# **Flux growth of silicates with vapour transported silicon**

## **B. M.** WANKLYN

*Clarendon Laboratory, University of Oxford, UK* 

## Z. HAUPTMAN

*Department of Geophysics and Planetary Physics, School of Physics, University of Newcastle upon Tyne, UK* 

As a result of a proposed vapour transport mechanism, silicate crystals have been grown from fluxed melts which originally contained only trace amounts of silicon. The melts were contained in platinum crucibles in a sillimanite, AI<sub>2</sub>SiO<sub>5</sub>, muffle, and the flux consisted of PbF<sub>2</sub>, or PbF<sub>2</sub> + PbO, occasionally with additional MoO<sub>3</sub>. It is postulated that a volatile siliceous species resulted from the reaction of PbF<sub>2</sub> vapour with the muffle and that this species transported Si into the fluxed melts. The silicate crystals produced include  $E_r$ SiO<sub>s</sub>, Dy<sub>2</sub>SiO<sub>s</sub>, Mg<sub>2</sub>SiO<sub>4</sub>·MgF<sub>2</sub>, a new material of formula Dy<sub>4</sub>SiO<sub>s</sub>, and several new rare earth compounds with the apatite structure.

#### **1. Introduction**

The event which initiated the research described in this paper was the appearance of crystals several millimetres in size, identified as  $Er<sub>2</sub>SiO<sub>5</sub>$ , in an experiment intended to produce  $Er<sub>2</sub>MoO<sub>8</sub>$ by flux evaporation. The crucible was contained in a sillimanite,  $Al_2SiO_5$ , muffle, and the flux was  $PbF<sub>2</sub>$ .

The occurrence of silicon in the crystals could have been the result of its presence as an impurity in the starting materials or its accidental introduction; or it could have been due to vapour transport of a phase containing silicon into the crucible. The introduction of sufficient silicon either as an impurity or by accident could not be explained, but the third possibility was feasible, since the literature indicates that species such as  $SiF_4$  and  $SiOF_2$  are effective transport agents. For example,  $SiOF<sub>2</sub>$  and  $SiF<sub>4</sub>$ have been reported to be transport agents in the growth of  $Be_2SiO_4$  by vapour transport [1].  $SiF<sub>4</sub>$  has also been reported to be a transport agent in the growth of  $Co<sub>2</sub>SiO<sub>4</sub>$  [2] and of topaz [3] in sealed quartz tubes, where the reaction between HF and  $SiO<sub>2</sub>$  supplied the vapour species, and HF was provided by the hydrolysis of  $CoF<sub>2</sub>$  and  $AlF<sub>3</sub>$  respectively. An

experimental investigation into the growth of silicate crystals in sillimanite muffles is reported, and the results are discussed.

## **2. Equipment and chemicals**

The furnaces and flux growth technique have been described previously [4]. In a typical experiment, six platinum crucibles, each  $10 \text{ cm}^3$ in volume and with a loosely fitting lid, were supported in Morgan M.I. 3000 refractory brick in a sillimanite muffle which was placed in a furnace. The open end of the muffle was blocked with a brick plug. The muffle protected the furnace and elements from the highly reactive  $PbF_2$  vapour, and was generally used only once. The volume of a melt was usually about 5 cm<sup>3</sup>.

The chemicals used were: Rare Earth Products 99.9% pure  $Er_2O_3$  and  $Dy_2O_3$ , BDH AnalaR  $MoO<sub>3</sub>$ , PbO<sub>2</sub> and PbO, "Extra Pure" PbF<sub>2</sub>, "Optran"  $PbF_2$ , and Johnson, Matthey "Specpure" MgO. The amounts of Si in the above chemicals are as follows:

99.9  $\%$  R<sub>2</sub>O<sub>3</sub> : 2 ppm approx. BDH AnalaR  $MoO<sub>3</sub>$ : < 1000 ppm BDH AnalaR  $PbO<sub>2</sub>$  : < 90 ppm BDH AnalaR PbO  $\div$   $\lt$  2 ppm

*9 1974 Chapman and Hall Ltd* 



## **3. Experiments and observations**

## **3.1. Er**<sub>2</sub>SiO<sub>5</sub>

In the first experiment in which silicate crystals were produced, hereafter referred to as experiment A, a mixture containing 1.8 g  $Er_2O_3$ , 0.7 g  $MoO<sub>3</sub>$ , 20 g "Extra Pure" PbF<sub>2</sub> and 5 g PbO was placed in a crucible. A loosely fitting lid was placed over the crucible to prevent accidental contamination of the melt and to reduce the rate of evaporation of the flux. The crucible was placed with five other crucibles, each containing similar quantities of  $PbF_2$  and various oxides as solutes in the muffle. The muffle was heated to  $1285^{\circ}$ C and cooled at 1 K h<sup>-1</sup> for five days.

The experiment produced pink crystals, about 1.9 g in total weight. Chemical analysis indicated their formula to be  $Er<sub>2</sub>SiO<sub>5</sub>$  (required, 75.8%) Er,  $6.4\%$  Si; found,  $75\%$  Er,  $6\%$  Si) and this result was substantiated by comparing the X-ray powder pattern with that of sintered  $Er_sSiO_s$ and with published data [5]. EPMA confirmed the analysis. Since 1.9 g  $Er<sub>2</sub>SiO<sub>5</sub>$  consists of 1.65  $g Er<sub>2</sub>O<sub>3</sub>$  and 0.25 g SiO<sub>2</sub>, and in view of the Si concentration in the starting materials, this quantity of silica could not be accounted for in terms of impure starting materials.

To check whether silica had been accidentally introduced into the melt, the experiment was repeated twelve times using "Optran"  $PbF_2$ instead of the "Extra Pure"  $PbF_2$ , and in ten cases  $Er<sub>2</sub>SiO<sub>5</sub>$  crystals large enough to be separated by visual inspection were obtained. In the other two experiments, evaporation was insufficient for crystal growth. Since samples of the same batches of all the starting materials had been used for the growth of other materials prior to the use of the sillimanite muffle and silicates had not occurred, it was concluded that the muffle was the source of Si. In particular, in many evaporation experiments in which  $R_2O_3$ , PbO and  $PbF_2$  were initially present in the crucibles, only  $R_2O_3$  and ROF had been obtained.

To investigate whether  $MoO<sub>3</sub>$  was necessary for the formation of the silicate crystals, experiment A was repeated without it, and in only one of five experiments were the crystals of  $Er_sSiO_5$ large enough to separate visually. It was thus evident that  $MoO<sub>3</sub>$  was not necessary for the formation of the silicate crystals, but it con-

tributed to their size.  $MoO<sub>3</sub>$  has been reported in flux growth literature as an additive to  $PbF_2$ flux in the growth of good quality  $Al_2O_3$  crystals [6], and one of the authors (B.W.) has frequently used it as an additive with good results.

A platinum crucible containing the same mixture as in experiment A was sealed into a heavy walled quartz tube and held at  $1100^{\circ}$ C for 200 h in a region of uniform temperature in a tubular furnace. Evaporation was relatively slight, and no  $Er<sub>2</sub>SiO<sub>5</sub>$  crystals were obtained. However, EPMA showed an average concentration of about 5 wt  $\frac{6}{6}$  Si in the solidified melt (approximately  $1.4 \text{ g Si}$ ).

There is as yet no evidence as to the nature of the vapour species which transported the silicon, but assuming only a reaction involving simple molecules, the most probable reaction to occur under the conditions of the experiment in the closed quartz tube is:

$$
2PbF_{2(g)} + SiO_{2(s)} \rightleftharpoons SiF_{4(g)} + 2PbO_{(1)},
$$

 $\Delta G_{\rm R}^{0} = -4.1$  kcal mol<sup>-1</sup> at 1400 K [7]. The change of standard free enthalpy,  $\Delta G_{\rm R}^{\rm o}$ , is compatible with chemical transport. Conventionally, the chemical activities of the condensed phases,  $a_{\rm SiO_2}$  and  $a_{\rm PbO}$ , are equal to unity, and the equilibrium constant  $K_{\rm p}$  (1400K)  $\approx P_{\text{SiF}_4}/P_{\text{PbF}_2}$ . From the relation  $\Delta G_R^0 = -RT$  $\log_e K_p$ ,  $K_p$  (1400K)  $\approx$  4.4 atm<sup>-1</sup>. The partial pressure of  $PbF_2$  in equilibrium with the liquid phase is  $P_{\rm PbF_2}$  (1400K)  $\Rightarrow$  0.2 atm and hence  $P_{\text{SiF}_4}$  (1400 K)  $\approx$  0.17 atm. Even if this has been overestimated by an order of magnitude, it would still result in an effective transport of silicon.

The fact that vapour transport of Si into the melt occurred under nearly isothermal conditions indicates that the driving force for the transport is the free energy of a reaction between the gaseous siliceous species and the melt.

## 3.2. Mg<sub>2</sub>SiO<sub>4</sub> . MgF<sub>2</sub>

Many experiments on the flux growth of MgO have been carried out in this laboratory [8]. Typically, 20 g "Optran" or "Specpure" PbF<sub>2</sub> + 2.4 g MgO were mixed and heated to 1250 to  $1280^{\circ}$ C in a 10 cm<sup>3</sup> platinum crucible, and a gap between the crucible and lid allowed the  $PbF<sub>2</sub>$ to evaporate. The crucibles were heated either in a large chamber furnace or in a platinum tube, and only MgO was obtained from more than 50 such experiments.

When a crucible containing the same com-



*Figure 1* Crystals from 5 cm<sup>3</sup> melts in 10 cm<sup>3</sup> crucibles: (a)  $Dy_4SiO_8$  (2 mm  $\times$  1 mm grid); (b)  $Dy_2SiO_5$  (1 mm  $\times$ 1 mm grid); (c)  $Pb_{0.2}Gd_{4.8}(Si_{2.6}Al_{0.2})O_{12.8}F_{0.2}$  (1 mm  $\times$ 1 mm grid). Apatite structure.

ponents was heated in the sillimanite muffle with seven other crucibles, each containing similar amounts of  $PbF_2$  and solute, it was subsequently found to contain a colourless crystal, 6 mm across. On examination the crystal showed birefringence between crossed polarisers

and thus was not MgO. The X-ray powder pattern showed very close agreement with the data for  $Mg_2SiO_4.MgF_2$ , Norbergite [9], and EPMA confirmed the result. (Required,  $13.8\%$ Si,  $35.9\%$  Mg,  $18.7\%$  F. Found,  $12.4\%$  Si, 33.9  $\%$  Mg, 20.5  $\%$  F.)

## **3.3. New silicate crystals**

Besides  $Er<sub>2</sub>SiO<sub>5</sub>$  and  $Dy<sub>2</sub>SiO<sub>5</sub>$ , several new silicates have been grown by the "vapour-flux" method. EPMA indicates that the formula of one of these corresponds approximately to  $Dy_4SiO_8$ , and several new rare-earth silicates of the apatite family have also been produced (Fig. 1). This work will be published elsewhere.

## 3.4. Effect of the reaction with **the**  sillimanite muffle

After the evaporation experiment, the interior of the muffle was yellowish, shiny and crystalline to a depth of  $1$  to  $2$  mm. A thin section was polished for microscopic examination and this showed virtually no isotropic material. This result was confirmed by the X-ray powder pattern of scrapings of the surface. The powder photograph showed no sign of glass, which is typically seen as a darkened diffuse ring on the film, but showed a considerable increase in the amount of free alumina [10] and the presence of  $PbAl<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>$ [ll].

The increase in free alumina was confirmed by EPMA. Before reaction with  $PbF_2$ , the backscattered electron image showed voids, seen as black spots with adjacent light areas (Fig. 2a). The A1 scan (Fig. 2b) showed little variation, while the Si scan (Fig. 2c) showed small Si-rich regions.

After reaction with  $PbF_2$ , the back-scattered electron image showed dark areas corresponding to Al-rich regions, and light areas corresponding to regions rich in Si and Pb (Fig. 3a). This observation was confirmed by comparison with the A1 scan (Fig. 3b) and the silicon scan (Fig. 3c). EPMA showed that the Al-rich regions consist of  $Al_2O_3$ :PbO in the molar ratio 11:1 approximately, and that the regions rich in Pb and Si correspond to a lead-aluminium-silicate of approximately composition PbO. $Al_2O_3$ .  $3SiO<sub>2</sub>$ . These results show that the muffle surface had altered chemically and physically.

When a muffle was used for the first time, it was subsequently found that, in addition to a considerable amount of Si transport, a smaller amount of A1 transport also occurred, since







*Figure 2* (a) Back-scattered electron image of muffle before use. (b) A1 scan. (c) Si scan.

aluminates were produced in melts which did not initially contain alumina. During subsequent use, AI transport continued but Si transport no longer occurred. It appeared that the Si ceased to be available for transport after combining with PbO. The growth of aluminate crystals by the "vapour-flux" method will be published elsewhere.

## **4. Discussion**

The presence of  $Al_2O_3$  crystals (Fig. 3b) in the muffle surface after reaction is consistent with the postulated transport reaction:



*Figure 3* (a) Back-scattered electron image of muffle after reaction. (b) AI scan. (c) Si scan.

$$
2PbF_{2(g)} + Al_2SiO_{5(e)} \rightleftharpoons Al_2O_{3(e)} + SiF_{4(g)} + 2PbO_{(e)},
$$

 $\Delta G_{\rm R}^{0}$  = - 0.6 kcal mol<sup>-1</sup> at 1500 K [7]. This complies with the requirement for chemical transport that  $\Delta G$  should be near zero.

In the absence of complete thermochemical data, reactions such as the following are proposed:

in the simplest case,

$$
SiF_{4(g)} + 4PbO_{(1)} \rightleftharpoons Pb_2SiO_4 + 2PbF_{2(g)},
$$
  
\n
$$
\Delta G_R^0 = -7.1 \text{ kcal mol}^{-1} \text{ at } 1500 \text{ K [7]}
$$

or, assisted by atmospheric moisture,

$$
SiF4(g) + 2H2O(g) + 2PbO(1) \rightleftharpoons Pb2SiO4
$$
  
+ 4HF<sub>(g)</sub>,  

$$
\Delta G_{R}^{0} = -15.6 \text{ kcal mol}^{-1} \text{ at } 1500 \text{ K [7]}.
$$

In either case, the equilibrium would shift to the right when crystallization of a silicate occurred, thereby depleting the melt of  $SiO<sub>2</sub>$ .

In the experience of one of the authors, direct addition of silica to melts containing  $PbF_2$  has not been found to result in crystals of the expected stoichiometry. During evaporation of the flux in the absence of a muffle, it appears that Si is lost from the melt possibly as  $SiF<sub>4</sub>$ , and that when  $SiF<sub>4</sub>$ , or other siliceous species, is present in the atmosphere, as we suggest is the case in the sillimanite muffle, the equilibrium is altered so that the concentration of the melt with respect to Si is increased.

The following sequence is postulated:

1. Pb $F_2$  evaporates and reacts with the muffle to form  $\text{SiF}_4$  or more complex siliceous species;

2. the siliceous species diffuses back into the melts;

3. silicates crystallize when the melts become supersaturated.

#### **5. Conclusions**

1. It has been shown that when a sillimanite muffle is used to protect a furnace from corrosive vapour, transport of material from the muffle into the crucibles may occur and result in phases which contain silica.

2. This "vapour-flux" transport method may be a useful way of growing crystals of silicate materials, since the crystals which have been obtained are of greater size and better quality than those reported in the literature [12-14].

3. Several new compounds have been grown as single crystals with dimensions of several millimetres, from melts only  $5 \text{ cm}^3$  in volume.

## **Acknowledgements**

The authors are indebted to Dr G. Garton and to Dr S. H. Smith for helpful discussions; to the latter for technical assistance; to Mr F. R. Wondre for the X-ray powder patterns; to Mr W. Davison of the School of Physics, Newcastle University, for EPMA; and to Mr J. A. Roberts of the Mullard Research Laboratories for the chemical analysis of  $Er<sub>2</sub>SiO<sub>5</sub>$ . This work was supported in part by the S.R.C.

#### **References**

- 1. A.v. NOV o S ELOVA, *Kristall und Technik* 2 (1967) 511.
- 2. H. sCrtMID, *Z. fiir Anorg. und Allgem. Chem.* 327 (1964) 110.
- 3. g. SCHOBER and E. THILO, *Ber. dtsch. Chem. Ges.*  73 (1940) 1219.
- 4. G. GARTON, S. H. SMITH and B. M. WANKLYN, *J. Crystal Growth* 13/14 (1972) 588.
- 5. L. A. HARRIS and c. B. FINCH, *Amer. Min.* 50 (1965) 1493.
- 6. A. B. CHASE and J. A. OSMER, *J. Amer. Ceram. Soc.*  53 (1970) 343.
- 7. JANAr Thermochemical Tables. 2nd Edition, (U.S. Dept. of Commerce, National Bureau of Standards, 1971).
- 8. G. GARTON, B. F. HANN, B. M. WANKLYN and s. H. SMITH, *Y. Crystal Growth* 12 (1972) 66.
- 9. A.S.T.M. Powder Diffraction File No. 11-686.
- 10. A.S.T.M. Powder Diffraction File No. 10-173.
- 11. A.S.T.M. Powder Diffraction File No. 14-590.
- 12. I. A. BONDAR, L. N. KOROLEVA, and N. A. TOROPOV, *Growth of Crystals 6A* (1968) 101.
- 13. i. A. BONDAR and N. A. TOROPOV *Mat. Res. Bull.*  2 (1967) 479.
- 14. I. A. BONDAR and L. N. KOROLEVA, *Russian J. lnorg. Chem.* 13 (1968) 3172.

Received 16 October 1973 and accepted 31 January 1974.