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Crystal Growth and Magnetic Susceptibility of Some Rare-Earth Compounds

Part 1 *Crystal Growth*

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Single crystals of the following types of rare-earth compounds have been obtained by the fluxed-melt method of crystal growth: ROF, $R_2Ti_2O_7$, R_2TiO_5, $RNbO_4$, R_3NbO_7 (R = rare-earth metal). The experimental conditions are described and X-ray diffraction data are presented for compounds not previously reported.

1. Introduction

Compounds containing closely-spaced rare-earth ions are of interest as they may become magnetically ordered at low temperatures. In recent years, the magnetic properties of rare-earth garnets have been intensively investigated. This paper describes the preparation as small crystals of several other groups of rare-earth compounds which, because they are sufficiently concentrated as regards their rare-earth ion content, may be of interest for magnetic experiments.

A number of the compounds we have prepared as crystals have a range of compositions. This non-stoichiometry makes chemical analysis necessary before calculations concerning their magnetic properties can be carried out. Though the chemical composition of sintered samples is known, such samples often lead to unreliable results because of incomplete combination, producing more than one phase, or surface effects when the particle size is small.

Flux-grown material has the disadvantage that ions from the flux are invariably incorporated into the crystals. However, the amount incorporated is usually too low to affect the magnetic behaviour.

Although it may be possible to prepare some of the compounds described by melting the components, it would first be necessary to establish that congruent melting occurred. The melting points of these complex oxides are likely to be high, leading to container problems during melting.

The fluxed-melt method thus seemed the most advantageous and widely applicable for the preparation of a range of compounds of different types, particularly as the products were intended for preliminary magnetic investigations.

Representatives of the following groups of rare-earth compounds: (i) ROF, (ii) $R_2Ti_2O_7$, (iii) R_2TiO_5, (iv) $RNbO_4$, (v) R_3NbO_7, (R = rare-earth metal) have been obtained from a fluxed-melt in the form of single crystals which are large enough to be useful for epr or optical experiments.

2. Experimental

Platinum crucibles with tightly fitting lids were used in a furnace heated from above. Compositions and conditions for preparation of crystals of the size described are given in table I. 1% PbO_2 was included in each PbO/PbF_2 melt, to provide initially an oxidising atmosphere. Crucibles were held overnight at the maximum temperature before cooling was started.

In some cases, evaporation at constant temperature yielded the desired phase, whereas slow cooling produced compounds with the flux. Evaporation was facilitated by pressing inwards a portion of the upper rim of the crucible,

TABLE I Conditions for flux growth of ROF, $R_2Ti_2O_7$, R_2TiO_5, R_3NbO_7, $RNbO_4$.

Compound	Composition	Cooling conditions or temperature of evaporation	Product
YOF	21 g Y_2O_3, 200 g PbF_2	1340 to 900° C at 3°/h	Platelets 3 × 2 mm
GdOF	7.4 g Gd_2O_3, 1.5 g Al_2O_3, 30 g PbO, 20 g PbF_2	1280 to 845° C at 3°/h	$GdAlO_3$ + GdOF
TbOF	10 g Tb_4O_7, 2 g Al_2O_3, 34 g PbO, 34 g PbF_2	,,	$TbAlO_3$ + TbOF
DyOF	12 g Dy_2O_3, 3 g Al_2O_3, 65 g PbO, 35 g PbF_2	,,	$Dy_3Al_5O_{12}$ + DyOF
HoOF	12 g Ho_2O_3, 2 g Al_2O_3, 45 g PbO, 35 g PbF_2	,,	$HoAlO_3$ + HoOF
ErOF	9.3 g Er_2O_3, 2.4 g Al_2O_3, 48 g PbO, 32 g PbF_2	,,	$Er_3Al_5O_{12}$ + ErOF
$R_2Ti_2O_7$, R = Gd, Tb, Dy, Ho	3.6 g Gd_2O_3, 1.6 g TiO_2, 36 g PbF_2	Held at 1235° C for 1 week	Octahedra up to 3 mm across
R_2TiO_5, R = Gd, Dy	8.4 g Dy_2O_3, 3.6 g TiO_2, 140 g PbO	1280 to 940° C at 3°/h	Transparent platelets or rods up to 3 mm long
$RNbO_4$, R = La to Yb, and Y	7.4 g Yb_2O_3, 5 g Nb_2O_5, 64.3 g Bi_2O_3, 2.2 g B_2O_3	1340 to 1050° C at 3°/h	Bipyramids up to 5 mm across
	6.8 g Gd_2O_3, 5 g Nb_2O_3, 75 g PbF_2	Held at 1260° C for 1 week	Platelets, 4 mm across
R_3NbO_7, R = Nd, Gd, Tb, Dy, and Hp	10.2 g Gd_2O_3, 7.5 g Nb_2O_5, 30 g PbF_2, 150 g PbO	1285 to 950° C at 2°/h	Pseudo-cubes, 1 mm$_3$

leaving a gap under the lid. Best results were obtained when evaporation was allowed to proceed to completion.

X-ray diffraction powder diagrams were obtained either with a Philips 11.84 cm diameter camera or a Philips PW diffractometer fitted with a single-crystal monochromator.

2.1. Rare-Earth Oxyfluorides ROF

The stoichiometric oxyfluorides have a fluorite structure[1-3] which is rhombohedrally distorted. Fluoride ions may substitute partially for O^{2-}, necessitating the incorporation of an equal number of F^- ions elsewhere in the lattice; in this case, the unit cell dimensions increase slightly, and the structure undergoes a tetragonal distortion.

Several methods were attempted to crystallise ROF, based on Nielsen's observation [4] of rod-like crystals of YOF when yttrium iron garnet was grown from a PbO/PbF_2 melt, rich in Y_2O_3.

(*a*) Solution of R_2O_3 in PbF_2/PbO flux at about 1340° C, followed by cooling at 3°/h to 900° C: this was successful only in the case of YOF, producing tabular crystals up to 4 × 2 mm. The powder pattern corresponded to that of tetragonal YOF [5]. Cooling from 1400° at 2/3 resulted in glossy cubes of Y_2O_3 at the melt surface.

(*b*) Complete evaporation of the solvent from a solution of Dy_2O_3 in PbF_2/PbO at 1230° C resulted in granular material which had the powder pattern of Dy_2O_3.

(*c*) Solutions of R_2O_3 + Al_2O_3 in PbF_2/PbO, richer in R_2O_3 than required to produce the corresponding aluminates or garnets, were cooled slowly from 1280 to 900° C. The flux was dissolved in dilute HNO_3, allowing crystals of ROF to be separated from garnet or aluminate, either visually or with the aid of a polarising microscope. Pseudo-cubes, up to 1 mm on edge, of GdOF, TbOF, DyOF, HoOF, and ErOF, were obtained, but the method failed with YOF. The X-ray powder patterns of GdOF, DyOF, and ErOF corresponded closely to that of tetragonal YOF [5]. The powder patterns of TbOF and HoOF corresponded to that of rhombohedral TbOF [6]. As all these oxyfluorides were prepared under similar conditions, it is not clear why only TbOF and HoOF should have the stoichiometric rhombohedral form. Table II gives the observed unit cell dimensions of these compounds.

(*d*) Oxyfluoride crystals were also produced when the rare-earth orthoferrites were crystallised from $PbO/PbF_2/B_2O_3$ melts containing excess rare-earth oxide. HoOF was prepared in this way as thin plates up to 6 × 1 mm, using a

TABLE II Unit cells of rare-earth oxyfluorides

Tetragonal		Rhombohedral (hexagonal unit cells given)	
GdOF	$a_0 = 3.96$ Å, $c_0 = 5.50$ Å	TbOF	$a_0 = 3.85$ Å, $c_0 = 18.97$ Å
DyOF	$a_0 = 3.91$ Å, $c_0 = 5.45$ Å	HoOF	$a_0 = 3.79$ Å, $c_0 = 18.86$ Å
ErOF	$a_0 = 3.88$ Å, $c_0 = 5.39$ Å		

50 cm^3 crucible. Its X-ray powder pattern closely resembled that of tetragonal YOF [5].

2.2. Rare-Earth Titanates, $R_2Ti_2O_7$

The system Y_2O_3/TiO_2 contains two compounds, Y_2TiO_5 and $Y_2Ti_2O_7$ [7], each of which has a limited range of composition. $Y_2Ti_2O_7$ [8], $Gd_2Ti_2O_7$ and $Dy_2Ti_2O_7$ [9] have been investigated in the form of ceramic samples. $Y_2Ti_2O_7$ has a pyrochlore structure with $a_0 = 10.09$ to 10.13 Å [7, 8] corresponding to a variation in mole % Y_2O_3 from 29 to 42.

Attempts to prepare $R_2Ti_2O_7$ by slowly cooling its solution in PbF_2 or PbF_2/PbO were unsuccessful, owing to partial combination of the components with the flux. Octahedral crystals of $R_2Ti_2O_7$ up to 3 mm across were prepared by evaporating to completion their solution in PbF_2 at 1230° C.

The crystals were yellow or brownish, and isotropic. Their powder patterns were similar to that of the mineral pyrochlore [10] and were identical to those of samples produced by sintering (R_2O_3 + $2TiO_2$) at 1250° C. The unit cell dimensions found for $Gd_2Ti_2O_7$ and $Dy_2Ti_2O_7$ were close to those given by Roth [9]. Table III gives the unit cell dimensions of $Gd_2Ti_2O_7$, $Tb_2Ti_2O_7$, $Dy_2Ti_2O_7$, and $Ho_2Ti_2O_7$ crystals as prepared in this way.

TABLE III Unit cells of $R_2Ti_2O_7$

Cubic
$Gd_2Ti_2O_7$, $a_0 = 10.17$ Å
$Tb_2Ti_2O_7$, $a_0 = 10.14$ Å
$Dy_2Ti_2O_7$, $a_0 = 10.09$ Å
$Ho_2Ti_2O_7$, $a_0 = 10.07$ Å

2.3. Rare-Earth Titanates, R_2TiO_5

Y_2TiO_5 was prepared in polycrystalline form by Ault and Welch [7] who described it as an anomalous fluorite compound, because a fluorite structure would not be expected from the radius ratio of Y and Ti. Powder samples were also used by Collongues *et al* [11] who assigned a monoclinic unit cell to the compound. A single-crystal study by Guillen and Bertaut [12] of La_2TiO_5 (grown by the Verneuil method) showed it to be orthorhombic, with $a_0 = 10.97$ Å, $b_0 = 11.37$ Å, $c_0 = 3.93$ Å, space group Pnam. This has 5-co-ordinated Ti-ions.

Dy_2TiO_5 and Gd_2TiO_5 were prepared as platelets or rods by cooling a solution of composition (R_2O_3 + $2TiO_2$) in PbO. The transparent platelets, up to 1 × 2 mm in size, had colours characteristic of the rare-earth ions and showed sharp extinction under the polarising microscope. The strong lines of their powder patterns indicated a fluorite type of pseudo-cell, but there were many additional lines.

A sample of composition (Y_2O_3 + TiO_2) was sintered at 1250° C, but complete combination did not occur. Besides X-ray diffraction lines presumably due to Y_2TiO_5, as they corresponded closely to those of the R_2TiO_5 crystals, the lines of Y_2O_3 and $Y_2Ti_2O_7$ were present.

The molar percentage of Y_2O_3 in the Y_2TiO_5 phase has been found to vary from 46 to 61 [7]. X-ray fluorescence analysis of Gd_2TiO_5 crystals showed them to contain 55 mole % Gd_2O_3 and 45 mole % TiO_2. About 4% PbO by weight was also present in the sample analysed, either as occluded flux or substituting for Gd^{3+} in the lattice.

Single-crystal X-ray photographs of Gd_2TiO_5 crystals showed the unit cell to be orthorhombic, with $a_0 = 10.48$ Å, $b_0 = 11.25$ Å, $c_0 = 3.70$ Å, space group Pnam, like La_2TiO_5 [12].

Table IV gives the unit cell dimensions and X-ray powder pattern data for Y_2TiO_5, Gd_2TiO_5, and Dy_2TiO_5.

2.4. Rare-Earth Orthoniobates, $RNbO_4$

The system R_2O_3/Nb_2O_5 contains three compounds [13], R_3NbO_7 [14], $RNbO_4$ [15], and RNb_3O_9 [16]. The crystal growth of $NdNbO_4$ by cooling its solution in PbF_2 has been described [17].

$RNbO_4$ at room temperature has a monoclinic unit cell, resulting from a crystallographic transition from the tetragonal, scheelite form at 800° C [15]. We found that cooling a solution of $HoNbO_4$ in PbF_2 did not produce $HoNbO_4$ crystals; large crystals of lead niobate, containing perhaps some Ho^{3+}, were produced.

TABLE IV X-ray powder pattern data for R_2TiO_5.

hkl intensity*	Gd_2TiO_5 $d(hkl)_{obs}$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	Dy_2TiO_5 $d(hkl)_{obs}$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	Y_2TiO_5 $d(hkl)_{obs}$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$
110 m	7.690	0100	0100	7.630	0102	0101	7.580	0104	0102
200 w	5.220	0218	0211	5.140	0225	0216	5.150	0225	0216
120 w	4.980	0239	0240	4.910	0246	0242	4.920	0245	0246
210 w	4.750	0264	0258	4.680	0271	0263	4.670	0272	0265
011 m	3.550	0471	0474	3.520	0480	0479	3.510	0482	0485
130			0473			0477			0485
310 vw *Cukβ*	3.360	0526	0521	3.390	0518	0533	3.320	0538	0533
201 vs	3.060	0635	0638	3.020	0653	0648	3.010	0658	0654
320 w	2.970	0674	0661	2.940	0685	0674	2.970	0673	0677
400 m	2.662	0838	0841	2.636	0855	0854	2.628	0861	0861
031			0847			0855			0867
330 w	2.560	0907	0894	2.542	0919	0909	2.578	0894	0916
321 w	2.333	1090	1088	2.304	1120	1106	2.295	1128	1117
340 w	2.207	1220	1222	2.192	1237	1238	2.186	1244	1252
331 mw	2.112	1332	1321	2.091	1359	1341	2.084	1368	1353
060 w	1.876	1688	1680	—	—	—	—	—	—
002 s	1.862	1715	1708	1.848	1740	1728	1.837	1760	1750
450 w	1.737	1971	—	1.725	1998	—	1.711	2030	—
620 vvw	1.695	2069	2080	—	—	—	1.671	2126	2128
360 m	1.600	2154	2154	1.649	2187	2177	1.642	2204	2204
601 m	1.600	2321	2320	1.584	2371	2367	1.575	2395	2377
232			2339			2377			2391
322 mw	1.582	2375	2369	1.566	2425	2402	1.560	2445	2430
332 w	1.510	2609	2602	1.505	2627	2637	1.497	2651	2660
Orthorhombic	$a_0 = 10.61$ Å			$a_0 = 10.49$ Å			$a_0 = 10.50$ Å		
Pnam	$b_0 = 11.27$ Å			$b_0 = 11.26$ Å			$b_0 = 11.14$ Å		
	$c_0 = 3.73$ Å			$c_0 = 3.70$ Å			$c_0 = 3.68$ Å		

*w = weak; s = strong; m = medium; v = very.

Evaporation of a solution of $RNbO_4$ in PbF_2 at 1230° C produced highly twinned, transparent plates, which gave powder patterns in agreement with that given in the ASTM data file for the $DyNbO_4$ [18], and with powder patterns of samples prepared by sintering (R_2O_3 + Nb_2O_5) at 1250° C.

Well-formed bipyramidal crystals up to 5 mm in size, with perfect basal cleavage, were grown from Bi_2O_3/B_2O_3 flux, cooled from 1340 to 900° C. This flux severely attacked the crucibles. Cleaved plates were transparent; under the polarising microscope lamellar twinning due to the transition at 800° C [15, 17] could be observed. The colours of the crystals corresponded to those of the constituent rare-earth ions.

2.5. Rare-Earth Niobates, R_3NbO_7

Compounds of the type R_3NbO_7 are reported to have a defect fluorite lattice [14]. Rooksby and White [14], who made sintered samples, suggested that with Nd and La, ordering of the weberite type occurred; with rare-earth ions smaller than Nd, they were unable to observe super-lattice lines, but argued that ordering of the pyrochlore type was likely; thus, the formula might be expressed as $R_2(R, Nb)O_7$. They did not determine the composition boundaries of the phase R_3NbO_7. Savchenko and Godina [13] investigated calcined mixtures of R_2O_3 and Nb_2O_5 in various proportions (R = La, Ce, Pr). They found that a single phase existed between 75% R_2O_3/25% Nb_2O_5 (R_3NbO_7), and 65% R_2O_3/35% Nb_2O_5. To prepare R_3NbO_7 crystals, a melt containing (R_2O_3 + Nb_2O_5) in PbO/PbF_2 flux ($PbO:PbF_2$ = 100:20) was cooled slowly from 1285 to 950° C.

As with R_2TiO_5, the formation of compounds with the flux necessitated non-stoichiometric melts. The crystals were extracted with dil HNO_3. They were transparent, pseudo-cubic in some cases, and about 1 mm on edge. The colours were characteristic of the constituent rare-earth ions. X-ray fluorescence analysis of Gd_3NbO_7 crystals showed them to contain Gd_2O_3 and Nb_2O_5 in the molar ratio 67:33. 5.0 wt % Pb also present in the crystals may substitute for Gd in the lattice or occur in occluded flux. The composition of the crystals is near the Nb_2O_5-rich boundary of the R_3NbO_7 phase [13] (65% R_2O_3, 35% Nb_2O_5). Our crystals were grown from a melt containing R_2O_3 and Nb_2O_5 in equal molar proportions, and thus would be expected to have a high Nb_2O_5 content.

Crystals of Nd_3NbO_7 showed sharp extinction under the polarising microscope but appeared twinned. Due to this twinning in even the smallest fragments examined by X-rays it has not been possible to fix the space group of the crystal structure. The unit cell appears to be tetragonal, with a_0 = 5.69 Å, c_0 = 5.66 Å.

Crystals containing the smaller rare-earth ions (Gd, Tb, Dy, Ho) showed no extinction, but like the neodymium compound were multiply twinned, and the information from oscillation and Weissenberg photographs was ambiguous. The powder patterns could be indexed for the most part on the basis of the cubic unit cells proposed by Rooksby and White. A number of faint lines which appeared in similar positions on photographs of all of these compounds could be accounted for only by adopting a larger hexagonal cell which is related to the cubic pseudo-cell by distortion along the body diagonal of the latter. According to the analysis quoted above, the crystals are rather far removed from the "ideal" composition, which may account for the distortion from cubic symmetry.

Table V gives the observed X-ray powder pattern data for Nd_3NbO_7, and table VI gives

TABLE V X-ray powder pattern data for Nd_3NbO_7

hkl	Intensity*	$d(hkl)_{obs}$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$
111	vs	3.280	0552	0552
200	m, broad	2.841	0736	0733
002				0740
112	w	2.321	1103	1107
212				1101
202	vs, broad	2.008	1474	1473
220				1466
311	ms	1.718	2016	2018
113	s	1.712	2030	2032
222	m	1.640	2210	2206
320	vw	1.581	2378	2383
312	vvw	1.518	2580	2573
213				2581
400	vw	1.429	2915	2932
004	w	1.418	2956	2960
322	vvw	1.380	3123	3123
223				3131
330	vw	1.345	3286	3299
313	m, broad	1.305	3492	3498
331				3484

Tetragonal, a_0 = 5.68(7) Å; c_0 = 5.66(2) Å.

*w = weak; s = strong; m = medium; v = very.

TABLE VI X-ray powder pattern data for R_3NbO_7

hkl intensity*	Gd_3NbO_7			Tb_3NbO_7			Dy_3NbO_7			Ho_3NbO_7		
	$d(hkl)_{obs}$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	$d(hkl)_{obs}$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	$d(hkl)_{obs}$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$	$d(hkl)_{obs}$	$\sin^2\theta_{obs}$	$\sin^2\theta_{calc}$
006 mw	3.140	0600	0600	3.100	0.618	0608	3.090	0621	0620	3.080	0627	0620
112 vs	3.070	0630	0627	3.050	0639	0637	3.040	0641	0640	3.030	0647	0640
202 w	—	—	—	—	—	—	2.667	0835	0831	2.661	0839	0831
114 ms	2.667	0835	0828	2.652	0845	0839	2.641	0853	0847	2.629	0860	0847
118 w	1.914	1621	1631	1.893	1658	1650	1.895	1666	1672	1.889	1666	1672
300 s	1.882	1679	1679	1.874	1693	1705	1.865	1711	1716	1.860	1719	1716
221 w	—	—	—	1.615	2277	—	1.614	2287	—	1.609	2295	2304
1.1.10									2293			2293
222 s	1.605	2306	2307	1.598	2328	2343	1.590	2353	2356	1.587	2360	2356
311 w	—	—	—	1.545	2491	2481	—	—	—	1.542	2499	2493
224 mw	1.539	2520	2508	1.531	2536	2545	1.523	2564	2563	1.519	2574	2563
307			2499			2538			2560			
3.0.10 mw	1.333	3344	3354	1.326	3380	3395	1.319	3422	3437	1.316	3430	3437
	Hexagonal			Hexagonal			Hexagonal			Hexagonal		
	$a_0 = 6.51$ Å			$a_0 = 6.48$ Å			$a_0 = 6.44$ Å			$a_0 = 6.44$ Å		
	$c_0 = 18.81$ Å			$c_0 = 18.73$ Å			$c_0 = 18.55$ Å			$c_0 = 18.55$ Å		

*w = weak; s = strong; m = medium; v = very.

the unit cell dimensions and powder pattern data for Gd_3NbO_7, Tb_3NbO_7, Dy_3NbO_7, and Eo_3NbO_7 prepared in this way.

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