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Flux growth of R_2MoO_6 and compounds in the systems R_2O_3–MoO_3–PbO

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Compositions and conditions for the growth of crystals of R_2MoO_6, Pb_2MoO_5, and for the new compounds $MoGd_2Pb_4O_{10}$ and $Mo_3Gd_6Pb_4O_{22}$ are described. Gd_2O_3 crystallized under non-equilibrium conditions.

X-ray powder patterns for the compounds R_2MoO_6(R = Gd, Tb, Dy, Ho, Er), and for the two new fluorite-related compounds, $MoGd_2Pb_4O_{10}$ and $Mo_3Gd_6Pb_4O_{22}$, are given.

1. Introduction

The systems R_2O_3–MoO_3, where R is a rare-earth ion, are known to contain the congruently melting, ferroelectric phase, $R_2(MoO_4)_3$ [1-3] and the phase R_2MoO_6. The rare earth ions in the latter compounds are sufficiently concentrated to make magnetic ordering at low temperatures probable. This paper reports an investigation into crystalline phases in the systems R_2O_3–MoO_3–PbO, and the flux growth of R_2MoO_6 from PbF_2–MoO_3.

R_2MoO_6 compounds (R = Sm to Lu) have a monoclinic structure, *C2/c* [4, 5] and have melting points in the range 1600 to 2100°C [5, 6]. Crystals of $(Gd,Bi)_2MoO_6$ which were suitable for X-ray analysis have been prepared by sintering a mixture of this composition at 1400°C [5].

2. Experimental

2.1. Equipment and materials

The furnaces, control equipment and flux growth technique have been described previously [7]. The crucibles were of pure platinum and had flanged lids which were a tight push fit. The chemicals used were: Rare Earth Products 99.9% R_2O_3, BDH "Analar" grade MoO_3, PbO_2 and PbO, and "Optran" grade PbF_2.

2.2. Flux growth

Preliminary attempts to grow R_2MoO_6 were made using several flux systems without success. It was then found that R_2MoO_6 could be crystallized from the systems R_2O_3–MoO_3–PbO, and from melts which contained PbF_2, R_2O_3 and excess MoO_3 by allowing the PbF_2 to evaporate.

Table I lists starting compositions and growth conditions for some of the phases in the systems R_2O_3–MoO_3–PbO. The components were weighed out, mixed, and placed in 20 cm^3 platinum crucibles; 5 wt % of PbO was included as PbO_2 to provide oxidizing conditions during heating. The closely fitted lids reduced evaporation of the flux. The crucibles, embedded in M.I. 3000 brick, were heated in a furnace to 450°C, held at this temperature for 2 to 3 h to ensure complete oxidation of the crucible contents, and then heated at 100K h^{-1} to 1290°C. After 22 h the furnace was cooled at 2 to 7K h^{-1} to 1000°C, and then at 100K h^{-1} to room temperature. Where (PbF_2 + MoO_3) was used as flux, the crucible lids were loosely fitted to allow the flux to evaporate during very slow cooling.

During exploratory work, the flux and crystals were removed from the crucible mechanically. This usually broke up the material to some extent, and a bar magnet was then used to separate the phases. To avoid breaking the crystals a hot draining technique was adopted, since the flux was not readily soluble in aqueous reagents. At the conclusion of the cooling programme, each crucible was inverted and placed in the furnace on a slab of refractory brick. The temperature was then raised to 1150°C at 100K h^{-1} and then reduced at the same rate. It was then easy to remove the flux, which had drained onto the crucible lid, and recover the crystals.

The residual flux was removed from R_2MoO_6

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TABLE I Starting compositions and procedures for flux growth

Crystal	Starting composition	Maximum temperature (°C) and cooling programme	Result
Dy_2MoO_6	1.8 g Dy_2O_3, 3.2 g MoO_3, 18 g PbF_2, 5 g PbO, 0.5 g PbO_2 (5 mm × 0.2 mm aperture between lid and crucible on one side)	1270, cooled at 0.7K h^{-1} to 1160	2 to 4 m spherulitic structures composed of many needles
Dy_2MoO_6	1.8 g Dy_2O_3, 4.2 g MoO_3, 18 g PbF_2, 5 g PbO, 0.5 g PbO_2 (5 mm × 0.1 mm aperture between lid and crucible on one side)	1270, cooled at 0.7 K h^{-1} to 1160	Rods up to 5 mm × 2 mm × 0.5 mm, with cracks; did not show uniform extinction
Ho_2MoO_6	7.2 g Ho_2O_3, 24.3 g MoO_3, 30.3 g PbO, 3.6 g PbO_2	Held 2 h at 450 then heated at 100K h^{-1} to 1290. Held 24 h at 1290, then cooled at 2K h^{-1} to 1000	Rods up to 8 mm × 5 mm × 1 mm, mostly cracked, but some untwinned
$MoGd_2Pb_4O_{10}$	4.2 g Gd_2O_3, 10.3 g MoO_3, 52 g PbO, 2 g PbO_2	Held 9 h at 1280, cooled at 5K h^{-1} to 800	Flat, polycrystalline "discs", 2 to 3 mm in diameter (Fig. 3)
Gd_2O_3	6.2 g Gd_2O_3, 1.9 g MoO_3, 20.6 g PbO, 1.2 g PbO_2	Held 12 h at 1280, cooled at 6 h^{-1} to 600	Transparent, platy rods of Gd_2O_3 up to (2 × 1) mm^2. The crucible leaked, altering the composition. Batches which did not leak did not produce Gd_2O_3
$Mo_3Gd_6Pb_4O_{22}$	14.3 g Gd_2O_3, 2.9 g MoO_3, 29.2 g PbO, 2.2 g PbO_2	Held 24 h at 1270, then cooled at 6 h^{-1} to 870	Complete melting did not occur; many crystal rods, up to 1 mm × 0.2 mm × 0.2 mm, were separated

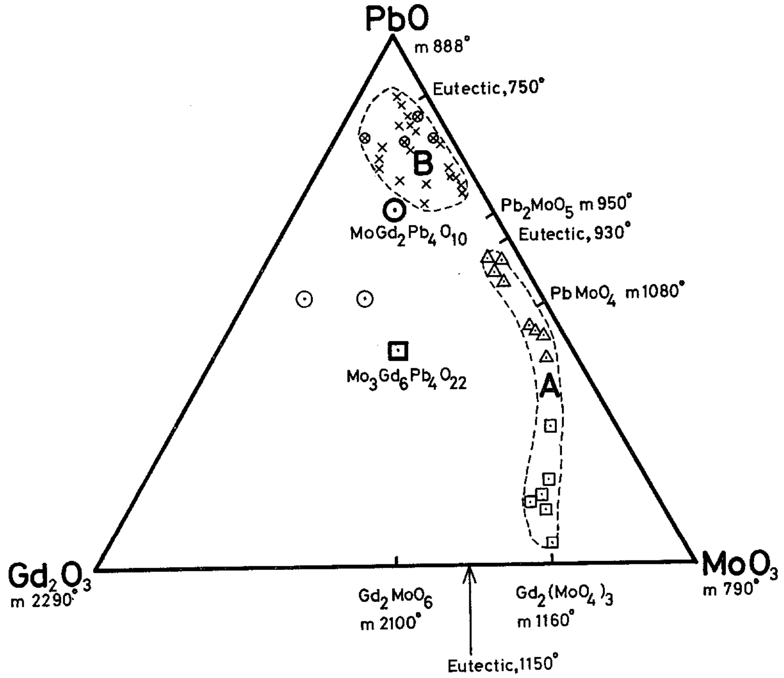

Figure 1 Starting compositions for crystal growth by slow cooling in the system Gd_2O_3–MoO_3–PbO. Region A: Gd_2MoO_6, primary phase; △: $PbMoO_4$, secondary phase; ⊡: $Gd_2(MoO_4)_3$, secondary phase. Region B: × $MoGd_2Pb_4O_{10}$, primary phase, and Pb_2MoO_5, secondary phase; ⊗: Gd_2O_3 crystallized at high temperatures, and was only obtained at low temperatures after the crucible had leaked. The compositions marked ⊙ : these did not entirely liquefy. On cooling, small rods of $Mo_3Gd_6Pb_4O_{22}$ were obtained.

Figure 2 Er_2MoO_6 crystals on the base of a 50 cm^3 crucible.

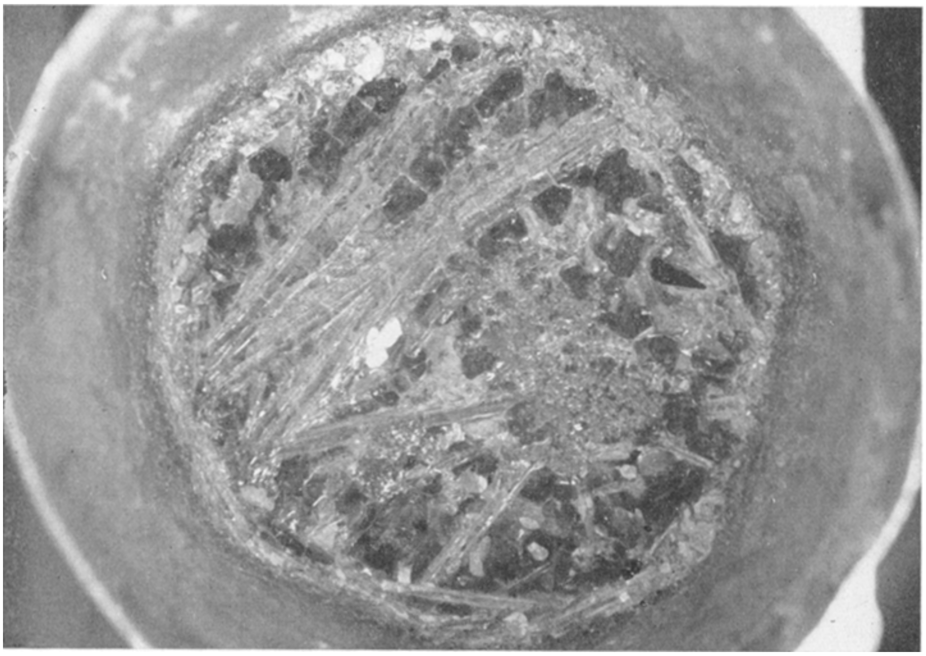

Figure 3 Rods of Pb_2MoO_5 and "discs" of $MoGd_2Pb_4O_{10}$ at the surface of the melt in a 50 cm^3 crucible.

by heating in hot 1:10 nitric acid solution. Care was necessary since R_2MoO_6 crystals dissolved in hot concentrated acid, and $R_2(MoO_4)_3$ and $MoGd_2Pb_4O_{10}$ dissolved even in dilute acid.

3. Results

3.1. Crystallization of R_2MoO_6

3.1.1. (PbF_2 + MoO_3) as flux

A considerable excess of MoO_3 was necessary to produce R_2MoO_6 crystals. With an R_2O_3:MoO_3

TABLE II X-ray powder pattern data for R_2MoO_6 (R = Gd to Er)

I/I_0	Gd_2MoO_6 d (Å)	Tb_2MoO_6 d (Å)	Dy_2MoO_6 *d* (Å)	Ho_2MoO_6 d (Å)	Er_2MoO_6 *d* (Å)
1	4.10	4.09	4.09	4.08	4.07
4	3.44	3.41	3.40	3.39	3.38
10	3.12	3.10	3.09	3.08	3.06
10	3.09	3.08	3.06	3.05	3.04
5	2.795	2.784	2.765	2.753	2.751
4	2.713	2.705	2.680	2.670	2.668
5	2.609	2.607	2.594	2.583	2.576
1	2.209	2.204	2.185	2.177	2.170
1	2.112	2.106	2.090	1.087	2.080
1	2.002	1.994	1.988	1.976	1.973
5	1.946	1.937	1.925	1.918	1,914
6	1.909	1.901	1.893	1.886	1.884
3	1.896	1.892	1.879	1.869	1.864
3	1.870	1.864	1.855	1.848	1.846

molar ratio of 1:4.5, the crystals were similar in form to those described in Section 3.1.2. below. They did not show simultaneous extinction. Rapid evaporation of the flux at 1270°C produced spherulitic structures.

3.1.2. The systems R_2O_3–MoO_3–PbO

Under the conditions described, the weight loss due to evaporation was less than 1 %. To identify the phases, X-ray powder patterns of the crystals were compared with published data [8] and with powder patterns of sintered material of known composition. This enabled the composition diagram (Fig. 1) to be plotted.

In region A of the diagram, R_2MoO_6 crystallized as the primary phase. The crystals grew as rods or plates, with brown superimposed on the colour characteristic of the constituent rare earth ion. The crystals were translucent but were always cracked even when care was taken to cool to room temperature at 100K h^{-1}. A few crystals showed uniform extinction and Läue back-reflection photographs showed these to be untwinned. Fig. 2 shows crystals of Er_2MoO_6 which grew at the base of a 50 cm^3 crucible from which the flux had been hot-poured. Table II gives X-ray powder pattern data for some of the compounds R_2MoO_6. EPMA showed that the lead content of Gd_2MoO_6 was 0.16%.

From preliminary a.c. susceptibility measurements on powder samples, Dy_2MoO_6, Tb_2MoO_6 and Ho_2MoO_6 show deviations from a Curie-Weiss law at temperatures between 1 and 4.2K. Measurements are currently being made down to 0.5K and will be reported elsewhere.

3.2. Crystallization of $MoGd_2Pb_4O_{10}$

In region B a new compound crystallized in the form of small discs, with yellow rods of Pb_2MoO_5, often more than 1 cm in length, as the secondary phase. Fig. 3 shows both phases at the surface of a melt. EPMA indicated that the composition of the new phase corresponded to the formula $MoGd_2Pb_4O_{10}$ (required, 6.9% Mo, 22.5% Gd, 59.3% Pb; EPMA found 6.9% Mo, 25.2% Gd, 61.3% Pb). A mixture corresponding to the formula was sintered at 1200°C in a platinum crucible with a closely fitting lid. The X-ray powder pattern of the sinter agreed closely with that of the crystal "discs".

An attempt was made to determine the melting point of $MoGd_2Pb_4O_{10}$ with a hot stage microscope but the volatilization of MoO_3 from the sample was large under these conditions and melting was not observed on raising the temperature. The powder pattern of the residue indicated mainly Gd_2O_3. Fig. 4 shows a few "discs" between crossed polarizers. They were polycrystalline, flat above and below, with no sign of facets, and often consisted of segments with a point in common. The "discs" did not nucleate at sites on the crucible wall or at the melt surface, as usually occurs in flux growth, but apparently grew on nuclei already present in the melt, possibly Gd_2O_3 particles, which are very refractory.

Powder patterns indicated that this material has a fluorite-related structure. Single crystal oscillation and Weissenberg photographs showed a more complicated structure in which a pseudo-orthorhombic subcell of dimensions 3.94, 3.90, 16.40 Å (± 0.1 Å) formed part of a larger orthogonal cell of lower symmetry. The powder lines have been indexed on the basis of the small orthorhombic subcell and the single crystal photographs (Table III).

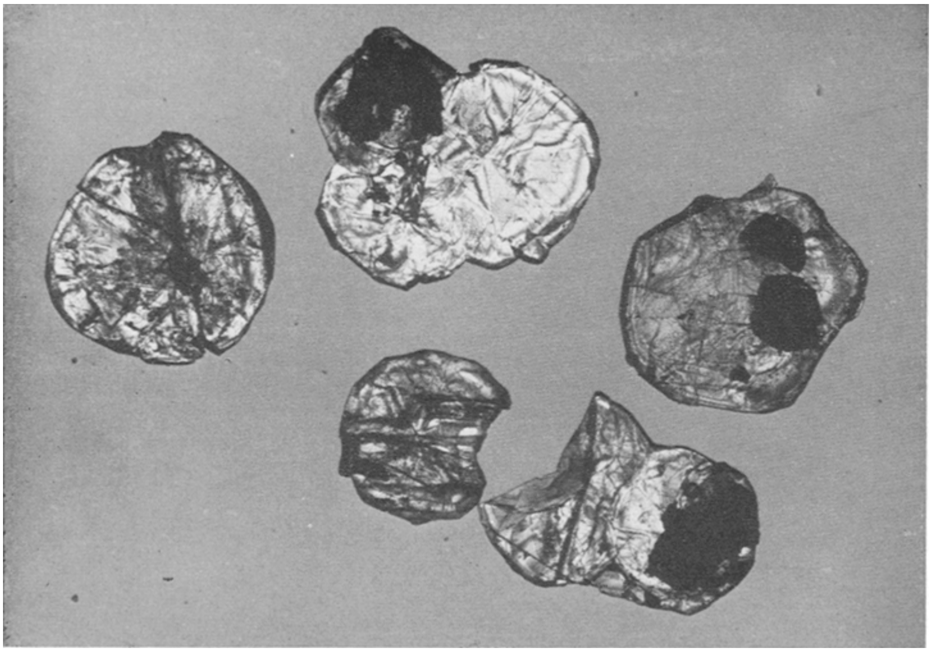

Figure 4 "Discs" of $MoGd_2Pb_4O_{10}$ (1.5 to 2 mm in diameter).

TABLE III X-ray powder pattern data for $MoGd_2Pb_4O_{10}$ and $Mo_3Gd_6Pb_4O_{22}$

	$MoGd_2Pb_4O_{10}$*			$Mo_3Gd_6Pb_4O_{22}$	
I	d_0	d_{calc}	hkl	I	d_0
1	3.90	3.90 3.94	010 100	7	3.13
1	3.46	N.I.		10	3.09
10	3.13	3.17	013	3	2.78
4	2.79	2.77	110	1	2.70
4	2.62	2.63	112	3	2.57
1	1.97	1.97	200	3	1.94
6	1.91	1.92	202	9	1.90
5	1.67	1.67	213	3	1.86
5	1.60	1.60	206	6	1.67
3	1.58	1.59	026	3	1.64
2	1.39	1.39	011	4	1.59
2	1.31	N.I.		5	1.58
2	1.28	1.28	303	3	1.57
3	1.25	1.24	310	3	1.55
				3	1.50
				2	1.40
				3	1.31

*Pseudo-orthorhombic subcell, $a_0 = 3.94$ Å, $b_0 = 3.90$ Å, $c_0 = 16.40$ Å.

3.3. R_2O_3

The batches marked ⊗ on the composition diagram produced platelets or small rods which were identified as Gd_2O_3 from their X-ray powder patterns. EPMA confirmed this identification and also indicated 2.4% Mo and 1.1% Pb as impurities. The growth process was particularly non-reproducible, since with the high PbO concentrations needed, leakage of the crucibles frequently occurred, and it was these batches that produced Gd_2O_3 crystals. It appeared that re-solution occurred when the run was not interrupted, and further work will be directed towards establishing reproducible growth conditions.

3.4. $Mo_3Gd_6Pb_4O_{22}$

Batches of compositions indicated ⊙ in the diagram did not entirely melt, but each produced rods approximately 1 mm in length which gave a new X-ray powder pattern (Table III). By sintering small batches at 1270°C for 12 h, grinding, and resintering, the composition which gave the same powder pattern as the rods was found to correspond to the formula $Mo_3Gd_6Pb_4O_{22}$.

This material has a fluorite-related structure. Preliminary single crystal oscillation and Weissenberg photographs show the symmetry to be monoclinic.

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