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Flux growth of rare earth silicates and aluminosilicates

B. M. WANKLYN, F. R. WONDRE
Clarendon Laboratory, University of Oxford, UK
G. B. ANSELL
Code 60, Michaelson Laboratories, US Naval Weapons Center, China Lake, California, USA
W. DAVISON
School of Physics, The University, Newcastle upon Tyne, UK

Crystals of R_2SiO_5, $R_2Si_2O_7$, rare earth apatites, and square-faceted rare earth aluminium garnets containing silicon have been grown from fluxed melts. Silicon was provided in two ways: by vapour transport of a siliceous vapour species which diffused into the melts ("vapour-flux" method), and by including SiO_2 in the initial mixtures. The results of these two methods are compared.

The materials have been characterized by X-ray diffraction and, in some cases, by EPMA. Powder pattern data for some of the rare earth apatites are included.

1. Introduction

The rare earth silicates are of interest for several reasons: (1) the concentration of rare earth ions is sufficient for magnetic interactions at low temperatures to be expected; (2) the structures allow a variety of substitutions at cationic as well as anionic sites, and so are suitable for a number of physical studies, including those concerned with potential laser action [1]; (3) the variety of arrangements of the small SiO_4 tetrahedra leads to a multiplicity of structures, and many of the compounds are known to have temperature-dependent structures above room temperature. Structural transitions at low temperatures may also occur. The structures of rare earth silicates have been comprehensively reviewed by Felsche [2].

Crystals of $CaY_4(SiO_4)_3O$ have been grown by the Czochralski method at 2060° C [1]. Crystals, initially described as $Sm_4(SiO_4)_3$ and later shown to have the apatite structure, were obtained as rods or whiskers when Sm_2O_3 and Sm were heated in sealed quartz tubes at 1250° C [3].

The flux growth of R_2SiO_5 crystals from Bi_2O_3 [4] and from Li_2O–MoO_3 [5] has been described. The crystals from Li_2O–MoO_3 were large enough for X-ray studies; those grown from Bi_2O_3 flux contained 7.2% Bi. Some members of the series R_2SiO_5 and $Yb_2Si_2O_7$ have been grown from KF as flux, but the crystals were small and not well defined [6]. Small crystals of Er_2SiO_5 have been grown from PbO–PbF_2 flux by cooling from 1500 to 900° C [7].

Rare earth silicate crystals have recently been grown from fluxed melts which initially contained no silicon, by a "vapour-flux" method. The silicon was provided via a vapour species which resulted from a reaction between PbF_2 and sillimanite, Al_2SiO_5, and which diffused back into the melts [8]. This paper reports the growth of rare-earth silicates and aluminosilicates by two methods. In the first, silicon was provided by the "vapour-flux" method and in the second, SiO_2 was initially included in the starting materials.

2. Materials and equipment

The chemicals were: Rare Earth Products 99.9% pure R_2O_3 (R = Er, Ho, Dy, Tb, Gd, La); Trona Industrial grade Pr_4O_7 and Nd_2O_3; BDH Laboratory Reagent B_2O_3 and precipitated SiO_2 and "Analar" PbO, Al_2O_3, PbO_2, $CaCO_3$, and MoO_3; Johnson Matthey Grade 2 PbF_2.

The SiO_2 contained 12 wt% H_2O and the

TABLE I Starting compositions, experimental conditions and crystal products

Composition of mixture		Crucible volume (cm^3)	Soak temp. (°C)	Holding time (h)	Cooling rate (K h^{-1})	Final temp. (°C)	Crystal products
Apatites							
Pr	2.2 g Pr_4O_7, 0.51 g SiO_2, 35 g PbF_2, 0.7 g PbO_2, 1.5 g MoO_3	20	1240	6	0.8	1120	Transparent rods 1.5 mm in thickness which grew right across the crucible
Gd	1.8 g Gd_2O_3, 18 g PbF_2, 0.5 g PbO_2, 3.2 g MoO_3, 5 g PbO	10	1280	20	1	1150	Rods 10 mm in length
Gd	2 g Gd_2O_3, 0.35 g SiO_2, 26 g PbF_2, 6 g PbO, 1.4 g PbO_2, 1.2 g MoO_3	20	1240	6	0.7	1120	Rods 10 mm in length
Er	1.5 g Er_2O_3, 0.25 g SiO_2, 20 g PbF_2, 1 g PbO_2, 0.2 g $CaCO_3$	10	1270	6	0.2	1200	Needles of apatite
Er	1.2 g Er_2O_3, 0.6 g SiO_2, 14 g PbO, 1.1 g PbO_2, 9 g MoO_3, 0.1 g $CaCO_3$	10	1270	4	1	1130	2 mm rods of apatite
R_2SiO_5							
Dy	1 g Dy_2O_3, 0.2 g SiO_2, 13 g PbF_2, 3 g PbO, 0.7 g PbO_2, 0.7 g MoO_3	10	1270	4	1	1130	Large plates shown in Fig. 2, 10 mm across
Er	1 g Er_2O_3, 0.35 g SiO_2, 13 g PbF_2, 3 g PbO, 0.7 g PbO_2, 0.6 g MoO_3	10	1250	4	0.7	1120	Platelets 3 to 4 mm across, 1 mm thick
Er	1.8 g Er_2O_3, 20 g PbF_2, 3 g PbO, 2.5 g PbO_2, 1.4 MoO_3	20	1290	6	1	1180	Crystals up to (3 × 4) mm^2
$R_2Si_2O_7$							
Er	1.8 g Er_2O_3, 20 g PbF_2, 0.2 g PbO_2, 5 g PbO	10	1280	4	0.5	1200	Crystals of $Er_2Si_2O_7$ on lid and upper walls (Fig. 1b and c). (Er_2SiO_5 grew at the crucible base)
Er	2.4 g Er_2O_3, 0.29 g SiO_2, 15 g PbO, 1 g PbO_2, 15 g MoO_3	20	1270	4 days	—	1270	Large transparent plate, 9 mm across (Fig. 1a)
Rare-earth aluminium/silicon garnets							
Er	1.2 g Er_2O_3, 0.4 g SiO_2, 0.7 g Al_2O_3, 1 g PbO_2, 15 g PbF_2, 6 g MoO_3	10	1270	5 days	—	1270	Pale blue crystals up to 1.3 mm on edge with square facets

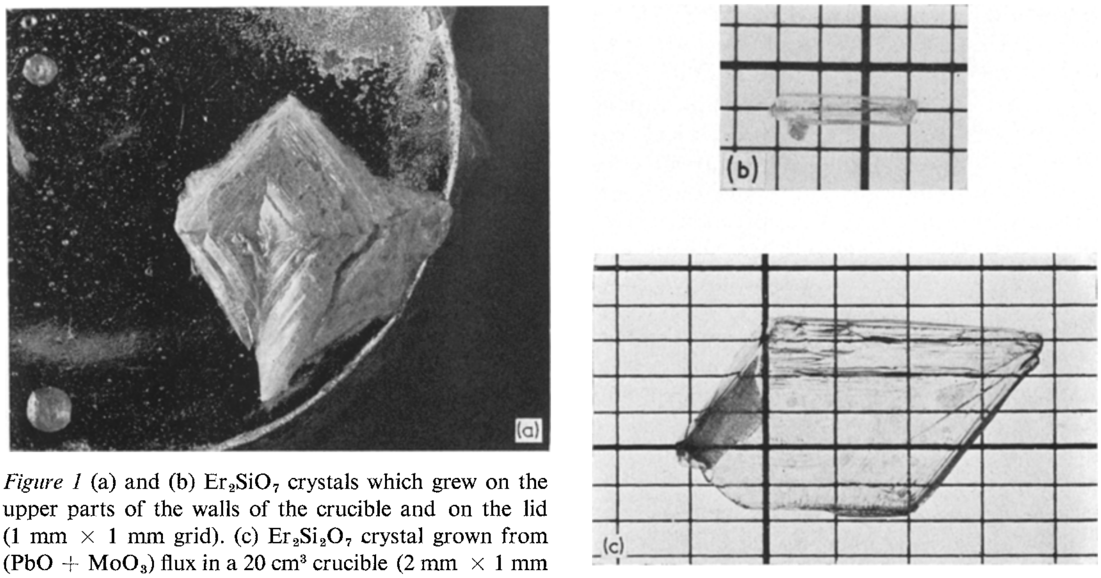

Figure 1 (a) and (b) Er_2SiO_7 crystals which grew on the upper parts of the walls of the crucible and on the lid (1 mm × 1 mm grid). (c) $Er_2Si_2O_7$ crystal grown from ($PbO + MoO_3$) flux in a 20 cm^3 crucible (2 mm × 1 mm grid).

weights and ratios reported here have been corrected for this.

The furnaces and control equipment have been described previously [9]. The melts were contained in platinum crucibles of 10, 20 or 50 cm^3 capacity which were provided with loosely fitting lids. The crucibles were placed in shallow hollows in Morgan M.I. 3000 refractory bricks, and alumina powder was packed around the bases. The crucible and brick assemblies were placed in a sillimanite D-muffle which was closed at one end. The muffle was placed in the furnace and the open end was blocked with 4 in. of refractory brick.

3. Experimental

Table I gives starting compositions, experimental conditions and crystal products. PbO_2 was included to provide oxidising conditions during heating. A small quantity of MoO_3 was usually added since this was found to contribute to the growth of larger crystals of better quality, apparently by reducing the number that nucleated and grew. The furnace was initially heated and finally cooled at 100 K h^{-1} to protect the muffle of sillimanite (Al_2SiO_5) from thermal shock. The heating programme also ensured that the chemicals were fully oxidized before reaching high temperatures. In batches where the silica

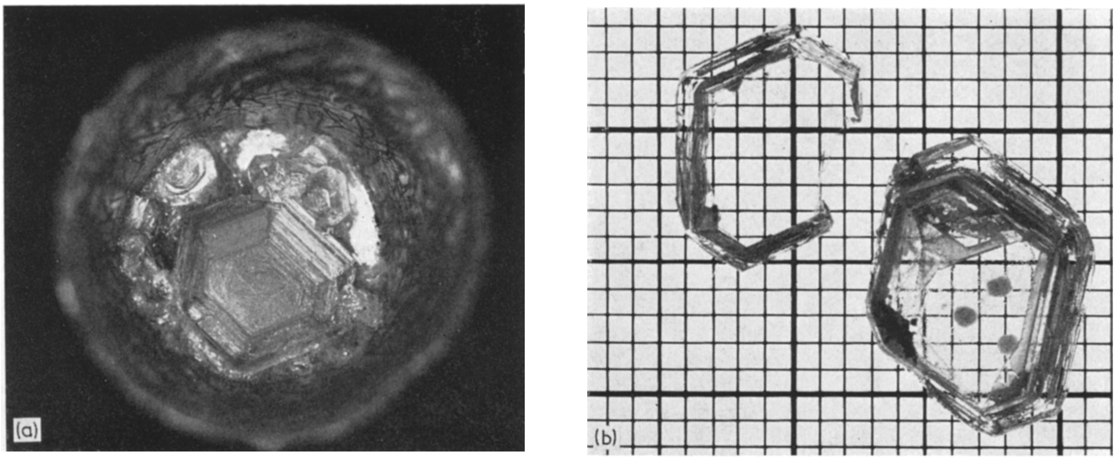

Figure 2 (a) Crystals of Dy_2SiO_5 in a 10 cm^3 crucible. (b) Crystal plates of Dy_2SiO_5. (1 mm × 1 mm grid.)

was provided by the "vapour-flux" method [8], a vapour species containing aluminium was also produced by a reaction between PbF_2 and Al_2SiO_5, and both this and the siliceous vapour species diffused into the melts [10]. Under these conditions, it was not possible to avoid contamination by aluminium, but it was found that Si was only transported to an appreciable extent when the muffle was new. When silicon was provided as SiO_2 in the initial mixtures, a previously used muffle was satisfactory. However, the reaction of PbF_2 with older muffles continued to produce the aluminous vapour species and thus batches were contaminated with Al to some degree.

To obtain crystals free from Al and to discover whether the rare earth apatites would crystallize equally well in its absence, one batch of crucibles was placed in a silica tube which was 2 in. in diameter, sealed at one end and plugged at the other with vitreosil and quartz wool. The apatites grew equally well in either the quartz tube or the sillimanite muffle, showing that Al was not necessary for their growth.

Evaporation was usually carried to completion but sometimes it was necessary to clean the crystals by soaking in hot, 1:20 aqueous HNO_3. Of all the rare earth silicates, only the apatites which contained the larger rare earth ions tended to dissolve during this treatment.

X-ray powder patterns were used to characterize R_2SiO_5 [2, 5, 11, 12], $R_2Si_2O_7$ (type C) [2] and the rare earth apatites [2, 3, 13, 14, 15]. EPMA provided quantitative information as to composition and degree of contamination by the flux, and the results are given in Table II. X-ray powder pattern data for some of the apatite phases are given in Table III.

A stoichiometric mixture corresponding to gadolinium apatite was sintered at 1200 and 1250°C, but this did not combine to form the apatite phase.

4. Results

Many experiments were carried out in which silicate crystals grew by the "vapour-flux" method, thus substantiating previous results [8]. In Table IV the products obtained from batches with and without silicon initially are readily compared. When Si was included, the results were generally more reproducible and certainly better for R_2SiO_5. In only four out of more than 40 experiments, a new rare earth silicate crystallized in the form of faceted platelets up to (12 × 2 × 0.2) mm³. This material will be characterized elsewhere.

TABLE II Identification of phases by EPMA

Formula	Formula requires (%)		EPMA indicates (%)		X-ray powder pattern agrees with data in references
Dy_2SiO_5	Dy	75.2		75.3	2, 5, 11, 12
	Si	6.5		5.9	
			F	0.1	
$Er_2Si_2O_7$ (type C)	Er	66.5		63.0	2
	Si	11.2		10.0	
$Er_{2.93}(Al_{4.8}Si_{0.2})O_{12}$ (garnet)	Er	56.5		57.3	16
	Si	0.65		0.73	
	Al	14.9		15.6	
$Y_5(Si_{1.5}B_{1.5})O_{12.5}F_{0.5}$ (apatite)	Si	5.9		5.9	2, 3, 13, 14, 15
	Y	62.4		62.4	
	B	2.3		not measureable	
	F	1.3		2.0	
			Al	0.1	
$Pb_{0.2}Dy_{4.8}Si_{2.8}O_{13}$ (apatite)	Dy	70.4		68.3	2, 3, 13, 14, 15
	Si	7.1		6.8	
	Pb	3.7		3.4	
$Pb_{1.16}La_{3.36}Er_{0.49}Si_{2.4}Al_{0.6}O_{12.2}F_{0.8}$ (apatite)	Pb	22.2		22.3	2, 3, 13, 14, 15
	La	43.0		43.2	
	Er	7.5		8.1	
	Si	6.2		6.5	
	Al	1.5		1.6	
	F	1.4		2.3	

TABLE III X-ray powder pattern data for some rare earth apatite phases

hkl	I/I_0	d_{obs}			
		$Y_5Si_{1.5}B_{1.5}O_{12.5}F_{0.5}$	$Pb_{0.2}Dy_{4.8}Si_{2.8}O_{13}$	$Pb_{0.19}Gd_{4.81}Si_{2.6}Al_{0.2}O_{13}$	$PbLa_{3.37}Er_{0.63}Si_{2.4}Al_{0.6}O_{12.5}F_{0.5}$
110	1	4.55	4.69	4.71	4.87
020	4	3.95	4.06	4.09	4.23
111	2	3.78	3.86	3.90	4.03
002	2	3.37	3.40	3.44	3.58
012	5	3.103	3.130	3.176	3.300
120	5	2.979	3.070	3.088	3.192
121	10	2.712	2.800	2.825	2.912
112	6	2.725	2.751	2.786	2.883
030	5	2.623	2.707	2.727	2.819
022	1	2.568	2.600	2.646	2.701
131	1	2.076	2.124	2.146	2.219
113	1	2.016	2.039	2.069	2.145
040	1	1.973	2.024	2.052	2.112
222	1	1.888	1.931	1.954	2.017
132	3	1.835	1.878	1.901	1.962
230	2	1.811	1.863	1.882	1.939
123	3	1.795	1.820	1.848	1.917
231	2	1.748	1.798	1.815	1.874
140	3	1.724	1.775	1.790	1.843
042	3	1.704	1.744	1.765	1.819

TABLE IV Initial ratios R_2O_3:SiO_2, flux mixtures, crystal products, and comparison of results

Rare earth, R	Molar ratio R:Si in initial mixture	Flux	Product	Comparison of results	
				"Vapour-flux"	Si initially in crucible
Er	up to 1:1.1	$PbF_2/PbO/MoO_3$	Er_2SiO_5 only, in the melt $Er_2Si_2O_7$, on the upper crucible wall and lid (Fig. 1a and b)	The methods produced comparable results Some of the material was transparent	
	up to 1:2.2	PbO/MoO_3	$Er_2Si_2O_7$ only (Fig. 1c)		Large crystals grew by combined evaporation and slow cooling (loosely fitting crucible lid)
	1:1.6	$PbF_2/PbO + CaCO_3$	Apatite		Er apatite was not obtained in the absence of Ca^{2+}
Dy	up to 1:0.9	PbF_2/PbO	Dy_2SiO_5 (Fig. 2a and b) or apatite	Small crystals	Large plates of Dy_2SiO_5
	up to 1:3.1	PbF_2/PbO	Apatite	The apatites were comparable by both methods	
	1:1	PbF_2/PbO	Apatite + Tb_2SiO_5		Poorly formed, inter-grown Tb_2SiO_5
Tb	up to 1:1.1	PbF_2/PbO	Apatite	The apatite crystals were comparable by both methods	
Pr, Nd, La	up to 1:0.8	PbF_2/PbO	Apatite (Fig. 3)		Thicker crystals were obtained with larger rare earth ions

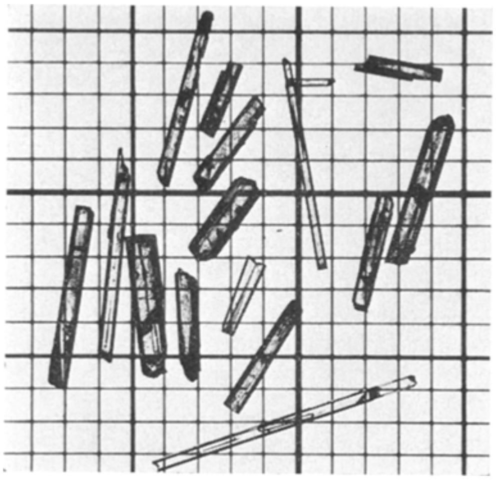

Figure 3 Hexagonal prisms of praeseodymium apatite grown from a melt containing silicon in a 20 cm^3 crucible. These are typical of all the apatites (1 mm × 1 mm grid).

$Er_2Si_2O_7$ crystals grew at the upper walls and lids of crucibles from which Si was initially absent. To determine whether Er was transported by PbF_2, a crucible containing Er_2O_3 and PbF_2, contained in a large platinum tube with a platinum rod supported so that its tip was near the crucible, was held for three days at a temperature above 1220° C. No material containing Er was deposited on the rod or on other parts of the platinum tube. Thus vapour transport of Er by PbF_2 can be discounted and apparently the melt was conveyed to the site of crystallization by a creeping process. Silicon then diffused into the thin layer of melt, resulting in the silicon-rich phase $Er_2Si_2O_7$, while in the bulk material in the crucible only Er_2SiO_5 crystallized.

Silicon-doped erbium aluminium garnets were first obtained by the "vapour-flux" method and were found to have a composition corresponding to $Er_{2.93}Al_{4.8}Si_{0.2}O_{12}$ [16]. The crystals were optically isotropic and were characterized by rectangular {100} facets, similar to those reported for rare-earth gallium garnets containing 5.5% Si [17]. When SiO_2 was initially present in the melt, larger crystals of similar habit were obtained, some of which are shown in Fig. 4. These "square" garnets did not have the colours usually shown by compounds of the rare earth ions, but were a pale blue-green when R = Er or Ho. The surface features shown in Fig. 4 were very different from those seen on garnets free from silicon. The latter have growth hillocks surrounded by vicinal faces. The {1 0 0} faces were only observed on rather small garnets as shown in Fig. 4. Crystals from still larger Si-doped batches showed instead a complex set of small facets, quite different from the usual habit of rare earth aluminium garnets. The Si-doped garnets also differed in that their solubility in hot 1 : 5 nitric acid solution was sufficiently high for the surfaces to be appreciably etched. A private communication from V. A. Timofeeva reports that she observed {1 0 0} faces in yttrium aluminium garnet grown from melts with a high B_2O_3 content, and that her colleagues have observed similar facets in garnets containing germanium[18].

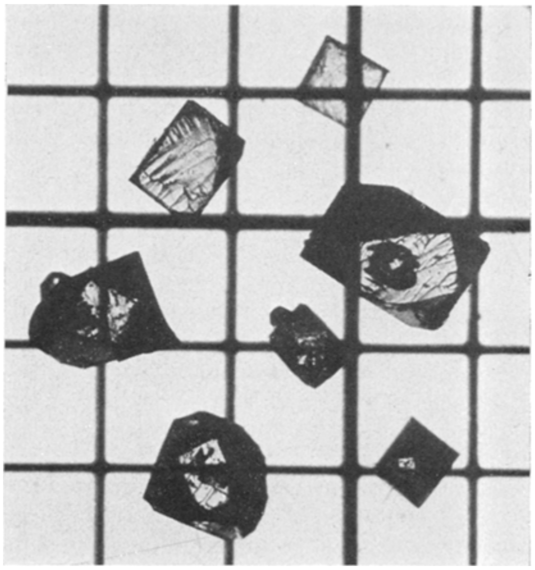

Figure 4 Square-faceted, Si-doped erbium aluminium garnets (1 mm × 1 mm grid).

In the sillimanite muffle, silicon entered melts by the "vapour-flux" process, at a rate which depended on the quantity of PbF_2 evaporating and reacting with the muffle surface. It is thus most probable that crystals grew under non-equilibrium conditions.

5. Conclusion

1. In many experiments silicate crystals were obtained both by the "vapour-flux" method [8] and from melts which initially contained Si. More consistent results were obtained in the latter case, but if the transport of silicon into a non-volatile flux were controlled, it would be possible to use the "vapour-flux" method to produce large crystals of predetermined composition.

2. Square-faceted rare earth aluminium garnets containing 0.7% Si have been grown. This habit has not previously been reported and the fact that incorporation of a small amount of silicon results in a change of habit, and especially in the growth of {100} faces, may be of value in epitaxial studies.

3. The silicates which possessed the apatite structure contained more Pb^{2+} in the lattice when the larger rare earth ions were present. This is probably a consequence of the fact that the ionic radius of Pb^{2+} is only slightly larger than that of La^{3+}, and considerably larger than the ionic radii of the smaller rare earth ions.

4. The rare earth silicate crystals were larger and of better quality than those reported previously. In particular, with R_2SiO_5, the addition of small amounts of MoO_3 to the starting material was found to result in the nucleation and growth of only a few large crystals.

5. Sillimanite muffles are useful in that they protect the furnace and elements from corrosive flux materials. With new muffles, contamination of melts in unsealed crucibles with both Si and Al is unavoidable, and with older muffles, Al is still transported into the melts, as previously reported [10].

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