13.361 ± 13	8.486 ± 4	7.115 ± 5	99.88 ± 0.10	794.8	5.65
Gd	13.389 ± 6	8.500 ± 2	7.106 ± 2	99.73 ± 0.03	797.1	5.68[c]
Tb	13.356 ± 13	8.482 ± 5	7.072 ± 6	99.60 ± 0.08	789.9	5.75
Dy	13.291 ± 8	8.446 ± 4	7.034 ± 3	99.68 ± 0.05	778.4	5.86
Ho	13.283 ± 6	8.425 ± 4	7.010 ± 3	99.67 ± 0.05	773.3	5.92
Er	13.262 ± 12	8.441 ± 4	7.003 ± 5	99.72 ± 0.07	772.7	5.95
Tm	13.226 ± 12	8.408 ± 4	6.964 ± 5	99.65 ± 0.08	763.5	6.03
Yb	13.230 ± 6	8.390 ± 3	6.962 ± 3	99.72 ± 0.03	761.7	6.08
Lu	13.207 ± 6	8.398 ± 3	6.944 ± 3	99.82 ± 0.03	758.9	6.12
Y	13.275 ± 41	8.440 ± 5	7.003 ± 9	99.60 ± 0.15	773.6	5.26[d]

[a] Error values here and elsewhere in this paper without decimal point correspond to the least significant digit.

[b] For four formula weights per unit cell, in space group $P2_1/a$.

[c] $Dm = 5.70 \pm 10$ g cm^{-3} for $Gd(IO_3)_3$.

[d] $Dm > 5.0$ g cm^{-3} for $Y(IO_3)_3$.

O_I compounds may be prepared by dehydration of the appropriate hydrate. Crystals of anhydrous Eu to Tm iodate only are obtained from boiling HNO_3 (*6*). The single crystal diffraction patterns show systematic absences only in $h0l$ with $h = 2n + 1$ and in $0k0$ with $k = 2n + 1$, corresponding to the space group $P2_1/a$. The lattice constants, given in Table I, were obtained by the method of least squares, using the program of Evans *et al.* (*8*). The input spacings were measured on Straumanis-mounted Debye–Scherrer photographs, taken with CrKα ($\lambda = 2.2909$ Å) radiation, and are listed in Table II. For well-resolved high-angle lines, wavelength values $\lambda\alpha_1 = 2.2896$ and $\lambda\alpha_2 = 2.2935$ Å were used. The unit cell of each O_I crystal contains four formula weights. The only density measured was for $Gd(IO_3)_3$, Type I at 5.70 ± 0.10 g cm^{-3}. The normal lanthanide contraction with increasing atomic number is clearly seen in Fig. 1, with no volume differing significantly from the mean.

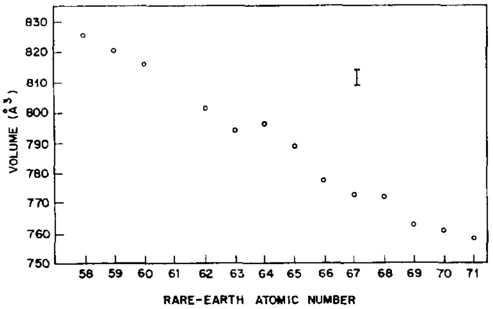

FIG. 1. Variation in unit cell volume of the anhydrous 4f-iodates, Type I, with atomic number of 4f-transition element. The error bar denotes one standard deviation in unit cell volume.

As expected for centrosymmetric crystals, no generation of second harmonics was observed.

3. Anhydrous Type II 4f-Iodates, Yb and Lu

$Yb(IO_3)_3$ and $Lu(IO_3)_3$ crystallize polymorphically in the monoclinic system, with the O_{II} form produced from solution in boiling HNO_3. The systematic absences

TABLE II. OBSERVED AND CALCULATED DEBYE–SCHERRER d-SPACINGS IN ÅNGSTROMS AND OBSERVED RELATIVE INTENSITIES OF THE ANHYDROUS 4f-IODATES OF TYPE I

	$Ce(IO_3)_3$			$Pr(IO_3)_3$			$Nd(IO_3)_3$			$Sm(IO_3)_3$			$Eu(IO_3)_3$			$Gd(IO_3)_3$			$Tb(IO_3)_3$		
$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)	I	d_{obs} (Å)	d_{calc} (Å)	I	d_{obs} (Å)	d_{calc} (Å)	I	d_{obs} (Å)	d_{calc} (Å)	I	d_{obs} (Å)	d_{calc} (Å)	I	d_{obs} (Å)	d_{calc} (Å)	I	d_{obs} (Å)	d_{calc} (Å)	I
2 1 0	—	5.268	< 1	—	5.329	< 1	—	5.245	< 1	—	5.217	< 1	—	5.201	< 1	—	5.212	< 1	5.189	5.201	1
3 1 0	3.951	3.952	1	3.947	3.941	1	—	3.933	< 1	—	3.910	< 1	—	3.897	< 1	—	3.907	< 1	3.910	3.898	3
0 2 1	3.668	3.669	2	3.666	3.663	1	3.646	3.655	1	3.637	3.641	4	3.633	3.630	3	3.362	3.633	4	3.626	3.623	5
0 0 2	3.576	3.556	5	3.563	3.546	5	3.451	3.541	4	3.521	3.519	6	3.500	3.505	6	3.501	3.502	6	3.487	3.487	7
1 2 1	3.459	3.462	2	3.448	3.455	1	3.438	3.446	2	3.422	3.433	2	3.416	3.422	3	3.426	3.427	4	3.410	3.419	2
$\bar{2}$ 0 2	3.409	3.384	3	3.396	3.380	3	3.379	3.380	3	3.349	3.352	3	3.331	3.340	4	3.333	3.337	5	3.319	3.319	1
$\bar{2}$ 2 1	—	3.340	< 1	—	3.414	< 1	—	3.332	< 1	—	3.314	< 1	—	3.305	< 1	—	3.308	< 1	—	3.298	< 1
4 0 0	3.338	3.341	10	3.332	3.330	10	3.324	3.324	10	3.305	3.302	10	3.392	3.291	10	3.297	3.299	10	3.292	3.292	10
$\bar{1}$ 1 2	—	3.310	< 1	—	3.323	< 1	—	3.302	< 1	—	3.280	< 1	—	3.268	< 1	3.264	3.265	1	—	3.250	< 1
2 2 1	3.102	3.104	8	3.095	3.096	8	3.087	3.087	8	3.075	3.076	8	3.065	3.065	8	3.072	3.071	9	3.060	3.064	9
$\bar{3}$ 2 1	2.950	2.961	2	2.956	2.957	2	—	2.953	< 1	2.935	2.936	1	2.923	2.927	1	2.932	2.931	2	2.921	2.923	1
2 0 2	—	2.940	< 1	2.927	2.928	2	2.923	2.921	2	2.907	2.907	2	2.895	2.894	1	2.898	2.897	3	2.891	2.888	2
1 3 0	2.793	2.792	1	2.789	2.789	1	2.780	2.782	1	2.774	2.773	1	2.758	2.766	1	2.769	2.770	2	2.764	2.764	1
$\bar{4}$ 0 2	2.693	2.669	1	2.679	2.667	1	2.667	2.667	1	2.646	2.643	1	—	2.635	< 1	2.634	2.634	2	2.621	2.622	2
$\bar{4}$ 2 1	—	2.584	< 1	—	2.615	< 1	—	2.577	< 1	—	2.561	< 1	—	2.554	< 1	—	2.557	< 1	—	2.549	< 1
$\bar{2}$ 3 1	—	2.518	< 1	—	2.590	< 1	—	2.510	< 1	2.500	2.499	1	2.493	2.492	1	2.496	2.495	1	2.488	2.489	1
0 0 3	2.371	2.370	1	—	2.364	< 1	2.361	2.361	2	2.346	2.346	3	2.338	2.336	3	2.335	2.338	2	2.341	2.324	
5 2 0	—	2.267	< 1	—	2.285	< 1	—	2.257	< 1	—	2.244	< 1	—	2.237	< 1	—	2.242	< 1	—	2.237	< 1
$\bar{5}$ 2 1	2.259	2.255	1	2.250	2.252	1	2.243	2.249	4	2.232	2.234	5	2.224	2.227	4	2.226	2.230	5	2.220	2.224	4
0 4 0	2.142	2.141	2	2.139	2.139	2	2.136	2.133	2	2.128	2.127	4	2.122	2.122	3	2.154	2.125	4	2.122	2.121	3
$\bar{3}$ 3 2	2.088	2.081	6	2.080	2.079	4	2.071	2.076	6	2.058	2.064	7	2.050	2.058	7	2.048	2.059	7	2.041	2.052	7

	$Dy(IO_3)_3$			$Ho(IO_3)_3$			$Er(IO_3)_3$			$Tm(IO_3)_3$			$Yb(IO_3)_3$			$Lu(IO_3)_3$			$Y(IO_3)_3$		
$h\,k\,l$	d_{obs} (Å)	d_{calc}(Å)	I	d_{obs}(Å)	d_{calc}(Å)	I	d_{obs}(Å)	d_{calc}(Å)	I	d_{obs}(Å)	d_{calc}(Å)	I	d_{obs}(Å)	d_{calc}(Å)	I	d_{obs}(Å)	d_{calc}(Å)	I	d_{obs}(Å)	d_{calc}(Å)	I
2 1 0	—	5.176	< 1	—	5.170	< 1	—	5.167	< 1	—	5.152	< 1	—	5.148	< 1	—	5.144	< 1	—	5.172	< 1
3 1 0	3.880	3.879	1	—	3.876	< 1	—	3.872	< 1	—	3.861	< 1	—	3.860	< 1	—	3.854	< 1	—	3.876	< 1
0 2 1	3.605	3.607	5	3.597	3.597	5	3.600	3.601	3	3.582	3.585	3	3.582	3.579	3	3.576	3.579	3	3.596	3.609	2
0 0 2	3.464	3.467	7	3.452	3.455	6	3.453	3.451	4	3.428	3.433	3	3.433	3.431	4	3.420	3.421	3	3.451	3.490	3
1 2 1	3.397	3.402	4	3.392	3.394	2	3.389	3.396	2	3.380	3.382	2	3.375	3.376	2	3.365	3.375	2	3.387	3.401	2
$\bar{2}$ 0 2	—	3.302	< 1	—	3.293	< 1	—	3.290	< 1	—	3.272	< 1	—	3.272	< 1	—	3.266	< 1	—	3.288	< 1
$\bar{2}$ 2 1	—	3.283	< 1	—	3.276	< 1	—	3.278	< 1	—	3.265	< 1	—	3.261	< 1	—	3.261	< 1	—	3.277	< 1
4 0 0	3.276	3.275	10	3.274	3.274	10	3.271	3.268	10	3.257	3.260	10	3.261	3.260	10	3.252	3.253	10	3.272	3.273	10
$\bar{1}$ 1 2	3.235	3.234	1	3.224	3.223	1	3.225	3.221	1	3.205	3.204	1	3.203	3.203	1	3.199	3.197	1	—	3.221	< 1
2 2 1	3.049	3.049	8	3.043	3.042	8	3.042	3.043	8	3.029	3.032	9	3.027	3.027	8	3.025	3.024	8	3.041	3.046	8
$\bar{3}$ 2 1	2.908	2.909	1	2.900	2.903	1	2.904	2.904	1	2.889	2.893	1	2.892	2.891	1	2.892	2.890	1	2.903	2.914	1
2 0 2	2.871	2.871	4	2.862	2.864	3	2.858	2.859	2	2.851	2.847	2	2.844	2.845	2	2.836	2.836	2	2.867	2.877	1
1 3 0	2.751	2.752	1	2.747	2.746	1	2.751	2.751	1	2.740	2.740	1	2.734	2.735	1	2.736	2.737	1	2.749	2.748	1
$\bar{4}$ 0 2	2.609	2.610	2	2.605	2.605	1	2.600	2.602	1	2.591	2.590	1	2.591	2.592	1	2.587	2.588	1	—	2.601	< 1
$\bar{4}$ 2 1	2.537	2.538	1	2.537	2.534	1	2.538	2.534	1	2.527	2.524	1	—	2.523	< 1	2.523	2.522	1	—	2.534	< 1
$\bar{2}$ 3 1	2.482	2.478	1	2.481	2.472	1	2.478	2.475	1	—	2.465	< 1	2.470	2.461	1	2.462	2.462	1	2.477	2.479	1
0 0 3	2.313	2.311	1	2.305	2.304	1	—	2.301	< 1	2.315	2.288	1	—	2.287	< 1	2.310	2.281	1	2.327	2.326	1
5 2 0	—	2.227	< 1	2.225	2.224	1	—	2.222	< 1	—	2.216	< 1	—	2.215	< 1	—	2.212	< 1	—	2.225	< 1
$\bar{5}$ 2 1	2.209	2.214	6	2.204	2.211	3	2.200	2.210	4	2.193	2.203	3	2.192	2.202	2	2.185	2.200	3	2.203	2.217	2
0 4 0	2.112	2.111	5	2.112	2.106	3	2.110	2.110	4	2.103	2.102	2	2.106	2.098	2	2.104	2.099	3	2.111	2.108	1
$\bar{3}$ 3 2	2.034	2.043	8	2.027	2.038	8	2.025	2.039	6	2.015	2.030	6	2.015	2.028	6	2.010	2.028	6	2.026	2.049	6

TABLE III

CRYSTALLOGRAPHIC DATA FOR $Yb(IO_3)_3$ AND $Lu(IO_3)_3$, TYPE II

	$Yb(IO_3)_3$	$Lu(IO_3)_3$
a (Å)	8.685 ± 5	8.689 ± 11
b (Å)	6.066 ± 2	6.057 ± 5
c (Å)	16.687 ± 9	16.678 ± 10
β	115.0 ± 0.2°	114.3 ± 0.2°
Volume (Å^3)	796.7	800.1
Z	4	4
Dx (g cm^{-3})	5.82	5.81
Dm (g cm^{-3})	>5.0	—
S.G.	$P2_1/c$	$P2_1/c$

observed in single crystal precession photographs are in $0k0$ only for $k = 2n + 1$ and in $h0l$ only for $l = 2n + 1$, corresponding to the space group $P2_1/c$. The lattice constants, obtained as for the O_I compounds, are given in Table III, the indexed powder-pattern spacings in Table IV. The slightly smaller volume of the respective O_I unit cells indicates a correspondingly more efficient packing arrangement. The b-lattice constant for O_I and $c/2$-lattice constant for O_{II} types are of comparable size.

4. Anhydrous Type III 4*f*-Iodates from Ce to Sm

Polycrystalline material only of $Ce(IO_3)_3$, $Pr(IO_3)_3$, $Nd(IO_3)_3$, and $Sm(IO_3)_3$, Type III was obtainable (*7*) by dehydration of the monohydrate. The unit cell dimensions were not determined, but the d-spacings of $Nd(IO_3)_3$, Type III are given as representative of O_{III} in Table V. It may be noted that the O_{III} compounds rapidly hydrate to form the corresponding monohydrate (*7*).

TABLE IV

OBSERVED AND CALCULATED d-SPACINGS[a] AND OBSERVED INTENSITIES OF $Yb(IO_3)_3$ AND $Lu(IO_3)_3$, TYPE II

	$Yb(IO_3)_3$			$Lu(IO_3)_3$		
$h\,k\,l$	d_{obs} (Å)	d_{calc} (Å)	I	d_{obs} (Å)	d_{calc} (Å)	I
$\bar{1}$ 1 1	4.91	4.96	1	—	4.97	< 1
0 1 2	4.74	4.73	1	—	4.74	< 1
1 1 1	4.21	4.27	5	4.21	4.27	1
0 0 4	3.78	3.78	7	3.79	3.79	5
1 1 2	3.67	3.65	2	—	3.66	< 1
$\bar{2}$ 0 4	3.59	3.59	2	—	3.60	< 1
2 0 1	3.47	3.47	4	3.48	3.48	4
$\bar{2}$ 1 3	3.35	3.36	10	3.35	3.36	10
2 1 0	3.27	3.30	9	3.27	3.31	8
0 2 0	3.03	3.03	4	3.03	3.30	3
0 2 1	2.97	2.97	3	2.97	2.97	2
$\bar{3}$ 0 2	2.89	2.89	6	2.89	2.89	6
1 2 0	2.82	2.83	4	2.83	2.83	2
$\bar{1}$ 2 2	2.79	2.79	4	2.80	2.79	2
$\bar{1}$ 0 6	2.75	2.76	5	2.74	2.76	8
0 1 5	2.72	2.71	1	2.72	2.17	1
$\bar{3}$ 1 3	—	2.60	< 1	2.60	2.60	2

[a] Absorption effects displace observed lines with $d > 4$ Å toward higher angles.

TABLE V

Observed *d*-Spacings and Intensities of $Nd(IO_3)_3$, Type III; $La(IO_3)_3$, Type IV; $Ce(IO_3)_3$, Type V; and $La(IO_3)_3$, Type VI

$Nd(IO_3)_3$, Type III		$La(IO_3)_3$, Type IV		$Ce(IO_3)_3$, Type V[a]		$La(IO_3)_3$, Type VI	
d_{obs} (Å)	*I*	d_{obs} (Å)	*I*	d_{obs} (Å)	*I*	d_{obs} (Å)	*I*
4.81	1	4.18	5	4.85	4	4.00	1
3.89	1	3.84	5	3.70	6	3.63	6
3.81	2	3.63	8	3.32	10	3.55	6
3.37	3	3.54	5	3.18	1	3.43	4
3.32	3	3.40	4	3.02	8	3.31	8
3.20	10	3.29	3	2.75	1	3.28	10
3.14	6	3.26	4	2.08	1	3.10	9
3.01	8	3.18	9	1.99	2	2.98	5
2.71	1	3.08	10	1.75	2	2.91	1
2.34	5	3.00	6	1.57	1	2.76	1
2.11	2	2.83	1			2.72	1
2.01	3	2.75	7			2.60	3
1.96	1	2.64	4			2.55	1
1.91	2	2.49	1			2.48	2
1.90	1	2.32	1			2.38	4
1.86	4	2.24	1			2.34	1
1.85	1	2.21	1			2.31	1
1.72	4	2.10	4			2.26	3
1.64	2	2.06	2			2.16	4
		2.03	4			2.12	5
		2.01	2			2.08	9
						2.02	2

[a] Pattern as given is complete to $d = 1.57$ Å.

TABLE VI

Observed and Calculated *d*-Spacings and Observed Intensities of La and $Ce(IO_3)_3 \cdot \frac{1}{2}H_2O$

	$La(IO_3)_3 \cdot \frac{1}{2}H_2O$			$Ce(IO_3)_3 \cdot \frac{1}{2}H_2O$		
h k l	d_{obs} (Å)	d_{calc} (Å)	*I*	d_{obs} (Å)	d_{calc} (Å)	*I*
1 1 1	4.83	4.83	1	4.82	4.84	1
2 1 1	4.39	4.43	5	4.37	4.39	3
3 1 1	3.97	3.94	6	3.96	3.93	5
5 0 0	3.86	3.85	2	3.84	3.79	5
0 2 0	3.70	3.70	1	3.69	3.71	1
1 2 0	3.62	3.63	4	3.62	3.64	3
4 1 1 2 2 0	3.44	3.47 3.45	3	3.43	3.44 3.45	3
0 0 2	3.38	3.38	1	3.37	3.40	3
1 0 2	3.31	3.33	10	3.30	3.34	9
3 2 0	3.26	3.21	6	3.25	3.20	5
6 0 0	3.22	3.21	6	3.23	3.16	5
2 0 2	3.16	3.19	7	3.16	3.16	6
5 1 1	3.05	3.05	9	3.04	3.01	10
3 0 2	3.02	3.00	1	2.96	2.96	1

5. Anhydrous Type IV 4*f*-Iodates, La, Ce and Pr; Anhydrous Type V 4*f*-Iodates, Ce to Sm; Anhydrous Type VI La Iodate

Only polycrystalline material from the three families in this section was obtainable.

TABLE VII

CRYSTALLOGRAPHIC DATA FOR $La(IO_3)_3 \cdot \frac{1}{2}H_2O$ AND $Ce(IO_3)_3 \cdot \frac{1}{2}H_2O$

	$La(IO_3)_3 \cdot \frac{1}{2}H_2O$	$Ce(IO_3)_3 \cdot \frac{1}{2}H_2O$
a (Å)	19.26 ± 1	18.93 ± 5
b (Å)	7.40 ± 1	7.34 ± 2
c (Å)	6.76 ± 1	6.71 ± 1
Volume (Å^3)	963.5	932.3
S.G.	$C222_1$	$C222_1$
Dx (g cm^{-3})	4.64	4.79
Dm (g cm^{-3})	4.7 ± 0.2	—
Z	4	4

Unindexed *d*-spacings and observed intensities for one member of each isostructural family are given in Table V.

Evidence for second harmonic generation has not been found in any of the six structural types in which the 4*f*-anhydrous iodates crystallize.

6. Hemihydrated 4*f*-Iodates, La and Ce

The only rare-earth iodate hemihydrates are formed by La and Ce (7). $La(IO_3)_3 \cdot \frac{1}{2}H_2O$ crystallizes from boiling water in the relatively uncommon space group $C222_1$ (with (hkl) systematically absent for $h + k = 2n + 1$ and $00l$ with $l = 2n + 1$). Under similar conditions, the Ce hemihydrate forms as microcrystalline spherulites, often accompanied by transparent yellow-green crystals of the monohydrate (see Section 7). In some batches, larger crystals of $Ce(IO_3)_3 \cdot \frac{1}{2}H_2O$ also grow. Ap-

TABLE VIII

OBSERVED AND CALCULATED *d*-SPACINGS AND OBSERVED INTENSITIES FOR THE RARE-EARTH IODATE MONOHYDRATES TYPE I

	$Ce(IO_3)_3 \cdot H_2O$			$Pr(IO_3)_3 \cdot H_2O$			$Nd(IO_3)_3 \cdot H_2O$			$Sm(IO_3)_3 \cdot H_2O$		
h k l	d_{obs} (Å)	d_{calc} (Å)	*I*	d_{obs} (Å)	d_{calc} (Å)	*I*	d_{obs} (Å)	d_{calc} (Å)	*I*	d_{obs} (Å)	d_{calc} (Å)	
1 0 0	9.59	9.52	1	—	9.38	< 1	—	9.40	< 1	—	9.29	< 1
0 0 1	—	6.82	< 1	6.67	6.76	1	6.71	6.74	1	—	6.68	< 1
2 0 0	—	4.76	< 1	4.73	4.68	1	4.72	4.71	3	4.65	4.64	1
$\bar{2}$ 1 1	3.95	4.00	1	3.92	3.93	6	3.90	3.92	5	3.88	3.88	5
1 1 1	3.86	3.86	1	3.83	3.83	5	3.82	3.83	4	3.78	3.80	4
$\bar{3}$ 0 1	3.41	3.41	10	3.38	3.38	6	3.37	3.37	5	3.34	3.35	7
0 2 0	3.38	3.38	2	3.35	3.35	4	3.34	3.34	4	3.31	3.32	2
2 0 1	—	3.32	< 1	3.28	3.29	5	3.28	3.30	5	3.26	3.26	6
$\bar{1}$ 1 2	—	3.27	< 1	3.22	3.22	10	3.21	3.21	10	3.18	3.18	10
3 0 0	3.17	3.17	2	3.15	3.12	4	3.14	3.13	4	3.11	3.10	5
$\bar{3}$ 1 1	3.04	3.04	1	3.02	3.02	9	3.01	3.01	9	2.99	2.99	8
2 1 1	2.97	3.02	1	2.95	2.95	7	2.94	2.94	7	2.93	2.90	5
3 1 0	—	2.87	< 1	2.83	2.83	1	2.83	2.84	1	2.79	2.81	1
$\bar{2}$ 2 1	—	2.79	< 1	2.76	2.76	2	2.75	2.75	2	2.72	2.73	3
1 2 1	—	2.75	< 1	2.72	2.72	2	2.72	2.72	2	2.70	2.70	2
$\bar{3}$ 1 2	—	2.75	< 1	2.70	2.70	2	2.69	2.69	1	—	2.66	< 1
$\bar{4}$ 0 1	—	2.60	< 1	2.55	2.55	1	—	2.54	< 1	2.52	2.52	1
$\bar{1}$ 2 2	—	2.50	< 1	2.48	2.48	1	2.47	2.47	1	2.45	2.45	1
0 2 2	—	2.40	< 1	2.38	2.38	3	2.37	2.37	3	2.36	2.36	1
2 2 1	—	2.37	< 1	2.35	2.38	3	2.34	2.35	3	2.33	2.33	1

proximate lattice constants, obtained from single-crystal diffraction photographs, were used as input terms in a least-squares refinement based on the *d*-spacings in Table VI to give the values of Table VII.

Both hemihydrates generate second harmonics, with an efficiency approaching an order of magnitude greater than that of quartz.

7. Monohydrated 4*f*-Iodates, Ce to Sm

The monohydrated 4*f*-iodates crystallize from boiling water in the monoclinic system. Powder patterns of $Ce(IO_3)_3 \cdot \frac{1}{2}H_2O$ (Table VI) and $Ce(IO_3)_3 \cdot H_2O$ (Table VIII) are very similar, although the single crystal diffraction symmetry reveals the difference in crystal systems. Accurate lattice constants measured for $Nd(IO_3)_3 \cdot H_2O$ (*9*) and given in Table IX allowed the powder patterns for the four members of this family to be indexed (Table VIII). Lattice constants for Ce, Pr, and Sm iodate monohydrate were thereby obtained using least-squares refinement (Table IX). A *B*-centered cell may be derived from the constants of Table IX to give $a' = 19.067$,

TABLE IX

CRYSTALLOGRAPHIC DATA FOR THE MONOHYDRATED 4*f*-IODATES, TYPE I, FROM Ce TO Sm

	$Ce(IO_3)_3 \cdot H_2O$	$Pr(IO_3)_3 \cdot H_2O$	$Nd(IO_3)_3 \cdot H_2O$[a]	$Pm(IO_3)_3 \cdot H_2O$[b]	$Sm(IO_3)_3 \cdot H_2O$
a (Å)	10.428 ± 17	10.198 ± 9	10.2012 ± 13	10.172 ± 13	10.080 ± 7
b (Å)	6.760 ± 33	6.706 ± 7	6.70530 ± 4	6.700 ± 20	6.642 ± 6
c (Å)	7.469 ± 7	7.357 ± 9	7.3538 ± 9	7.289 ± 24	7.250 ± 8
β	114.1 ± 0.1°	113.3 ± 0.1°	113.11 ± 0.02°	113.1 ± 0.2°	112.9 ± 0.1°
Volume (Å^3)	480.6	462.1	462.65	456.9	447.1
S.G.	$P2_1$	$P2_1$	$P2_1$	$P2_1$	$P2_1$
Dx (g cm^{-3})	4.72	4.91	4.93	5.00	5.15
Dm (g cm^3)	—	—	4.80 ± 0.1	—	—
Z	2	2	2	2	2

[a] Ref. (*9*).

[b] Data based on powder photograph *d*-spacings for $Pm(IO_3)_3 \cdot xH_2O$, Ref. (*10*); see text.

TABLE X

CRYSTALLOGRAPHIC DATA FOR THE RARE-EARTH IODATE DIHYDRATES
TYPE I

	$Tm(IO_3)_3 \cdot 2H_2O$	$Yb(IO_3)_3 \cdot 2H_2O$	$Lu(IO_3)_3 \cdot 2H_2O$
a (Å)	8.233 ± 13	8.217 ± 18	8.018 ± 12
b (Å)	10.134 ± 14	10.074 ± 19	9.956 ± 21
c (Å)	7.015 ± 13	7.037 ± 22	6.969 ± 16
α	100.5 ± 0.2°	100.0 ± 0.3°	99.8 ± 0.2°
β	94.9 ± 0.2°	94.1 ± 0.6°	93.8 ± 0.2°
γ	66.6 ± 0.1°	66.3 ± 0.2°	68.2 ± 0.2°
Volume (Å^3)	528.1	525.1	508.9
S.G.	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	2	2	2
Dx (g cm^{-3})	4.59	4.64	4.80
Dm (g cm^{-3})	4.5 ± 0.1	—	—

TABLE XI

OBSERVED AND CALCULATED *d*-SPACINGS AND OBSERVED INTENSITIES FOR THE RARE-EARTH IODATE DIHYDRATES TYPE I

	$Tm(IO_3)_3 \cdot 2H_2O$			$Yb(IO_3)_3 \cdot 2H_2O$			$Lu(IO_3)_3 \cdot 2H_2O$		
h k l	d_{obs} (Å)	d_{calc} (Å)	*I*	d_{obs} (Å)	d_{calc} (Å)	*I*	d_{obs} (Å)	d_{calc} (Å)	*I*
0 1 0	9.11	9.18	2	9.02	9.10	2	9.04	9.13	2
0 0 1	6.92	6.90	5	6.91	6.93	5	6.85	6.87	2
$\bar{1}$ $\bar{1}$ 1	5.39	5.46	8	5.31	5.44	8	5.31	5.32	4
0 1 1	5.13	5.13	3	5.13	5.14	3	5.11	5.11	2
0 2 0	4.55	4.59	1	—	4.55	< 1	4.55	4.56	1
0 $\bar{2}$ 1	4.14	4.14	1	4.12	4.12	1	4.14	4.11	2
$\bar{1}$ 1 1	3.87	3.89	3	3.86	3.86	2	3.85	3.86	3
2 0 0	3.77	3.78	3	3.76	3.76	2	3.73	3.72	2
0 2 1	3.57	3.56	5	3.56	3.55	5	3.56	3.55	5
$\bar{2}$ $\bar{2}$ 1	3.49	3.49	4	3.48	3.47	4	—	3.47	< 1
0 0 2	3.45	3.45	10	3.44	3.42	10	3.44	3.43	6
$\bar{1}$ 2 0	3.36	3.38	4	3.35	3.35	6	3.34	3.38	4
2 0 1	3.27	3.29	6	3.27	3.30	8	3.26	3.27	4
1 $\bar{2}$ 1	3.18	3.18	6	3.18	3.16	7	3.18	3.18	4
$\bar{2}$ 1 0	3.10	3.09	6	3.09	3.08	6	3.08	3.08	4
0 3 0	3.05	3.06	7	3.05	3.03	7	3.05	3.04	10
2 3 0	3.02	3.02	5	3.02	3.02	4	3.02	3.03	2
0 $\bar{3}$ 1	2.98	2.98	5	2.97	2.96	5	2.97	2.96	3
$\bar{1}$ 2 1	2.91	2.91	1	2.91	2.89	1	2.90	2.90	1
$\bar{2}$ 1 1	2.78	2.78	6	2.77	2.76	4	2.77	2.77	4
3 2 0	2.68	2.69	9	2.67	2.69	7	2.66	2.66	6
0 3 1	—	2.64	< 1	2.64	2.63	1	2.62	2.62	1

TABLE XII

CRYSTALLOGRAPHIC DATA FOR THE DIHYDRATED 4*f*-IODATES OF TYPE II FROM Nd TO Er, INCLUDING Y

Rare earth	*a* (Å)	*b* (Å)	*c* (Å)	*α* (°)	*β* (°)	*γ* (°)	Volume (Å^3)	*Dx* (g cm^{-3})[a]
Nd	7.56 ± 4	10.77 ± 5	7.34 ± 2	105.3 ± 0.4	110.8 ± 0.7	97.9 ± 0.6	520.7	4.50
Sm	7.53 ± 3	10.77 ± 4	7.35 ± 2	105.3 ± 0.3	110.5 ± 0.4	98.2 ± 0.5	519.7	4.54
Eu	7.47 ± 3	10.66 ± 3	7.33 ± 2	105.1 ± 0.2	110.9 ± 0.3	97.6 ± 0.3	510.1	4.64
Gd	7.51 ± 2	10.61 ± 2	7.34 ± 1	104.6 ± 0.1	110.8 ± 0.2	97.5 ± 0.2	513.1	4.65[b]
Tb	7.47 ± 2	10.66 ± 3	7.34 ± 1	104.8 ± 0.1	111.0 ± 0.3	97.5 ± 0.4	511.0	4.68
Dy	7.50 ± 3	10.69 ± 3	7.31 ± 2	105.1 ± 0.3	110.8 ± 0.3	97.9 ± 0.3	511.8	4.69
Ho	7.51 ± 2	10.68 ± 2	7.26 ± 1	104.4 ± 0.1	111.6 ± 0.2	98.3 ± 0.1	506.2	4.76
Er	7.50 ± 1	10.73 ± 2	7.28 ± 1	104.4 ± 0.2	111.5 ± 0.1	98.3 ± 0.2	509.1	4.75
Y	7.48 ± 2	10.70 ± 3	7.29 ± 2	104.6 ± 0.3	110.9 ± 0.3	98.3 ± 0.3	509.0	4.24

[a] For two formula weights per unit cell, in space group $P\bar{1}$.

[b] $Dm = 4.7 \pm 0.1$ g cm^{-3}.

TABLE XIII

Observed and Calculated Debye–Scherrer *d*-Spacings[a] in Ångstroms and Observed Relative Intensities of the Dihydrated 4*f*-Iodates, Type II, from Nd to Er, Including Y

	$Nd(IO_3)_3\cdot 2H_2O$			$Sm(IO_3)_3\cdot 2H_2O$			$Eu(IO_3)_3\cdot 2H_2O$			$Gd(IO_3)_3\cdot 2H_2O$			$Tb(IO_3)_3\cdot 2H_2O$			$Dy(IO_3)_3\cdot 2H_2O$			$Ho(IO_3)_3\cdot 2H_2O$			$Er(IO_3)_3\cdot 2H_2O$			$Y(IO_3)_3\cdot 2H_2O$		
$h\,k\,l$	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I	d_{obs}	d_{calc}	I
0 1 0	9.97	10.04	2	9.94	10.03	2	—	9.97	< 1	—	9.96	< 1	9.78	9.99	3	9.83	9.98	3	9.65	9.98	2	9.75	10.03	3	9.73	10.00	2
1 0 0	6.80	6.83	3	6.74	6.81	4	6.73	6.75	3	6.72	6.72	2	6.73	6.76	6	6.76	6.78	6	6.71	6.74	4	6.73	6.73	5	6.73	6.75	3
0 0 1	6.44	6.44	1	—	6.58	< 1	—	6.41	< 1	—	6.42	< 1	—	6.43	< 1	—	6.49	< 1	—	6.41	< 1	—	6.43	< 1	—	6.36	< 1
$\bar{1}\,\bar{1}\,1$	5.37	5.44	1	5.34	5.42	4	5.30	5.40	2	5.31	5.40	2	5.30	5.40	5	5.31	5.40	5	5.30	5.36	3	5.30	5.38	4	5.28	5.37	3
$\bar{1}\,\bar{2}\,1$	—	4.06	< 1	4.06	4.04	2	4.01	4.03	2	—	4.03	< 1	4.02	4.03	2	4.03	4.04	3	4.00	4.01	1	4.01	4.02	2	4.00	4.01	2
$\bar{2}\,0\,1$	3.72	3.71	9	3.70	3.70	10	3.68	3.67	10	3.69	3.69	10	3.68	3.67	10	3.68	3.68	10	3.66	3.69	10	3.68	3.68	10	3.67	3.67	8
1 2 0	3.64	3.63	8	3.63	3.61	7	3.60	3.60	5	3.62	3.62	4	3.62	3.61	3	3.62	3.61	2	3.61	3.59	1	3.63	3.60	2	3.61	3.60	1
$\bar{1}\,\bar{1}\,2$	—	3.61	< 1	—	3.61	< 1	—	3.60	< 1	—	3.60	< 1	3.60	3.60	3	3.59	3.59	2	3.57	3.57	1	3.58	3.58	2	3.57	3.58	2
$0\,\bar{3}\,1$	3.49	3.49	8	3.50	3.49	1	3.46	3.46	1	3.48	3.44	1	3.46	3.46	2	3.47	3.46	3	3.45	3.45	3	—	3.47	< 1	—	3.46	< 1
$0\,\bar{1}\,2$	—	3.43	< 1	3.45	3.44	8	3.43	3.43	7	3.43	3.43	3	3.43	3.42	7	3.42	3.42	5	3.40	3.39	4	3.42	3.39	6	3.41	3.40	3
$\bar{2}\,\bar{1}\,1$	—	3.39	< 1	3.38	3.37	5	3.36	3.36	4	3.38	3.38	5	3.36	3.36	7	3.37	3.36	6	3.36	3.36	4	3.36	3.35	7	3.35	3.35	2
0 3 0	3.36	3.35	10	3.34	3.34	5	3.32	3.32	6	3.32	3.32	5	3.32	3.33	7	3.31	3.33	4	3.30	3.30	4	3.30	3.34	5	3.30	3.33	3
$\bar{1}\,\bar{2}\,2$	3.29	3.27	2	3.26	3.27	3	3.25	3.26	3	3.25	3.25	3	3.25	3.26	5	3.24	3.25	4	3.23	3.23	4	3.24	3.24	4	3.23	3.24	2
$1\,\bar{3}\,1$	3.19	3.17	4	3.19	3.18	5	3.16	3.13	9	3.16	3.12	8	3.15	3.12	8	3.15	3.14	9	3.13	3.13	9	3.14	3.14	9	3.14	3.14	10
$\bar{1}\,1\,2$	3.11	3.11	4	3.11	3.11	4	3.11	3.11	7	3.12	3.12	3	3.12	3.12	6	3.11	3.10	4	3.10	3.10	9	3.11	3.11	10	3.11	3.11	9
$\bar{1}\,\bar{3}\,1$	3.05	3.05	3	3.04	3.04	4	3.04	3.03	2	—	3.02	< 1	3.04	3.03	2	3.04	3.03	2	3.03	3.02	3	3.04	3.03	3	3.03	3.02	4
$\bar{2}\,\bar{1}\,2$	—	3.00	< 1	—	2.99	< 1	3.02	2.98	2	—	2.98	< 1	3.02	2.98	1	3.00	2.98	2	—	2.97	< 1	3.00	2.98	3	—	2.96	< 1
2 1 0	—	3.01	< 1	2.99	3.00	1	2.98	2.98	2	—	3.01	< 1	2.98	3.00	2	2.98	2.99	1	2.97	2.97	2	2.99	2.97	3	2.97	2.97	3
$0\,\bar{3}\,2$	—	2.85	< 1	—	2.86	< 1	—	2.83	< 1	—	2.83	< 1	—	2.83	< 1	—	2.81	< 1	—	2.81	< 1	—	2.82	< 1	—	2.82	< 1
1 3 0	2.74	2.74	1	2.73	2.73	9	2.72	2.72	8	2.72	2.73	6	2.71	2.74	9	—	2.72	< 1	2.71	2.72	7	2.72	2.72	4	2.71	2.72	3
0 3 1	—	2.63	< 1	—	2.63	< 1	2.63	2.62	3	—	2.63	< 1	—	2.63	< 1	—	2.65	< 1	2.65	2.65	4	2.66	2.66	4	—	2.63	< 1
$\bar{1}\,2\,2$	2.63	2.61	1	—	2.61	< 1	2.61	2.61	3	2.62	2.62	2	—	2.62	< 1	—	2.60	< 1	2.60	2.60	7	2.62	2.62	6	2.60	2.61	5
2 2 0	2.53	2.54	2	—	2.53	< 1	2.52	2.52	4	2.52	2.54	1	—	2.54	< 1	—	2.52	< 1	—	2.51	< 1	2.50	2.50	2	—	2.50	< 1
$\bar{1}\,\bar{1}\,3$	2.44	2.44	4	—	2.44	< 1	—	2.44	< 1	2.42	2.44	7	—	2.44	< 1	—	2.43	< 1	—	2.42	< 1	2.41	2.41	8	—	2.41	< 1
$\bar{2}\,\bar{1}\,3$	2.31	2.33	4	—	2.33	< 1	—	2.33	< 1	2.32	2.33	2	—	2.33	< 1	—	2.32	< 1	—	2.32	< 1	—	2.31	< 1	—	2.31	< 1
$\bar{2}\,4\,0$	—	2.33	< 1	—	2.33	< 1	—	2.33	< 1	2.29	2.29	2	—	2.29	< 1	—	2.28	< 1	—	2.28	< 1	—	2.27	< 1	—	2.27	< 1

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[a] See footnote to Table IV.

TABLE XIV

OBSERVED *d*-SPACINGS AND INTENSITIES OF $Gd(IO_3)_3 \cdot 4H_2O$ AND $Lu(IO_3)_3 \cdot 4H_2O$

$Gd(IO_3)_3 \cdot 4H_2O$		$Lu(IO_3)_3 \cdot 4H_2O$	
d_{obs} (Å)	I	d_{obs} (Å)	I
9.43	3	—	
7.54	4	7.55	4
7.16	3	7.06	4
5.11	2	5.05	4
4.94	2	4.92	3
3.85	5	3.85	5
3.77	7	3.79	4
3.60	4	3.72	3
3.43	5	3.56	4
3.40	4	3.35	10
3.31	10	3.28	3
3.04	1	3.24	1
3.00	1	3.00	2
2.96	2	2.93	4
2.86	3	2.78	3
2.77	1	2.75	6
2.75	4	2.64	1
2.65	4	2.59	1
2.62	2	2.54	1
2.57	3		

$b' = 6.760$, $c' = 7.469$ Å and $\beta = 93.1°$ which, except for small distortions, is identical with the orthorhombic cell of the corresponding $Ce(IO_3)_3 \cdot \frac{1}{2}H_2O$. Table IX also contains the lattice constants of isomorphous $Pm(IO_3)_3 \cdot H_2O$, derived from the powder data given for "$Pm(IO_3)_3 \cdot xH_2O$" by Scherer (*10*) and refined by the method of least squares.

The detailed crystal structure of $Nd(IO_3)_3 \cdot H_2O$ has now been determined (*9*), but the structural effect of removing half the water has not yet been investigated.

The monohydrate structure is polar, with strong pyroelectric and piezoelectric coefficients (*11*), and it generates second harmonics with an efficiency about an order of magnitude greater than quartz.

8. Dihydrated 4*f*-Iodates, Type I: Tm to Lu

The rare-earth iodate dihydrates of Type I crystallize from boiling aqueous solution in the triclinic system. The reduced cell crystallographic data for the three members of this family are given in Table X, with lattice constants obtained (*8*), by the method of least

TABLE XV

OBSERVED *d*-SPACINGS AND INTENSITIES OF Ce, Pr, Nd, AND $Sm(IO_3)_3 \cdot 5H_2O$, TYPE I

$Ce(IO_3)_3 \cdot 5H_2O$[a]		$Pr(IO_3)_3 \cdot 5H_2O$		$Nd(IO_3)_3 \cdot 5H_2O$		$Sm(IO_3)_3 \cdot 5H_2O$[a]	
d_{obs} (Å)	I	d_{obs} (Å)	I	d_{obs} (Å)	I	d_{obs} (Å)	I
4.25	1	6.87	2	11.41	1	3.52	10
3.70	1	6.52	2	6.51	1	3.31	4
3.58	10	4.88	1	5.97	1	3.23	4
3.32	1	4.37	1	3.99	2	2.96	5
3.19	3	4.00	2	3.87	1		
3.18	2	3.75	3	3.74	3		
3.00	1	3.67	2	3.56	10		
2.85	1	3.57	10	3.37	1		
2.81	1	3.30	5	3.31	3		
2.76	1	3.18	8	3.17	3		
2.60	1	3.09	4	3.09	1		
2.45	1	3.00	5	2.99	2		
2.33	1	2.95	4	2.80	1		
2.23	2	2.89	2	2.60	1		
		2.81	3				
		2.75	3				
		2.68	2				
		2.61	3				

[a] Best patterns available.

squares by fitting precession- and Weissenberg-derived initial values to the *d*-spacings given in Table XI. The unit cell contains two formulas of rare-earth iodate dihydrate. The lack of second harmonic generation shows the space group to be the centrosymmetric $P\bar{1}$.

9. Dihydrated 4*f*-Iodates, Type II: Nd to Er

The eight isostructural Type II rare-earth and yttrium iodate dihydrates crystallize in the triclinic system, from boiling aqueous solution, as does the Type I family. Approxi-

TABLE XVI

OBSERVED AND CALCULATED *d*-SPACINGS AND OBSERVED INTENSITIES FOR RARE-EARTH IODATE PENTAHYDRATES TYPE II

	$La(IO_3)_3 \cdot 5H_2O$			$Pr(IO_3)_3 \cdot 5H_2O$		
h k l	d_{obs} (Å)	d_{calc} (Å)	*I*	d_{obs} (Å)	d_{calc} (Å)	*I*
0 2 0	11.55	11.57	6	11.49	11.56	6
0 0 1	6.64	6.58	1	—	6.56	< 1
0 4 0	5.79	5.79	1	5.74	5.78	1
$\bar{1}$ 2 1	5.19	5.14	1	5.16	5.16	1
$\bar{1}$ 3 1	4.56	4.60	5	4.58	4.62	3
1 4 0	—	4.24	< 1	4.18	4.24	1
$\bar{1}$ 4 1	4.01	4.07	2	—	4.08	< 1
0 6 0	3.89	3.86	4	3.87	3.85	4
1 5 0	3.71	3.71	6	3.69	3.72	6
$\bar{1}$ 5 1	—	3.60	< 1	3.60	3.61	2
$\bar{1}$ 0 2	3.50	3.51	3	3.52	3.51	2
$\bar{1}$ 1 2	—	3.47	< 1	3.48	3.47	2
1 3 1	3.45	3.45	8	3.41	3.44	8
1 6 0	—	3.28	< 1	3.28	3.28	1
$\bar{1}$ 3 2	3.21	3.20	2	3.20	3.20	1
0 2 2	3.17	3.17	7	3.15	3.15	5
$\bar{2}$ 3 1	3.07	3.07	2	—	3.09	< 1
0 3 2	3.03	3.03	10	3.01	3.02	10
0 7 1	2.95	2.95	4	2.94	2.95	2
$\bar{2}$ 4 1	2.89	2.90	1	—	2.91	< 1
$\bar{1}$ 5 2	2.82	2.80	2	2.81	2.80	1
$\bar{2}$ 3 2	2.71	2.69	1	2.69	2.70	1
0 8 1	2.66	2.65	1	—	2.64	< 1
1 0 2	2.54	2.54	1	2.53	2.53	1
0 6 2	2.50	2.50	1	—	2.50	< 1
1 3 2	2.43	2.41	1	2.41	2.40	1
0 9 1	2.39	2.39	1	—	2.39	< 1
1 9 0	2.37	2.38	1	—	2.38	< 1
$\bar{1}$ 3 3	2.27	2.27	3	2.26	2.26	2
$\bar{3}$ 0 1	2.25	2.24	2	2.25	2.25	2
0 3 3	2.11	2.11	1	2.10	2.10	1
$\bar{1}$ 9 2	2.08	2.07	2	2.06	2.07	3
1 10 1	1.987	1.983	2	1.974	1.981	5
$\bar{2}$ 10 1	1.903	1.903	8	1.897	1.906	7
2 8 1	1.878	1.880	2	1.874	1.879	1
1 11 1	1.848	1.846	3	1.836	1.844	4

mate lattice constants, obtained from single crystal diffraction photographs of $Nd(IO_3)_3 \cdot 2H_2O$, Type II, refined to the values given in Table XII using the method of least-squares (*8*) and the *d*-spacings of Table XIII. The powder pattern of the $Sm(2_{II})$ compound could thus be indexed (Table XIII) and the lattice constants refined as in Table XII, and so on, for the remaining members of the Type II family. The unit cell volume of $Er(2_{II})$ is significantly smaller than that of $Tm(2_I)$, indicating the packing in the Type II family to be appreciably more efficient than in Type I.

Type II dihydrates do not generate second harmonics; hence, the space group is taken to be $P\bar{1}$.

10. Tetrahydrated 4*f*-Iodates, Gd to Lu

The rare-earth iodate tetrahydrates are obtained at room temperature either by precipitation, by gel growth, or by evaporation of aqueous solution (*6*). The largest crystals grown had dimensions less than 10 μm; hence, single crystal data were not measured. Powder patterns for the end isostructural members of this family are given in Table XIV. No second harmonic generation is observed.

11. Pentahydrated 4*f*-Iodates, Type I: Ce to Sm

Polycrystalline pentahydrates of Type I are prepared by the same methods as the tetrahydrates, with maximum dimensions less than 10 μm. Powder patterns for the four Type I pentahydrates are given in Table XV. These powders do not generate second harmonics.

12. Pentahydrated 4*f*-Iodates, Type II: La and Pr

$La(IO_3)_3 \cdot 5H_2O$ and $Pr(IO_3)_3 \cdot 5H_2O$, Type II, crystallize by slow evaporation from aqueous solution or by gel growth (*7*) in the monoclinic system. Single crystal diffraction photographs show the only systematic absences to be in $0k0$ with $k = 2n + 1$, leading to the assignment of space groups $P2_1$ or $P2_1/m$. The lack of second harmonic generation indicates the centrosymmetric choice. Approximate lattice constants obtained from precession photographs were used both to index the *d*-spacings given in Table XVI, and as initial values in least-squares refinement (*8*), leading to the final values of Table XVII.

TABLE XVII

CRYSTALLOGRAPHIC DATA FOR $La(IO_3)_3 \cdot 5H_2O$ AND $Pr(IO_3)_3 \cdot 5H_2O$, TYPE II

	$La(IO_3)_3 \cdot 5H_2O$	$Pr(IO_3)_3 \cdot 5H_2O$
a (Å)	6.722 ± 9	6.768 ± 8
b (Å)	23.141 ± 16	23.120 ± 39
c (Å)	7.113 ± 6	7.107 ± 7
β	112.3 ± 0.1°	112.7 ± 0.1°
Volume (Å^3)	1023.7	1025.9
S.G.	$P2_1/m$	$P2_1/m$
Z	4	4
Dx (g cm^{-3})	4.89	4.89
Dm (g cm^{-3})	—	4.7 ± 0.2

13. Summary

Thirteen crystallographically distinct families of 4*f*-iodates, including hydrates, have been investigated. The hemihydrate and monohydrate are noncentrosymmetric, generating second harmonics. Small single crystals, large enough for measurement of lattice constants, were prepared for seven families, including the two that are noncentrosymmetric.

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