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The flux growth of some rare-earth and iron group complex oxides

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The flux growth of crystals of the following rare-earth complex oxides is reported here for the first time: (Nd, Pb)MnO_3, (Eu, Pb)MnO_3. $Tm_2Ge_2O_7$ and Pr_2MoO_6. Starting compositions for the flux growth of RBO_3 (R = Nd, Pr, La), (La, Pb)MnO_3, $Pb_3Mn_7O_{15}$, $R_2Ti_2O_7$ (R = Tm to Pr), R_2SiO_5 (R = Er, Ho, Dy) and $LiCoPO_4$ are also given; these compositions have yielded larger crystals than previously reported. In many cases, only a small number of crystals was obtained by spontaneous nucleation.

1. Introduction

The work described in this paper forms part of a study [1–3] of the flux growth of materials which are of interest on account of their magnetic, optical, and other properties. The starting compositions were calculated, or previous compositions were modified, in accordance with a previously published model for the prediction of favourable starting compositions [4, 5].

2. Chemicals

The following chemicals were used: Rare Earth Products 99.9% R_2O_3 (R = rare earths) except for La_2O_3 which was 99.99% pure; BDH Laboratory reagent grade B_2O_3, GeO_2, $MnCO_3$, LiCl and TiO_2; BDH "Analar" grade Al_2O_3, KF, K_2CO_3, MoO_3, PbO and PbO_2; BDH "extra pure" PbF_2; Johnson Matthey "Specpure" MnO_2, Mn_3O_4, Co_3O_4; Koch Light Laboratories Ltd 99% Li_2CO_3; BDH Silica gel, 60–120 mesh, dehydrated before use.

3. Experimental procedure

The starting compositions, furnace programmes and crystal products are given in Table I. Crucibles of pure platinum with tightly fitting lids were used to contain the mixtures. The crucibles were heated in D-shaped sillimanite muffles so that the furnaces were protected from attack by corrosive flux vapours [6]. The furnaces were heated at 100 to 200 $K h^{-1}$, and, after suitable soak periods, cooled according to the programmes in Table I. They were finally cooled to room temperature at 100 $K h^{-1}$.

The crystal products were identified by comparison of their X-ray powder patterns with published data.

4. Notes on the crystals

4.1. RBO_3 (R = La, Nd, Pr)

The flux growth of thin platelets of RBO_3 with the aragonite structure (R = Nd, Pr, La) from the systems R_2O_3–B_2O_3–PbO has been described [7]. Subsequently it was reported that increasing the ratio PbO:B_2O_3 resulted in crystals up to 2 mm thick [5], and that on increasing the concentration of La_2O_3, faceted prisms instead of platelets were obtained [8].

In Table I, the growth of large $NdBO_3$ and $PrBO_3$ crystals from the R_2O_3–PbO–B_2O_3 system is reported, and also the results of partial substitution of PbF_2 for PbO. As observed in other systems [4, 5], the solubility of R_2O_3 in the system increased greatly with PbF_2 present, by about 300% in this case.

A good yield of large, transparent crystals was obtained from both compositions given here for $LaBO_3$. Attack on the crucibles was appreciable when composition 2, with the higher (PbO + PbF_2) concentration relative to that of B_2O_3 was used.

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TABLE I Starting compositions, cooling programmes and crystal products

Composition no.	Formula	Starting composition (g)	Crucible volume (cm^3)	Maximum and final temperatures (° C)	Holding time at t_{max} and cooling rate	Notes on recipe and procedure	Notes on crystal products
1	$NdBO_3$	$6.5Nd_2O_3$, $4.4B_2O_3$, 87.2PbO, $20.0PbF_2$	50	1270 870	24 h 1.3 K h^{-1}	Hot-poured. Wt loss 7%. $PrBO_3$ crystals have been grown from a similar composition but with Pr_6O_{11} replacing Nd_2O_3	7 translucent, faceted, purple crystals, up to 10 mm × 10 mm × 3 mm, at the surface of the melt
2	$LaBO_3$/Pr	$8.0La_2O_3$, $0.08Pr_6O_{11}$, $3.2B_2O_3$, $20.0PbF_2$, 22.0PbO, $2.0PbO_2$	20	1270 700	26 h 1.2 K h^{-1}	Hot-poured. Wt loss approx. 20%, This recipe tended to attack crucibles, often resulting in leaks. (The molar concentration ($PbO + PbF_2$) was high relative to that of B_2O_3)	A 3 mm thick plate, mainly transparent, up to 2 cm across grew at the melt surface
3	$LaBO_3$	$9.0La_2O_3$, $4.0B_2O_3$, $15.0PbF_2$, 16.5PbO, $1.5PbO_2$	20	1270 730	8 h 1.0 K h^{-1}	Hot-poured. Wt loss approx. 20%. This recipe, with higher concentration B_2O_3, did not attack the crucibles	A clear, platy crystal 2 mm thick covered almost the whole melt surface. A few faceted crystals at base
4	$(La,Pb)MnO_3$	$6.3La_2O_3$, $8.0MnCO_3$, $1.0B_2O_3$, $35.3PbF_2$, 35.3PbO, $1.3PbO_2$	50	1270 700	20 h 1.2 K h^{-1}	Hot-poured. Wt loss 27 to 37%. The additive B_2O_3, as well as the large excess of Mn oxide (amphoteric), was essential for obtaining few, large crystals, which were also obtained from subsequent similar batches.	4 black, faceted crystals, up to 10 mm × 8 mm × 5 mm; 3 are shown in Fig. 1a
5	$(Nd, Pb)MnO_3$	$8.4Nd_2O_3$, $11.5MnCO_3$, $1.5B_2O_3$, $53.6PbF_2$, 53PbO, $2.0PbO_2$	50	1250 800	24 h 1.2 K h^{-1}		One black crystal, 15 mm × 15 mm × 8 mm, shown in Fig. 1b, and two smaller crystals
6	$(Eu, Pb)MnO_3$	$13.5Eu_2O_3$, $7.5Mn_3O_4$, $30.0PbF_2$, 30.0PbO, $3.0PbO_2$	50	1270 800	22 h 1.3 K h^{-1}	Wt loss 23%. Crystals were mechanically separated. Excess Mn oxide could not be used, since it resulted in $EuMn_2O_5$	Rough, ill-formed, black (Eu, Pb) MnO_3 crystals at the surface of the melt

TABLE I continued.

Composition no.	Formula	Starting composition (g)	Crucible volume (cm^3)	Maximum and final temperatures (° C)	Holding time at t_{max} and cooling rate	Notes on recipe and procedure	Notes on crystal products
7	$Pb_3Mn_7O_{15}$	3.3Nd_2O_3, 11.3$MnCO_3$, 1.1B_2O_3, 35.3PbF_2, 35.3PbO, 3.3PbO_2	50	1270 700	20 h 1.2 K h^{-1}	Wt loss 34%. Leached in hot water. These crystals resulted from an attempt to obtain $NdMn_2O_5$, which was not produced	Many multi-faceted black crystals, up to 3 mm × 3 mm × 3 mm. A few are shown in Fig. 2
8	$Tm_2Ti_2O_7$	7.2Tm_2O_3, 3.2TiO_2, 20.0MoO_3, 28.0PbF_2, 28.0PbO, 2.0PbO_2	50	1270 800	22 h 1.3 K h^{-1}	20 to 25% wt loss. Previously, $R_2Ti_2O_7$ was grown by evaporation of PbF_2, which resulted in smaller crystals of inferior quality	8 brown, translucent octahedra, all 5 mm on edge or larger, grew at the crucible base. Some are shown in Fig. 3
9	$Tb_2Ti_2O_7$	1.7Tb_4O_7, 0.8TiO_2, 5.0MoO_3, 7.0PbF_2, 7.0PbO, 0.5PbO_2	10	1250 800	26 h 1.0 K h^{-1}		Translucent brown crystals up to 5 mm × 4 mm × 3 mm
10	$Pr_2Ti_2O_7$	1.7Pr_6O_{11}. 0.9TiO_2, 5.0MoO_3, 7.0PbF_2, 7.0PbO, 0.5PbO_2	10	1250 800	25 h 1.0 K h^{-1}		Dichroic, emerald green to red or orange platelets, mostly twinned, but very thin platelets appear single
11	$Tm_2Ge_2O_7$	8.3Tm_2O_3, 6.6GeO_2, 13.6MoO_3, 3.2KF, 2.6K_2CO_3, 16.2PbF_2, 18.8PbO, 1.2PbO_2	50	1270 800	22 h 1.3 K h^{-1}		Only one, faceted crystal 6.4 g in wt, shown in Fig. 4. Large flux inclusions present
12	R_2SiO_5 (R = Er, Dy)	1.0R_2O_3, 0.36SiO_2, 3.2MoO_3, 8.6PbF_2, 7.6PbO	10	1270 800	24 h 2.4 K h^{-1}	Wt loss 30 to 33%. Hot-poured	A few, faceted crystals with flux inclusions but clear outer regions. Only one crystal, 4 mm × 3 mm × 3 mm, was obtained from one batch
13	Ho_2SiO_5	2.2Ho_2O_3, 1.4SiO_2, 6.4MoO_3, 32.0PbO	15	1265 900	12 h 4.0 K h^{-1}		Platelets up to 6 mm × 4 mm × 1 mm
14	Pr_2MoO_6	6.3Pr_6O_{11}, 10.3MoO_3, 13.5K_2SO_4	50	1270 870	12 h 1.2 K h^{-1}	Wt loss negligible (discounting SO_3)	Transparent green platelets up to 4 mm × 3 mm × 0.2 mm grew at the base of the crucible
15	$LiCoPO_4$	11.0Co_3O_4, 17.2P_2O_5, 18.0LiCl, 11.0Li_2CO_3	50	950 450	6 h 1.0 K h^{-1}		Many well-faceted crystals, up to 4 mm × 4 mm × 3 mm, some with a central twin plane. Scarlet in thin section

4.2. (R, Pb)MnO_3 (R = La, Nd, Eu)

These materials, with their orthorhombically distorted perovskite structure, have been the subjects of numerous physical and also chemical studies, since some are effective as catalysts.

When prepared from flux systems containing compounds of lead, some substitution of Pb^{2+} for R^{3+} readily occurs, especially in the compound with $R^{3+} = La^{3+}$ and to a lesser degree in the compounds of the smaller rare-earth ions. With (La, Pb) MnO_3, the effect is to produce a room-temperature ferromagnet [9, 10]. The flux growth of crystals of this material from $PbO + PbF_2$ (for example, 120 g PbO, 120 g PbF_2, 20 g La_2O_3 and 21 g MnO_2) was reported by Morrish *et al.* [11]. Such batches each produced more than 150 crystals, the maximum volume of one crystal being 0.15 cm^3. It was found that Pb occupied 25 to 40% of the La sites.

4.2.1. (La, Pb) MnO_3 and (Nd, Pb) MnO_3

The present starting compositions were not very different from those given by Morrish *et al.* [11], which also contained a large excess of manganese oxide, but boric oxide was now included. Small amounts of this "additive" have previously been found to reduce the number of crystals produced by spontaneous nucleation [6]. In the present experiments, only a few, large crystals were obtained, some of which are shown in Fig. 1a and b. The melts were hot-drained before the flux solidified [6]. Laue back-reflection photographs indicate twinning in these crystals, suggesting structural transitions above room temperature which have not as yet been reported. The domain structure of these crystals is at present being investigated [12].

4.2.2. (Eu, Pb)MnO_3

In the case of (Eu, Pb)MnO_3, it proved very much more difficult to obtain the desired phase, since RMn_2O_5 has a very strong tendency to form instead, as has been reported previously when the crystal growth of $RMnO_3$ (R = Er to Gd) was the subject of study [1]. It was found essential to avoid having excess manganese oxide, and to ensure that the evaporation of some flux occurred to concentrate the melt, thus encouraging growth at higher temperatures when conditions are more favourable to the formation of Mn^{3+}, as required for $EuMnO_3$. At lower temperatures, the concentration of Mn^{4+} is evidently greater, since $EuMn_2O_5$ then results. The crystals of $EuMnO_3$ which grew at the melt surface, were only a few millimetres in size, and were ill-formed with rough surfaces.

4.3. $Pb_3Mn_7O_{15}$

This compound is of interest as a catalyst [13], and also for its physical properties, since it becomes ferromagnetic at 63 K; both the magnetization curves and the dielectric properties show anomalies [14].

Small single crystals described as $PbMn_2O_4$ have been reported with the probable space group $D_{3h}^2 - C\bar{6}\mathrm{cm}$ or $D^2 - C6/mcc$ and unit cell parameters $a_0 = 10.01$ Å, $c_0 = 13.58$ Å [14]. These are evidently the same material as that recently studied by Latourrette *et al.* [13], whose structural analysis indicated the formula $Pb_3Mn_7O_{15}$ and hexagonal symmetry. However, in their table of powder pattern data indexed according to the orthorhombic unit cell, with $a_0 = 9.98$ Å, $b_0 =$ 17.28 Å $c_0 = 13.55$ Å, the a_0 and b_0 dimensions have been confused.

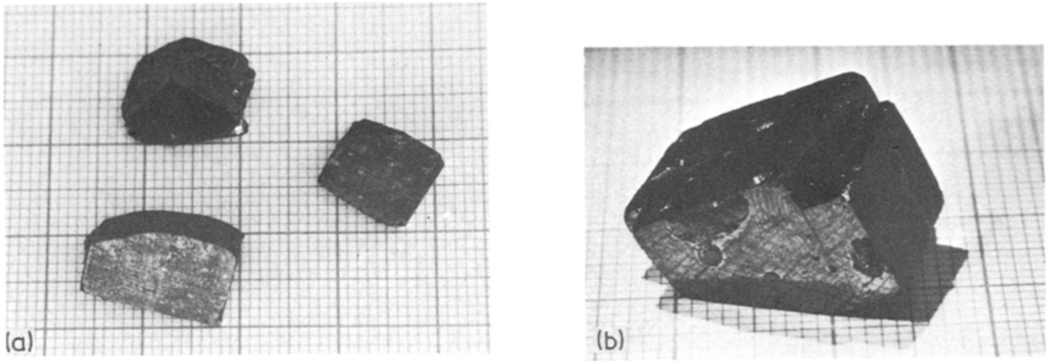

Figure 1 (a) Crystals of $LaMnO_3$ from a 50 cm^3 crucible (mm grid). (b) Crystal of $NdMnO_3$ from a 50 cm^3 crucible (mm grid).

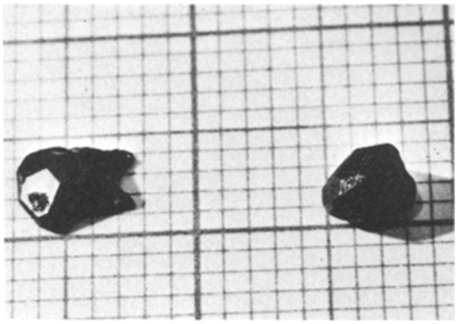

Figure 2 Hexagonal $Pb_3Mn_7O_{15}$ (mm grid).

The crystals described in Table I and shown in Fig. 2 gave powder pattern data in good agreement with that of Latourrette *et al.* [13]. EPMA data was consistent with the formula $Pb_3Mn_7O_{15}$ (formula requires 30.9%Mn, 30.6%Mn found; 50.0%Pb, 52.1%Pb found). Correctly indexed X-ray powder pattern data for the crystal are given in Table II.

4.4. $R_2Ti_2O_7$ (R = Tm, Er, Dy, Tb, Pr)

It has been shown [15] that $Dy_2Ti_2O_7$ orders antiferromagnetically at 1.3 K, but the physical properties of single crystals of this family have not yet been investigated.

The flux growth of some of these compounds by the evaporation of their solutions in PbF_2 has been reported [16], but the crystals were small, opaque, and contained many flux inclusions. The present starting compositions were modified to include a large proportion of acidic oxide, in accordance with previous proposals for modifying starting compositions to yield fewer, larger crystals [4, 5].

The resulting rare-earth titanates, $R_2Ti_2O_7$, were well-formed, translucent octahedra, although all had a brownish tint; from each of several batches, only a few crystals resulted, up to 8 mm on edge, as shown in Fig. 3. These contained a few inclusions, but had large clear regions. The polarizing microscope indicated the presence of internal strain. The crystal surfaces were microscopically rough, being covered with dendritic patterns.

4.5. $Tm_2Ge_2O_7$

The starting composition similar to that previously reported for $Ho_2Ge_2O_7$ [5] was further modified and resulted in the growth by spontaneous nucleation, of only one crystal, 6.4 g in weight.

TABLE II X-ray powder pattern data for $Pb_3Mn_7O_{15}$

I_{est}	hkl	d_{obs}(Å)	d_{calc}(Å)
W	0 0 2	6.75	6.78
W	2 0 0	4.95	4.99
S	0 0 4	3.39	3.39
S	1 5 1, 3 1 1	3.16	3.15
W	2 4 2	2.943	2.943
W	0 6 0	2.877	2.880
V.S	0 6 2	2.648	2.651
M	2 6 2, 4 0 2	2.342	2.341
W	0 0 6	2.254	2.258
W	0 6 4	2.194	2.196
W	1 7 3, 3 5 3	2.122	2.118

$a_0 = 9.98 \pm 0.02$ Å; $b_0 = 17.28 \pm 0.03$ Å; $c_0 = 13.57 \pm 0.03$ Å; space group: $Cmc2_1$.

4.6. R_2SiO_5 (R = Er, Ho, Dy)

These crystals were previously prepared by the "vapour-flux" method [17] and by slowly cooling the fluxed melts [18]. The present starting compositions which contain PbF_2 and a higher concentration of MoO_3, yielded thicker crystals. However, there was frequently some attack on the crucibles as a result of the rather high proportion of PbO, which was increased during slow cooling of the batches by hydrolysis and evaporation of PbF_2.

Previous investigation showed that compounds with lead, ($PbEr_4Si_5O_{17}$ and lead rare-earth oxyapatites) formed in the system Er_2O_3–PbO–SiO_2 [18]. However, with the addition of MoO_3, this problem has now been avoided and only Ho_2SiO_5 crystals were obtained from the composition given in Table I.

4.7. Pr_2MoO_6

The flux growth of the monoclinic R_2MoO_6 (R = Lu to Sm) compounds from the systems R_2O_3–PbO–MoO_3 has been reported [19]. For the growth of Pr_2MoO_6, however, the system

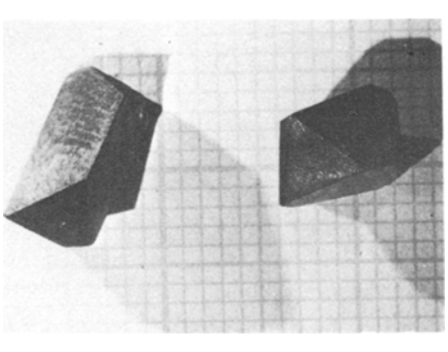

Figure 3 Octahedral crystals of $Tm_2Ti_2O_7$ (mm grid).

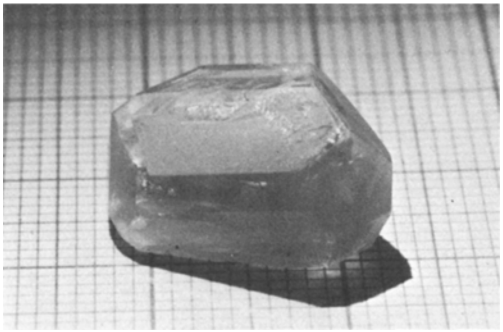

Figure 4 Crystal of $Tm_2Ge_2O_7$ from a 50 cm³ crucible (mm grid).

investigated was Pr_6O_{11}–MoO_3–K_2O, which does not attack platinum, unlike the system with PbO. The composition given in Table I yielded transparent green platelets, isotropic when viewed perpendicularly to the surfaces, in accordance with its tetragonal structure [20].

This system may be worth investigating also for the growth of the other rare-earth molybdates R_2MoO_6.

4.8. $LiCoPO_4$

These crystals are of interest because of their magnetoelectric properties which are currently being investigated by neutron diffraction [21]. The crystals reported here are substantially larger than those prepared before [22].

5. Discussion

It has been shown previously [4, 5] that starting compositions for the growth of compounds which contain a refractory and an acidic or amphoteric oxide can be calculated on the basis of a general ternary or pseudoternary composition diagram; also, fewer, larger crystals of more equidimensional habit may be expected when the excess acidic/amphoteric oxide is near the minimum needed to produce the desired compound. It was also shown that partial substitution of basic fluoride for basic oxide greatly increased the concentration of refractory oxide that could be dissolved in the melt at a given temperature.

The compositions reported in Table I are representative of a larger number of experiments. In many cases (as in compositions 1, 2, 3, 4, 5, 8, 11, 12), a few, (often less than 10, and occasionally only 1 or 2) crystals were obtained. These were relatively large and tended to contain flux inclusions, showing that the relative supersaturation of the melts was probably high [23] and growth immediately after nucleation was rapid. The outer parts of the crystal usually contained transparent regions free from inclusions.

Batches 2 and 3 illustrate again the great increase in solubility of R_2O_3 that usually occurs after substitution of PbF_2 for about half the PbO content (in this case, from 7 wt % to 24 wt % R_2O_3).

Compositions 8, 9 and 12 illustrate the notable improvement in quality, size and number of crystals that resulted on including MoO_3 in the melts [4, 5]. Compositions 4 and 5 resulted in much larger, fewer crystals than the previously published recipe [11]. It has been shown that a small percentage of an acidic oxide added to a fluxed melt is often helpful in reducing the numbers of crystals [6, 24] (the "additive effect"), and it appears that a few per cent of B_2O_3 has this effect in the growth of (La, Pb)MnO_3 and (Nd, Pb)MnO_3.

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