Flux growth of silicates with vapour transported silicon

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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, Al_2SiO_5, muffle, and the flux consisted of PbF_2, or $PbF_2 + PbO$, occasionally with additional MoO_3. It is postulated that a volatile siliceous species resulted from the reaction of PbF_2 vapour with the muffle and that this species transported Si into the fluxed melts. The silicate crystals produced include Er_2SiO_5, Dy_2SiO_5, $Mg_2SiO_4 \cdot MgF_2$, a new material of formula Dy_4SiO_8, 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_2SiO_5, in an experiment intended to produce Er_2MoO_6 by flux evaporation. The crucible was contained in a sillimanite, Al_2SiO_5, muffle, and the flux was PbF_2.

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, $SiOF_2$ and SiF_4 have been reported to be transport agents in the growth of Be_2SiO_4 by vapour transport [1]. SiF_4 has also been reported to be a transport agent in the growth of Co_2SiO_4 [2] and of topaz [3] in sealed quartz tubes, where the reaction between HF and SiO_2 supplied the vapour species, and HF was provided by the hydrolysis of CoF_2 and AlF_3 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 cm³ 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 cm³.

The chemicals used were: Rare Earth Products 99.9% pure Er_2O_3 and Dy_2O_3, BDH AnalaR MoO_3, PbO_2 and PbO, "Extra Pure" PbF_2, "Optran" PbF_2, and Johnson, Matthey "Spec-pure" MgO. The amounts of Si in the above chemicals are as follows:

99.9% R_2O_3	: 2 ppm approx.
BDH AnalaR MoO_3	: < 1000 ppm
BDH AnalaR PbO_2	: < 90 ppm
BDH AnalaR PbO	: < 2 ppm

"Extra Pure" PbF_2 : 12 ppm
"Optran" PbF_2 : < 2 ppm
"Specpure" MgO : < 1 ppm

3. Experiments and observations
3.1. Er_2SiO_5

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_3, 20 g "Extra Pure" PbF_2 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°C and cooled at 1 K h^{-1} for five days.

The experiment produced pink crystals, about 1.9 g in total weight. Chemical analysis indicated their formula to be Er_2SiO_5 (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_2SiO_5 and with published data [5]. EPMA confirmed the analysis. Since 1.9 g Er_2SiO_5 consists of 1.65 g Er_2O_3 and 0.25 g SiO_2, 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.
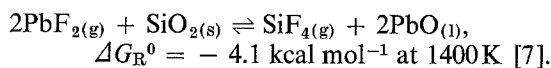
To check whether silica had been accidentally introduced into the melt, the experiment was repeated twelve times using "Optran" PbF_2 instead of the "Extra Pure" PbF_2, and in ten cases Er_2SiO_5 crystals large enough to be separated by visual inspection were obtained. In the other two experiments, evaporation 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_3 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_2SiO_5 large enough to separate visually. It was thus evident that MoO_3 was not necessary for the formation of the silicate crystals, but it con-

tributed to their size. MoO_3 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°C for 200 h in a region of uniform temperature in a tubular furnace. Evaporation was relatively slight, and no Er_2SiO_5 crystals were obtained. However, EPMA showed an average concentration of about 5 wt% Si in the solidified melt (approximately 1.4 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:

$$2PbF_{2(g)} + SiO_{2(s)} \rightleftharpoons SiF_{4(g)} + 2PbO_{(l)},$$
$$\Delta G_R^0 = -4.1 \text{ kcal mol}^{-1} \text{ at } 1400 \text{ K [7]}.$$

The change of standard free enthalpy, ΔG_R^0, is compatible with chemical transport. Conventionally, the chemical activities of the condensed phases, a_{SiO_2} and a_{PbO}, are equal to unity, and the equilibrium constant K_p (1400K) $\simeq P_{SiF_4}/P^2_{PbF_2}$. From the relation $\Delta G_R^0 = -RT \log_e K_p$, K_p (1400K) $\simeq 4.4$ atm^{-1}. The partial pressure of PbF_2 in equilibrium with the liquid phase is P_{PbF_2} (1400K) $\simeq 0.2$ atm and hence P_{SiF_4} (1400K) $\simeq 0.17$ 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. $Mg_2SiO_4 . MgF_2$

Many experiments on the flux growth of MgO have been carried out in this laboratory [8]. Typically, 20 g "Optran" or "Specpure" PbF_2 + 2.4 g MgO were mixed and heated to 1250 to 1280°C in a 10 cm^3 platinum crucible, and a gap between the crucible and lid allowed the PbF_2 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.
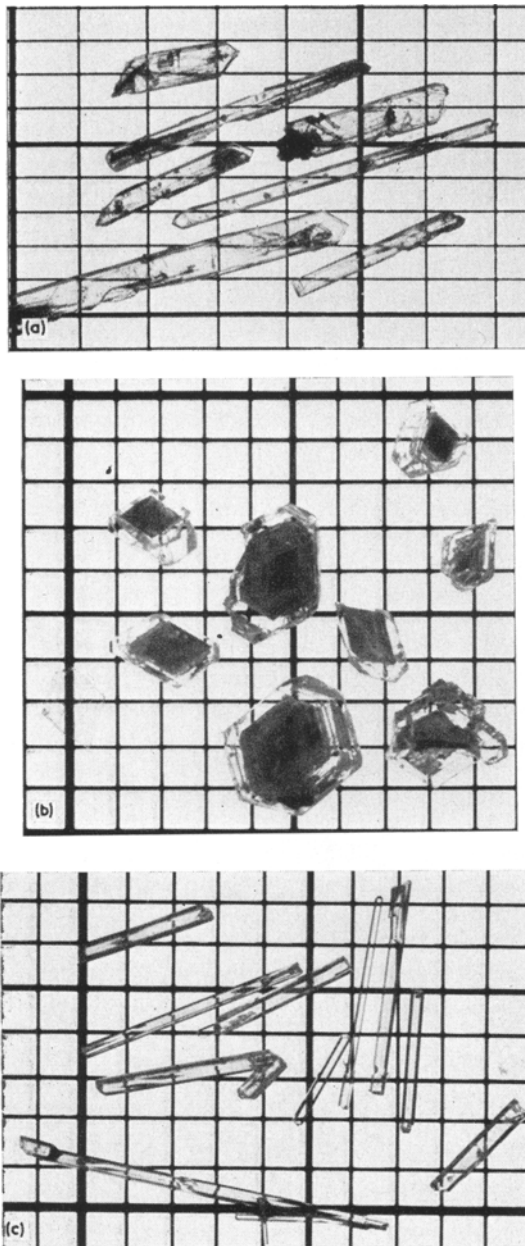
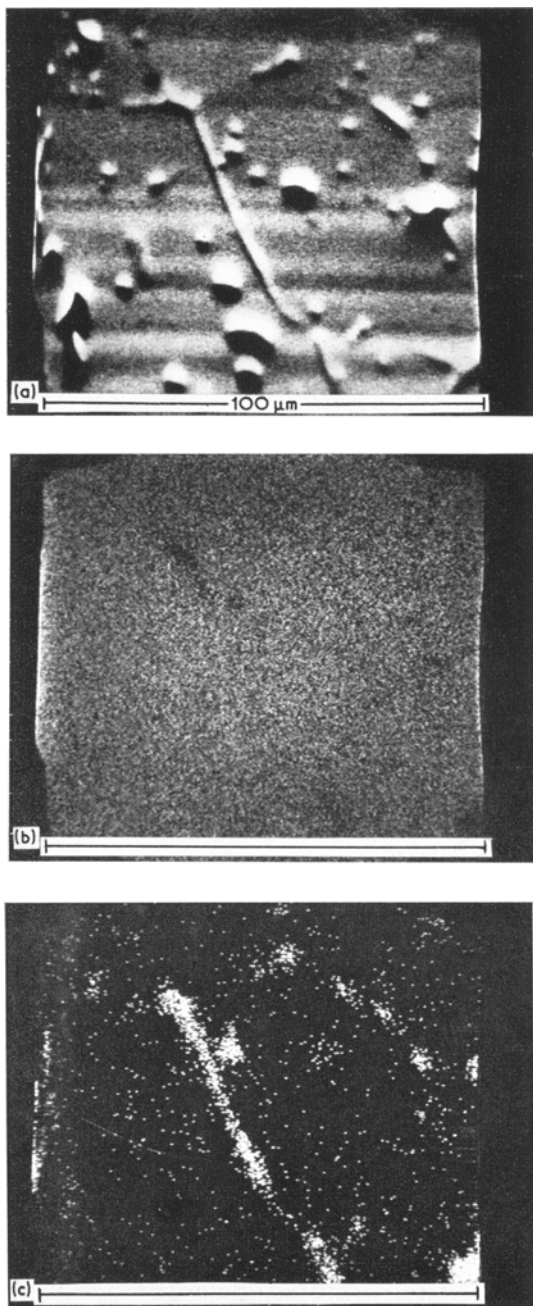When a crucible containing the same com-

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

aluminates were produced in melts which did not initially contain alumina. During subsequent use, Al 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:
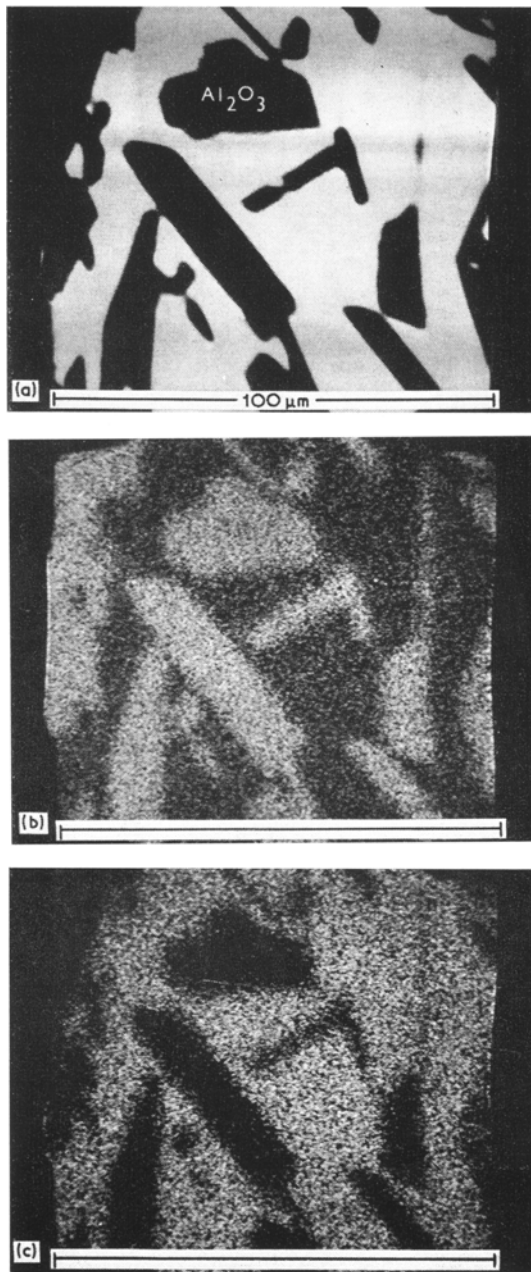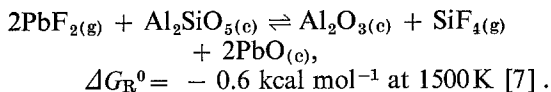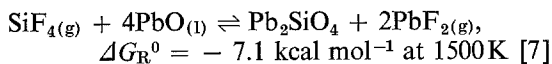

Figure 3 (a) Back-scattered electron image of muffle after reaction. (b) Al scan. (c) Si scan.

$$2PbF_{2(g)} + Al_2SiO_{5(c)} \rightleftharpoons Al_2O_{3(c)} + SiF_{4(g)}$$
$$+ 2PbO_{(c)},$$
$$\Delta G_R{}^0 = -0.6 \text{ kcal mol}^{-1} \text{ at } 1500 \text{ K } [7].$$
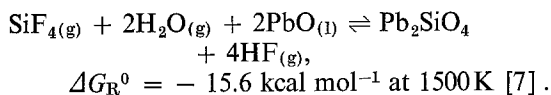
This complies with the requirement for chemical transport that ΔG should be near zero.

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

in the simplest case,

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

or, assisted by atmospheric moisture,

$$SiF_{4(g)} + 2H_2O_{(g)} + 2PbO_{(l)} \rightleftharpoons Pb_2SiO_4$$
$$+ 4HF_{(g)},$$
$$\Delta G_R{}^0 = -15.6 \text{ kcal mol}^{-1} \text{ at } 1500 \text{ K } [7].$$

In either case, the equilibrium would shift to the right when crystallization of a silicate occurred, thereby depleting the melt of SiO_2.

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_4, and that when SiF_4, 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. PbF_2 evaporates and reacts with the muffle to form 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 cm³ in volume.

Acknowledgements

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