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The flux growth of rare earth germanomolybdates and germanotungstates

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The growth of R_2GeMoO_8 and R_2GeWO_8 crystals from the flux systems R_2O_3-GeO_2-MO_3-PbO, where M = Mo or W, is described. A preliminary investigation of their magnetic properties is reported. The X-ray powder pattern data for R_2GeWO_8 with R = Gd, Tb, Dy, Ho and Er are given.

1. Introduction

The compounds R_2GeMoO_8 have the $CaWO_4$ (scheelite) structure, space group $I4_1/a$, with the smaller cation sites randomly occupied by tetravalent Ge and hexavalent Mo respectively [1]. The interest in these materials arises from the fact that the rare earth ions are sufficiently concentrated for magnetic transitions in the liquid helium temperature range to be expected.

The analogous compounds $RNaMo_2O_8$ and $RLiMo_2O_8$, which also have the scheelite structure but are magnetically more dilute, have been reported [2, 3]. The latter occurs as an epitaxial layer on R_2GeMoO_8 crystals grown from lithium ditungstate flux [4], and the possibility of some degree of solid solution of the two compounds cannot be excluded. It was decided to attempt to use a flux system less likely to contaminate the crystals, and to discover whether the magnetically concentrated analogues, R_2GeWO_8, could be prepared.

This paper reports the growth of the compounds R_2GeMoO_8 and R_2GeWO_8 where R = Gd, Tb, Dy, Ho and Er, and preliminary investigations of their magnetic properties. The four-component system R_2O_3-GeO_2-MO_3-PbO (M = Mo or W) has several advantages.

1. One of the authors had already grown $R_2Ge_2O_7$ from PbO-R_2O_3-GeO_2 [5] and R_2MoO_6 from PbO-R_2O_3-MoO_3 [6] and it seemed likely that R_2GeMoO_8 would crystallize from the combination of these systems.
2. The presence of three ions common to both crystal and flux greatly reduces the incorporation of impurities in the former.
3. Pb^{2+} usually replaces the smaller rare earth ions to the extent of only 0.02 to 0.3%.
4. The combined flux would probably be of low volatility.

2. Equipment

The furnaces, control equipment and flux growth technique have been described previously [7]. The crucibles were of 20 or 50 cm³ capacity and of pure platinum of 0.50 mm wall thickness. Each was provided with a tightly fitting lid.

The chemicals used were: Rare Earth Products 99.9% pure R_2O_3, BDH "Analar" MoO_3, PbO and PbO_2, and "Laboratory Reagent" WO_3 and GeO_2.

3. Crystal growth

In crystal growth from a four-component system, it is essential to reduce the number of variables to a minimum and this was achieved as follows:

1. The solubility of rare-earth complex oxides in PbO-based fluxes at 1260 to 1300°C is typically 3 to 5 wt% R_2O_3 (e.g. with RVO_4 from $Pb_2V_2O_7$ [8], $R_2Ge_2O_7$ and R_2GeO_5 from PbO-GeO_2 [5], R_2MoO_6 from PbO-MoO_3 [6], RPO_4 from $Pb_2P_2O_7$ [9]) and a solubility of this order was assumed.
2. In the PbO-GeO_2 system, the liquidus falls steeply with small additions of GeO_2 to PbO [10]. The liquidus temperature was accordingly reduced by adding more GeO_2 than is required for the formula R_2GeMoO_8, and an R_2O_3:GeO_2 ratio near 1:3 (molar) was used.

These assumptions were justified by the

TABLE I Starting compositions and flux growth conditions

Components	Crucible volume (cm^3)	Maximum temperature and holding time	Cooling programme	Results
1.8 g Gd_2O_3, 1.5 g GeO_2, 27.7 g PbO, 9 g MoO_3, 2.2 g PbO_2	20	1290°C (24 h)	2°C h^{-1} to 1240°C 3°C h^{-1} to 900°C	Clear, well-formed crystals
1.4 g Gd_2O_3, 2.2 g GeO_2, 20 g PbO, 14 g WO_3, 2.4 g PbO_2	20	1280°C (10 h)	4°C h^{-1} to 900°C	Clear crystals shown in Fig. 2

appearance of crystals up to 2 mm in length after only four trial experiments.

3. In attempts to produce R_2GeWO_8, similar considerations were applied with comparable results.

The crucibles were supported in groups of four in Morgan M1 3000 refractory brick. Each crucible was placed in a hollow in the brick, with alumina powder packed around it, and a slab of brick was placed over the top to protect the furnace from attack by PbO vapour and provide additional thermal insulation.

4. Results

4.1. R_2GeMoO_8

It was found that with PbO:MoO_3 = 2.4:1 or greater, and R_2O_3:GeO_2 as described above, rare earth germanates crystallized. At borderline compositions, the ionic radii of the rare earths were found to determine the phase obtained. With PbO:MoO_3 = 2.4:1, and the other molar proportions the same, with Tb_4O_7 in one batch and Ho_2O_3 in the other, the respective products were Tb_2GeMoO_8 and ($Ho_2Ge_2O_7$ + Ho_2GeO_5).

Table I gives the composition and growth conditions which produced the best crystals of Gd_2GeMoO_8. The loss in weight was usually less than 3 wt %.

A slow rate of cooling (2 to 4°C^{-1}) produced clear, well-formed crystals, even with only 20 cm^3 crucibles. Cooling at faster rates resulted in skeletal forms, platelets or dendrites.

The well-formed crystals were bipyramids with the characteristic colours of the trivalent rare earth ions. The germanomolybdates were dull in appearance even when the crystals were clear and free from flux inclusions. Microscopic examination showed this to be due to rough surfaces on the facets, which were sometimes scaly or corrugated.

The X-ray powder patterns for R_2GeMoO_8 agreed closely with published data [1]. EPMA showed that the lead content of Tb_2GeMoO_8 was 0.25%.

4.2. R_2GeWO_8

Table I gives the composition and growth conditions which produced the best crystals of Gd_2GeWO_8. The crystals grown from the system Gd_2O_3-GeO_2-WO_3-PbO had the same habit as R_2GeMoO_8. Their powder patterns

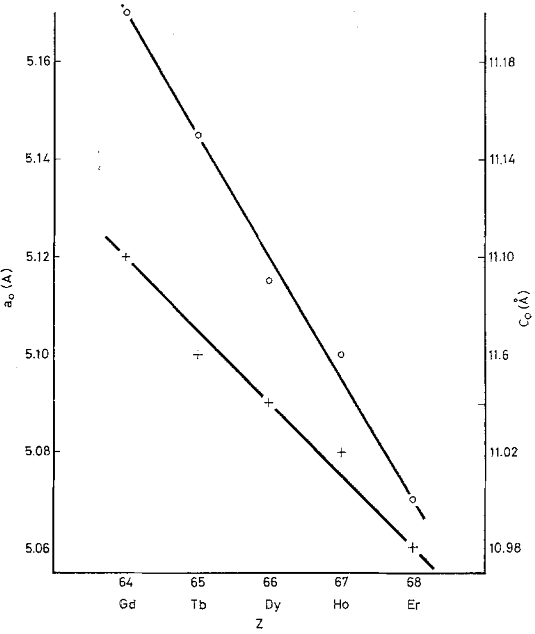

Figure 1 Unit cell parameters of R_2GeWO_8 plotted versus lanthanide atomic number: + : a_0, 0 : c_0.

TABLE II X-ray powder pattern data for the compounds R_2GeWO_8

hkl	Intensity (estimated)	d_{obs}				
		Er_2GeWO_8	Ho_2GeWO_8	Dy_2GeWO_8	Tb_2GeWO_8	Gd_2GeWO_8
101	M	3.38		3.32	3.35	3.37
112	VS	2.99	3.01	3.01	3.02	3.04
004	MS	2.74	2.77	2.77	2.92	2.80
200	S	2.52	2.54	2.54	2.55	2.56
121	M	2.21		2.22	2.24	2.25
114	W	2.18		2.20	2.20	2.22
105	W	2.02				2.05
123	W	1.92				1.95
204	VS	1.860	1.870	1.872	1.878	1.887
220	MS	1.785	1.795	1.794	1.800	1.811
301	VW	1.659		1.668	1.675	1.684
116	S	1.630	1.639	1.643	1.650	1.661
132	VS	1.532	1.542	1.542	1.547	1.554
107	MS	1.498	1.506	1.508	1.513	1.519
008	VW	1.373	1.383	1.386	1.393	1.402
400	W	1.263	1.268	1.270	1.275	1.279
136	S	1.205	1.213	1.214	1.220	1.225
413	M	1.164	1.171	1.171	1.175	1.180
404	MW	1.148	1.155	1.155	1.160	1.164
420	MW	1.131	1.137	1.138	1.140	1.145
		a_0 5.06 Å c_0 11.00 Å	a_0 5.08 Å c_0 11.06 Å	a_0 5.09 Å c_0 11.09 Å	a_0 5.10 Å c_0 11.15 Å	a_0 5.12 Å c_0 11.20 Å

corresponded closely to those of R_2GeMoO_8 and have been similarly indexed. Table II gives the X-ray powder pattern data and unit cell parameters for the compounds R_2GeWO_8, and in Fig. 1 the latter are plotted versus ionic radii of the rare earth ions.

A mixture of composition (Gd_2O_3 + GeO_2 + WO_3) was sintered by heating it in a Pt crucible for 6 h at 1250°C. The X-ray powder pattern of the product corresponded to that of the crystals and confirmed the formula Gd_2GeWO_8. With R_2GeWO_8, it was found possible to use relatively more GeO_2 and less WO_3 (as molar percentages) in this system without rare earth tungstates being produced.

The germanotungstates were shiny, the surfaces vitreous in appearance and somewhat curved (Fig. 2).

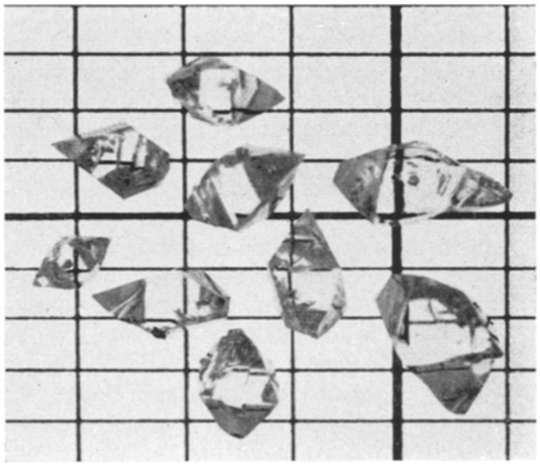

Figure 2 Crystals of Gd_2GeWO_8 (1 mm × 2 mm grid).

5. Magnetic susceptibility measurements

Measurements of the magnetic susceptibility of small quantities of the compounds have been made in the temperature range 0.5 to 4.2 K. In each case the sample consisted of many small crystallites, of typical mass 0.05 g, so that the data are representative of "powder" susceptibilities. The measurements were made by two methods; an a.c. (175 Hz) mutual inductance technique [11] and a d.c. low field (less than 1 kOe) method described by Cashion *et al.* [12].

TABLE III The experimental values of the Curie constant C (cgs units) and Weiss θ (K) together with the experimental and theoretical g-values.

	R_2GeWO_8				R_2GeMoO_8		
R	C	θ	g_{calc}	$g_{\mathrm{theoretical}}$	C	θ	g_{calc}
Tb	9.4	2.0	17.3	18	12.0	2.3	19.6
Dy	12.8	2.7	20.2	20	12.3	2.5	19.8
Ho	11.2	1.8	18.9	20	12.4	2.1	19.9
Er	7.7	1.6	15.7	18	7.9	1.8	15.9

The results have been analysed and, with the exception of the two gadolinium compounds, fitted to the simple Curie-Weiss law relationship

$$\chi = \frac{C}{T + \theta}.$$

The validity of such an analysis and the definition of the parameters have been given in a previous paper [13]. Gd_2GeMoO_8 and Gd_2GeWO_8 are not amenable to such a treatment as magnetic ordering occurs at approximately 1.4 K and the Curie-Weiss law is strictly only valid at temperatures well above the ordering temperature. Table III gives the measured values of the parameters C and θ and it should be noted that the susceptibility χ refers to the molar susceptibility per rare earth ion.

From the measured values of the Curie constant it is possible to obtain an estimate of the g-value associated with the rare earth ion. If we assume that the only occupied energy level is doubly degenerate (an assumption that is strictly valid for the Kramers ions Dy and Er) then the Curie constant is equal to $Ng^2\beta^2/4k$. For a powder susceptibility measurement a mean square g-value is obtained but if we consider that this arises from a single uniaxial g-value then we obtain the value denoted by g_c. This may be compared with the maximum theoretical value g_t, which is calculated on the assumption that the effect of the crystalline electric field is to split the free ion ground state such that the lowest level is a doublet with the maximum value of M_J. The results given in Table III show that our experimental results are compatible with the theoretical g-values calculated using the assumptions stated above.

For the Ho, Er and Tb compounds of each series the measurements were made down to 1 K; in each case there was no indication of any magnetic ordering occurring. The behaviour of the Gd and Dy compounds is shown in Fig. 3, where the reciprocal susceptibility per ion is plotted as a function of temperature. For Dy_2GeWO_8 (curve c) and Dy_2GeMoO_8 (curve d) the measurements were extended to the lowest temperature as there is clearly a departure from the Curie-Weiss law behaviour. At approximately 1 K for both compounds, the magnetic susceptibility becomes almost temperature independent indicating that some form of cooperative phenomenon is present. It is not possible to state the precise nature of the process although an antiferromagnetic state seems likely.

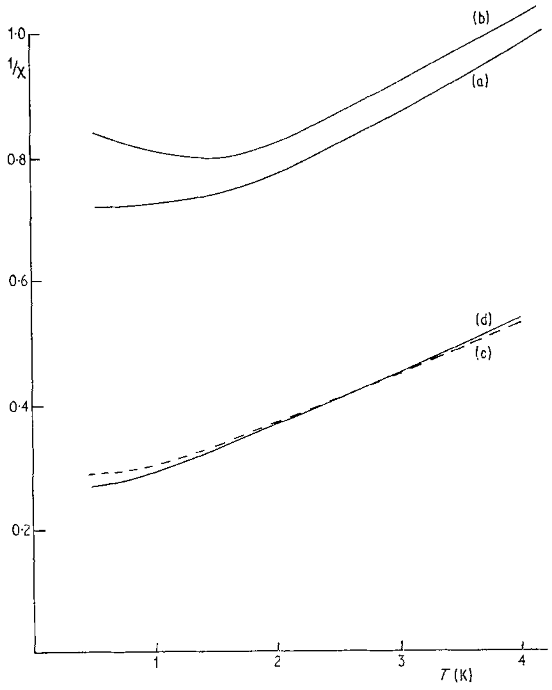

Figure 3 The reciprocal susceptibility versus temperature of the gadolinium and dysprosium compounds; (a) Gd_2GeWO_8, (b) Gd_2GeMoO_8, (c) Dy_2GeWO_8, (d) Dy_2GeMoO_8.

The environment of the rare earth ion in these compounds is not unique, being subject to the random occupation of the smaller cation site. This situation may result in local ordering of the rare earth ions with a corresponding broad peak in the susceptibility curve at the average transition temperature.

In Gd_2GeWO_8 (curve a) and Gd_2GeMoO_8 (curve b) the onset of magnetic ordering occurs at 1.5 and 1.4 K respectively. For the Gd^{3+} ion, which has an isotropic *g*-value, it is to be expected that after ordering to an antiferromagnetic state the powder susceptibility will decrease below the Néel point to a value which is $\frac{2}{3}$ of the susceptibility at the Néel temperature. This clearly does not happen in either of these two compounds. We speculate that this may be due to the random environment of the rare earth ions as with the dysprosium compounds.

6. Conclusion

A method has been described which produces good quality crystals of R_2GeMoO_8 and R_2GeWO_8. The flux system used is relatively non-volatile and it should be possible for larger crystals to be grown by top seeding. If a more adequate explanation of the magnetic behaviour is to be achieved then further experiments at low temperatures are necessary. However, the random occupation of the smaller cation site may well preclude a complete understanding.

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