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CRYSTAL GROWTH FROM THE FLUX SYSTEMS PbO-V_2O_5 AND Bi_2O_3-V_2O_5

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Fluxes of composition $2PbO \cdot V_2O_5$ and $4Bi_2O_3 \cdot V_2O_5$ have been found to be particularly suitable for crystal growth. Starting compositions and conditions for growth are given for Al_2O_3, Cr_2O_3, α-Ga_2O_3, β-Ga_2O_3, ThO_2, TiO_2, $GaFeO_3$, $NiFe_2O_4$, $NiTiO_3$, Fe_2TiO_5, $TbNbO_4$, $ThPbV_2O_8$ and RVO_4 (R = rare earth ion).

1. Introduction

The paper describes the application of lead and bismuth vanadate fluxes to the growth of a number of simple and complex oxides. The advantages of these fluxes have been described previously[1]); in particular the addition of V_2O_5 to the powerful solvents PbO and Bi_2O_3 greatly reduces the degree to which platinum is attacked. When these solvents are used alone, crucibles are prone to attack because the oxides are easily reduced and both lead and bismuth form low melting point alloys with platinum. On the addition of V_2O_5, however, any traces of free metal in the solvents are oxidized and the V_2O_5 is reduced only to a lower oxide. As a result prolonged experiments may be conducted, even at high temperatures (> 1350 °C). The vanadate fluxes are also nonvolatile, simple to prepare, readily soluble in dilute acids and permit the growth of a small number of large crystals by spontaneous nucleation.

2. Experimental

The crystals were grown in a muffle furnace which was heated by two vertical arrays of horizontal Morgan Crusilite elements, one on each side of the hearth. This arrangement produced a favourable temperature distribution for crystal growth and a small vertical temperature gradient which was sufficient to ensure that nucleation occurred at or near the bases of the crucibles.

The crucibles were provided with tightly fitting lids to minimize vaporization and the volumes of the melts were chosen so that each crucible was not more than half full. The latter measure enabled a hot-pouring technique to be used to facilitate the recovery of crystals.

In a typical experiment, several crucibles were embedded in a block of Morgan M.I.28 alumina brick and any spaces were packed with powdered alumina. The block was then heated in the furnace to such a temperature that complete dissolution of the solutes was assured and was maintained at this temperature for a predetermined period. At the end of the period, the furnace was cooled at a specified rate by means of a Eurotherm electronic programmer.

When the cooling programme had been completed, the block was withdrawn from the furnace, inverted and replaced. This sequence of operations was performed rapidly with the aid of a mechanical device so that the flux flowed into the lids of the crucibles before it could solidify. The furnace was then allowed to cool and the crucibles were removed from the block.

After a period of immersion in hot, dilute nitric acid, the lids were removed from the crucibles and each in turn was placed on a cone of perforated platinum foil which was mounted above a second, empty crucible. The assembly was then heated in the furnace to 1) C so that the flux melted and drained through the perforated cone into the lower crucible. By this means the flux was separated from the crystals, which remained either on the cone or on the inner surface of the upper crucible. The method had the advantage that crystals were recovered without recourse to tedious leaching procedures and, in the case of the rare earth vanadates,

TABLE 1

Starting compositions and experimental conditions for crystal growth from $2\ PbO \cdot V_2O_5$

Desired compound	Starting composition	Crucible volume (ml)	Initial temperature (°C)	Holding time (hr)	Final temperature (°C)	Cooling rate (°C hr^{-1})	Final product
(1) Fe_2TiO_5	16 g Fe_2O_3, 8 g TiO_2, 205 g PbO, 89 g V_2O_5	100	1330	1	950	1.7	Black plates up to 2.5 cm × 8 mm and rods
(2) $GaFeO_3$	2.5 g Ga_2O_3, 2.1 g Fe_2O_3 52 g PbO, 21 g V_2O_5	50	1300	14	900	5	Rods up to 1 cm × 0.3 mm × 0.3 mm and plates of β-Ga_2O_3 up to 4 mm in width
(3) $NiTiO_3$	5.6 g NiO, 6 g TiO_2 103 g PbO, 45 g V_2O_5	100	1320	14	950	1	Black rhombohedra up to 3 mm on edge and plates up to 1 cm in width
(4) α-Fe_2O_3	13 g Fe_2O_3, 202 g PbO, 94.5 g V_2O_5	100	1120	15	810	2.5	Thin basal plates up to 3 cm in width
α-Fe_2O_3	25 g Fe_2O_3, 202 g PbO, 94.5 g V_2O_5	100	1345	24	750	1.3	Thicker plates and rhombohedra
(5) TiO_2	4.2 g TiO_2, 51.4 g PbO, 24 g V_2O_5	50	1330	14	1000	1	Rods up to 2 cm × 1.5 mm × 1.5 mm
(6) ThO_2	14 g ThO_2, 95 g V_2O_5, 202 g PbO	100	1330	14	1000	1	Clear octahedra up to 2.5 mm on edge
(7) $ThPbV_2O_8$	14 g ThO_2, 112 g V_2O_5, 238 g PbO	100	1320	14	750	1.3	Thin, pale yellow plates up to 6 mm in width
(8) $DyVO_4$	9 g Dy_2O_3, 91 g V_2O_5, 214 g PbO	100	1330	14	950	1	Clear rods up to 2 cm × 1.5 mm × 1.5 mm

enabled the crystals to be recovered intact since these were prone to fracture if allowed to remain in contact with the flux until it solidified.

3. Results

3.1. Crystal growth from lead vanadate

The composition $2\ PbO \cdot V_2O_5$ was found to be the most suitable flux for the growth of crystals and the following materials have been prepared from it in accordance with the experimental procedures which are summarized in table 1.

(1) Fe_2TiO_5: This material occurs in nature as pseudobrookite. Large crystals were obtained, as shown in fig. 1, and E.P.M.A. has shown that these contained less than 0.3% V.

(2) $GaFeO_3$ and β-Ga_2O_3: Rods of $GaFeO_3$ up to 1 cm in length were obtained from a 78 g melt. A number of semi-transparent, brown, pseudo-hexagonal crystals were also formed and these were identified as β-Ga_2O_3.

(3) $NiTiO_3$: $NiTiO_3$ was found to grow in the form of rhombohedral crystals at high temperatures and basal plates at lower temperatures. Similar results were obtained for Cr_2O_3 and α-Fe_2O_3, which are structurally similar, and such behaviour has also been reported in the growth of the latter materials from PbO–$K_2B_4O_7$[2]).

(4) α-Fe_2O_3: When dilute solutions of Fe_2O_3 in $2\ PbO \cdot V_2O_5$ were cooled from below 1000 °C, large basal plates were formed. At higher temperatures the plates were thicker and rhombohedra were also produced. E.P.M.A. showed that the crystals contained less than 0.05% Pb and 1–2% V.

(5) TiO_2: Rods 2–3 cm in length were obtained of

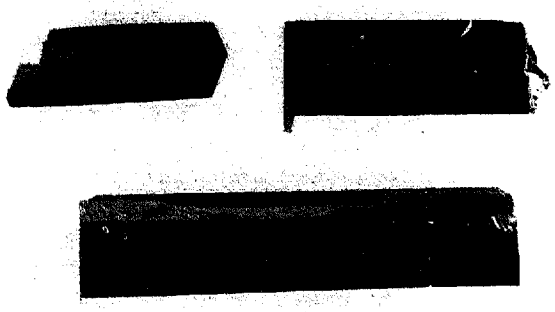

Fig. 1. Crystals of Fe_2TiO_5 (magnification 3×).

TABLE 2

X-ray powder pattern data for $ThPbV_2O_8$

hkl	*I*	$ThPbV_2O_8$	
		$\sin^2\theta$ (obs)	$\sin^2\theta$ (calc)
101	w	0.0199	0.0201
011	m	0.0253	0.0253
11$\bar{1}$	m	0.0314	0.0315
101	mw	0.0343	0.0341
111	m	0.0456	0.0455
200	s	0.0525	0.0526
120	vs	0.0582	0.0584
210	w	0.0634	0.0639
$\bar{1}$12	w	0.0660	0.0664
012	s	0.0674	0.0673
121	mw	0.0797	0.0794
211, $\bar{2}$12	mw	0.0907	0.0919
112	mw	0.0942	0.0944
220	vw	0.0969	0.0978
$\bar{1}$22	vw	0.0998	0.1004
130	mw	0.1151	0.1154
031	mw	0.1173	0.1158
31$\bar{1}$	mw	0.1213	0.1227
221, 22$\bar{2}$	mw	0.1249	0.1258
$\bar{1}$13	vw	0.1294	0.1298
131	vw	0.1348	0.1363
212	m	0.1471	0.1479
301	w	0.1531	0.1533

Unit cell dimensions for $ThPbV_2O_8$: $a = 6.96$ Å, $b = 7.25$ Å, $c = 6.75$ Å, $\beta = 105°$.

which the largest tended to contain flux inclusions. The crystals varied in colour from straw to deep red and some exhibited termination facets.

(6) ThO_2: Clear, colourless octahedra were obta ned of which the larger possessed an internal den itic structure and the (111) facets consisted of thin pl tes. When a melt was cooled below 1000 °C, resol ion occurred and a previously unreported phase, ThPb' $_2O_8$ was formed. That platinum dissolved in the melt to an appreciable extent was evident from the fact that small platelets of the metal were subsequently found a the base of the crucible.

(7) $ThPbV_2O_8$: This previously unreported ma rial crystallized in the form of transparent, yellow p ates which exhibited extinction under the polarizing m cro-scope. The X-ray powder pattern of the materia was found to be similar to that of monazite, $LaVO_4$, and has been similarly indexed. The X-ray diffraction data and the lattice parameters are included in table 2. No superlattice was observed, so it would appear that Th^{4+} and Pb^{2+} are randomly disposed in the lattice and thus the formula may be written (Th, Pb)VO_4. The crystals were analyzed and were found to contain 32.8% Pb and 14.2% V, a result which is in good agreement with the theoretical values of 31% and 15% respectively.

Similar but colourless crystals were produced on cooling a solution of ThO_2 in $Pb_2P_2O_7$, and the X-ray powder pattern of the material was consistent with a monazite-type structure of formula (Th, Pb)PO_4. Both materials rapidly decomposed on heating and attempts

TABLE 3

Starting compositions and experimental conditions for crystal growth from $4Bi_2O_3 \cdot V_2O_5$

Desired compound	Starting composition	Crucible volume (ml)	Initial temperature (°C)	Holding time (hr)	Final temperature (°C)	Cooling rate (°C hr^{-1})	Final product
(1) Cr_2O_3	20.4 g Cr_2O_3, 240 g Bi_2O_3, 24 g V_2O_5	100	1345	24	750	1.3	Rods and plates up to in width
(2) Al_2O_3	7 g Al_2O_3, 84 g Bi_2O_3, 8.5 g V_2O_5	50	1300	14	900	5	Rhombohedral platelet 5 mm on edge
(3) α-Fe_2O_3	12 g Fe_2O_3, 120 g Bi_2O_3, 12 g V_2O_5	50	1300	4	900	5	Rhombohedra up to 7 edge
(4) β-Ga_2O_3	7 g Ga_2O_3, 84 g Bi_2O_3, 8.5 g V_2O_5	50	1300	14	900	5	Platelets up to 6 mm × 1 mm
(5) $NiFe_2O_4$	3.7 g NiO, 8 g Fe_2O_3, 40 g PbO, 4 g V_2O_5	50	1350	24	950	1	Octahedra up to 3 mm
(6) $TbNbO_4$	20 g Tb_4O_7, 14 g Nb_2O_5, 200 g Bi_2O_3, 20 g V_2O_5	100	1330	14	900 500 then to	1 3	Bipyramids up to 5 m width
(7) $GdVO_4$	15 g Gd_2O_3, 180 g Bi_2O_3, 24 g V_2O_5	100	1320	14	950	1	Clear, yellow rods 7.5 mm × 2 mm × 2mm

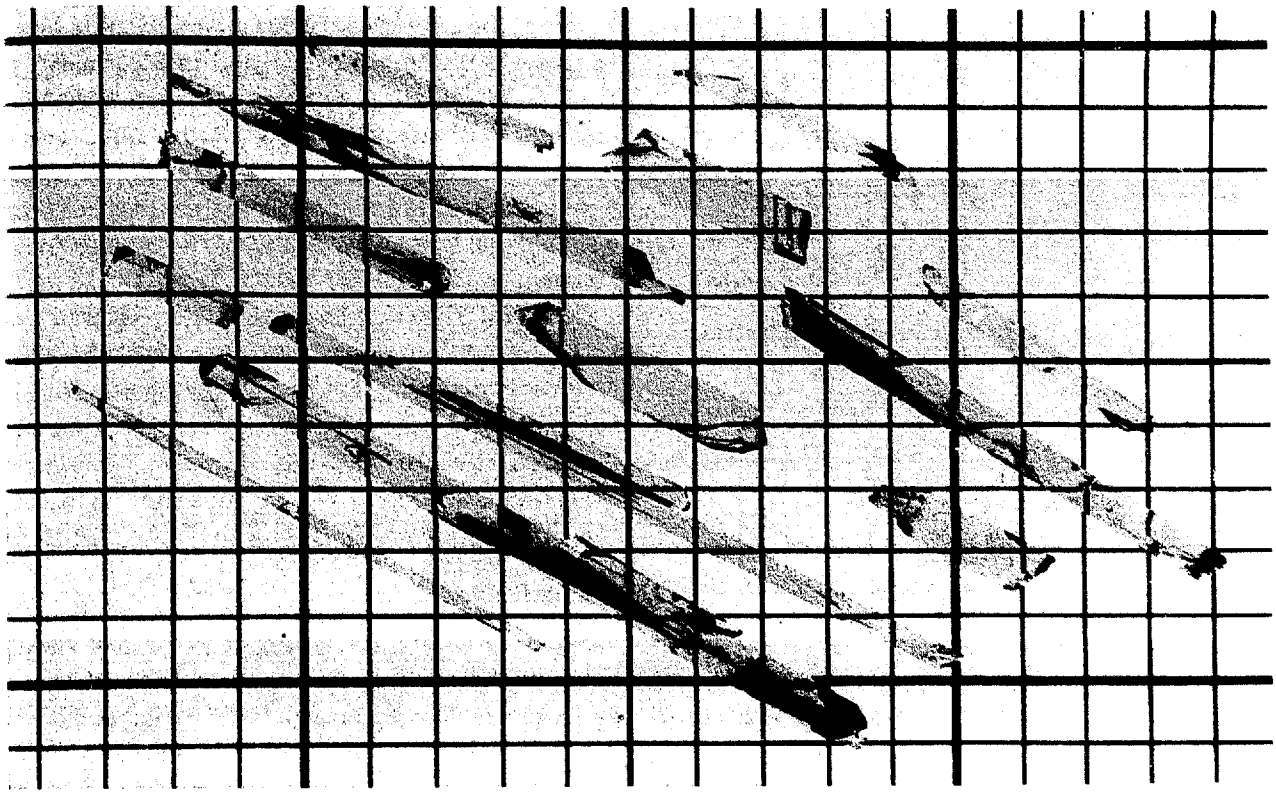

Fig. 2. Crystals of $DyVO_4$ (2.5 mm grid).

to synthesize them from the constituent oxides were unsuccessful.

(8) RVO_4 (R = rare earth ion and yttrium): All of the RVO_4 crystals grew in the form of long, clear rods from $2PbO \cdot V_2O_5$ alone as shown in fig. 2. However, as was reported for $GdVO_4$[3]), the growth habit was dependent on the composition of the flux and the presence of additives. For example, the addition of $NaVO_3$ and $Na_2B_4O_7$ to the flux caused the crystals to grow the form of plates or thick rods, while the addition V_2O_5 or B_2O_3 caused the rods to be elongated. The VO_4 crystals were analysed and found to contain 3% Pb.

2. CRYSTAL GROWTH FROM BISMUTH VANADATE

The composition $4Bi_2O_3 \cdot V_2O_5$ was found to be the most suitable flux and the following materials have been grown from it in accordance with the experimental procedures which are summarized in table 3. The preparation of the flux from an intimate mixture of its constituent oxides was shown to minimize damage to the crucibles.

(1) Cr_2O_3: As a result of the great difference in density between the flux and the solute, dissolution of the latter was usually incomplete and a layer of Cr_2O_3 remained at the surface of the melt. Despite the fact that this layer provided nucleation sites, large crystals grew at the base of the crucible, generally in the form of pseudo-hexagonal plates but also as rhombohedra. A hexagonal crystal in which grain boundaries are clearly defined is shown in fig. 3.

(2) Al_2O_3: As in the case of Cr_2O_3, nucleation occurred on undissolved material at the surface of the melt and also at the base of the crucible. The crystals

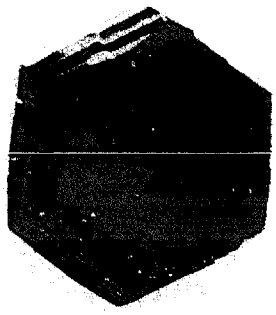

Fig. 3. Crystal of Cr_2O_3 showing grain boundaries.

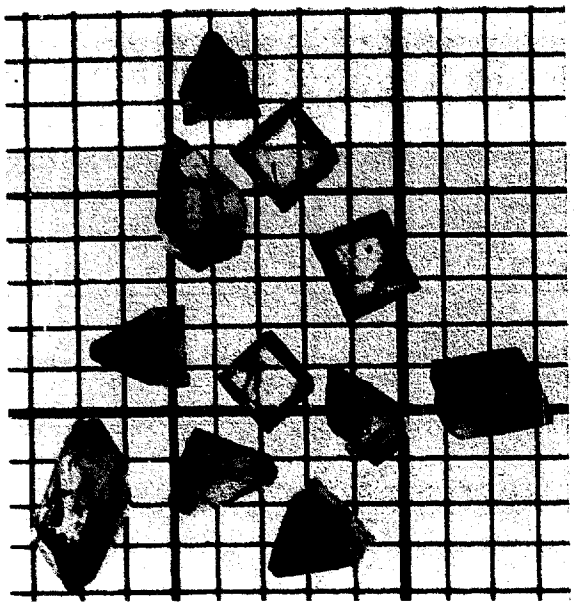

Fig. 4. Crystals of $TbNbO_4$ (mm grid).

grew in the form of rhombohedral platelets and some attained 5 mm on edge.

(3) α-Fe_2O_3: Only rhombohedral crystals were obtained and it was concluded that the presence of Bi_2O_3 inhibited the formation of basal plates. Under conditions which promoted rapid growth dendrites were formed. The crystals contained less than 0.1 % Bi and less than 1 % V.

(4) β-Ga_2O_3: Transparent, colourless plates up to 6 mm edge were obtained from a 100 g melt.

(5) $NiFe_2O_4$: Octahedra up to 3 mm on edge were grown from a 56 g melt.

(6) $TbNbO_4$: Bismuth fluxes are normally to be avoided for rare earth compounds because Bi^{3+} is similar in both size and charge to R^{3+}, as a result of which partial substitution can occur. However, it was shown that rare earth iron and aluminium garnets could be produced, but the extent of the substitution may be appreciated from the fact that, in an attempt to grow crystals of $Dy_3Fe_5O_{12}$, crystals of formula $Dy_{2.46}Bi_{0.52}Fe_{5.01}O_{12+\delta}$ were obtained. In the case of $RNbO_4$ however, the only known alternative solvent to bis uth vanadate is bismuth borate[4]), and in experiments ith $RNbO_4$–Bi_2O_3–B_2O_3 mixtures it was found tha the crucibles were attacked so severely that none rem ied intact. When bismuth vanadate was used, the cru les were not damaged and bipyramidal crystals of TbN O_4 were obtained, as shown in fig. 4. The crystals cor in- ed about 4 % Bi and 2 % V.

(7) RVO_4: The rare earth vanadate rods which ere grown from bismuth vanadate were considerably l ger in cross-section than those which were grown from ead vanadate. The degree to which the crystals were on- taminated by the flux was, however, consider bly greater. Analysis of $GdVO_4$ crystals showed that these contained about 7 % Bi.

4. Conclusions

Fluxes of composition $2\,PbO \cdot V_2O_5$ and $4\,Bi_2O_3 \cdot V_2O_5$ have been found to be suitable for the growth of a variety of oxide crystals. The properties of these fluxes, and in particular their low volatility at high temperatures, favour their use in epitaxial deposition and crystal-pulling experiments. Future work will be directed towards these ends.

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