$d_s = d_f$) relative to δ_s are superimposed on the curve in Fig. 2. The agreement is quite reasonable although it should be born in mind that the tungsten fibres are not perfectly reflecting. It is not anticipated, however, that some degree of absorption is likely to be significant.

Fig. 2 can also be used to determine the diameter of a real fibre. From Equation 1 we see that $\alpha_s = 2\pi s/\delta_s$. As $\delta_s \cong \delta_f$ and $d_s \approx d_f$ we get a good estimate of the parameter α in Fig. 2 by putting $\alpha = 2\pi s/\delta_f$. A corrected value for the real diameter d_f from the measured quantity δ_f is thus given by

$$d_f \cong 2\lambda \,.\, s/\delta_f \left[1 + \left(\frac{\delta_s - \delta_f}{\delta_s}\right)_{\mathrm{corr}}\right]$$

where $[(\delta_f - \delta_s)/\delta_s]_{\mathrm{corr}}$ was taken from Fig. 2. The relative error in the determination of d_f is now of the order of $[(\delta_f - \delta_s)/\delta_s]^2_{\mathrm{corr}}$.

We conclude that the diffraction pattern of a real fibre is sufficiently different from that of a slit to warrant the slit approximation being treated with caution. In principle, the laser diffraction method, as discussed here, is capable of high precision for diameter measurements. Another case where the difference is also significant occurs where one compares the diffraction pattern of a slit with that of a fibre as discussed elsewhere [6].

References

1. W. WATT, L. N. PHILLIPS and W. JOHNSON, *The Engineer* (May 27) (1966) 815.
2. R. MORETON, *Fibre Sci. Tech.* **1** (1969) 273.
3. M. KOEDAM, *Philips Tech. Rund.* **27** (1966) 182.
4. A. J. PERRY, K. PHILLIPS and E. DE LAMOTTE, *Fibre Sci. Tech.* **3** (1971) 317.
5. M. KERKER, "The Scattering of Light" (Academic Press, New York, 1969) p. 255.
6. R. DÄNDLIKER and B. INEICHEN, *ZAMP* **23** (1972) 163.

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Vapour transport of aluminium into fluxed melts, via reaction of PbF_2 with sillimanite

PbF_2 has been shown to react with sillimanite, Al_2SiO_5, producing a gaseous siliceous species which diffuses into fluxed melts and leads to the growth of silicate crystals by a "vapour-flux" process [1]. Since aluminium is also transported by PbF_2 [2], and since crystals of $ZnAl_2O_4$ and $BaO\,.\,6Al_2O_3$ have been grown above melts containing their components and PbF_2 [3], it seemed probable that the latter would react with sillimanite, transporting aluminium. This note describes the growth of aluminates and aluminosilicates by the "vapour-flux" process.

The chemicals used, and their content of Si and Al, are shown in Table I. The starting materials were contained in platinum crucibles of 10 cm³ capacity, with loosely-fitting lids. The crucibles, in batches of 4 or 6, were placed on slabs of Morgan M.I. 3000 refractory brick in a D-shaped sillimanite muffle which was 27 × 11 cm² in base area × 8 cm in height and closed at one end. The muffle was situated in a furnace and the open end blocked by a plug of refractory brick.

The starting compositions, experimental conditions and crystals obtained are shown in Table II. Details of the identification of the crystals by EPMA and X-ray powder patterns are given in Table III.

$MgAl_2O_4$. Transparent octahedra were found in a platinum crucible, which contained initially only high purity MgO and PbF_2, after the PbF_2 had evaporated in the muffle. The X-ray powder pattern of the crystals corresponded closely to that of $MgAl_2O_4$ [4], and the identification was confirmed by EPMA. $Mg_2SiO_4.MgF_2$ crystallized also from the same melt [1]. This result contrasts with many experiments with identical materials carried out in an open furnace or a platinum tube; here only MgO crystals were obtained.

Dy_2SiO_5, $DyAlO_3$, $Dy_3Al_5O_{12}$ and other aluminates. Three distinct phases grew in a melt

TABLE I Concentration of Al and Si in the chemicals (ppm)

	Al	Si
Rare Earth Products 99.9% R_2O_3	approx. 5	approx. 40
"Specpure" MgO	1	1
BDH "Optran" PbF_2	15	2
BDH "Analar" PbO	3	2
BDH "Analar" PbO_2	13	90
BDH "Analar" MoO_3	270	1000
BDH Lab. Reagent SiO_2	3000	

TABLE II Starting compositions, furnace programmes and crystalline products

Starting compositions	Initial temperatures and cooling programmes (°C)	Crystal products
2.3 g MgO, 19.5 g PbF_2	20 h at 1280, cooled at 0.5 K h^{-1} to 1220 (mainly flux evaporation)	$MgAl_2O_4$, 2 mm crystals, and Mg_2SiO_4, MgF_2 crystals [1]
1.8 g Dy_2O_3, 2.6 g MoO_3, 2 g PbO, 0.5 g PbO_2, 18 g PbF_2	20 h at 1280, cooled at 1 K h^{-1} to 1150.	Dy_2SiO_5 platelets, 2 to 3 mm on edge; $DyAlO_3$ rhombohedra, 1 mm on edge; $Dy_3Al_5O_{12}$, 1 mm crystals
1.8 g Gd_2O_3, 3.2 g MoO_3, 18 g PbF_2, 5 g PbO, 0.5 g PbO_2	20 h at 1280, cooled at 1 K h^{-1} to 1150.	$Pb_{0.19}Gd_{4.81}(Si_{2.6}Al_{0.2})O_{13}$, transparent hexagonal rods up to 8 mm × 0.3 mm × 0.3 mm
1 g Tb_4O_7, 0.2 g SiO_2, 13 g PbF_2, 0.7 g PbO_2, 3 g PbO, 0.6 g MoO_3	8 h at 1250, cooled at 1 K h^{-1} to 1120.	$Tb_3Al_5O_{12}$, as 3 mm crystals, (and rare-earth apatite rods)
1 g Er_2O_3, 0.4 g SiO_2, 13 g PbF_2, 0.7 g PbO_2, 3 g PbO, 0.6 g MoO_3	8 h at 1250, cooled at 1 K h^{-1} to 1120.	$Er_3Al_5O_{12}$, as 1 mm crystals, (and Er_2SiO_5)

TABLE III Identification of phases by analyses and X-ray powder patterns

Formula	Formula requires (%)	EPMA results (%)	X-ray powder pattern agrees closely with data in reference below
$MgAl_2O_4$	Mg 17.0 Al 37.4	Mg 16.6 Al 34.5 (Pb < .01)	[4]
$DyAlO_3$	Dy 68.4 Al 11.4	Dy 69.2 Al 10.8 (Pb < .01)	[5, 6]
Dy_2SiO_5	Dy 75.2 Si 6.5	Dy 75.3 Si 5.9	[7]
$Pb_{0.19}Gd_{4.81}(Si_{2.6}Al_{0.2})O_{13}$ (apatite structure)	Gd 69.9 Si 6.7 Al 0.5 Pb 3.6	Gd 70.6 Si 6.4 Al 0.4 Pb 3.7 (F not detectable)	[8, 9]

which initially contained only Dy_2O_3, PbF_2, PbO and MoO_3: faceted platelets of Dy_2SiO_5, small rhombohedra of $DyAlO_3$ and optically isotropic crystals which gave a powder pattern corresponding to garnet [10]. Other aluminate crystals obtained from melts which initially contained only trace amounts of aluminium include $PrAlO_3$ [11], $Tb_3Al_5O_{12}$ [12], $Er_3Al_5O_{12}$ [12], and several new rare-earth apatites of which $Pb_{0.19}Gd_{4.81}(Si_{2.6}Al_{0.2})O_{13}$ is an example. Photographs of the latter and of the Dy_2SiO_5 crystals have been published [1].

Transport of Al_2O_3 from sillimanite. The muffle itself appeared to be the only source of aluminium in these experiments; for the starting materials contained only trace amounts of Al, and they had all been frequently used in experiments in open furnaces without producing aluminates. Butcher and White reported that Al_2O_3 platelets were obtained on wires suspended over open crucibles containing mixtures of Al_2O_3 and PbF_2 [2]. A similar vapour species capable of transporting Al at high temperatures may be expected when PbF_2 reacts with Al_2SiO_5. It appears that this species diffused into fluxed melts to such an extent that aluminate and aluminosilicate crystals were formed. When a new muffle was used for flux growth experiments, it was found that much more silicate material than aluminate material was obtained by the "vapour-flux" mechanism; and the silicon content of the muffle surface was depleted, considerable amounts of free Al_2O_3 being observed on the surface after use [1]. When a muffle was used for subsequent experiments, little or no Si transport was observed, but the formation of aluminium garnets or aluminates showed that Al transport continued.

It is clear that the "vapour-flux" phenomenon sets significant limits to experimental procedures involving PbF_2 and aluminous muffles. It is possible that the "vapour-flux" process could be utilized to grow large crystals by controlling the rate of vapour transport into the flux.

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References

1. B. M. WANKLYN and Z. HAUPTMAN, *J. Mater. Sci.* **9** (1974) 1078.
2. M. M. BUTCHER and E. A. D. WHITE, *J. Amer. Ceram. Soc.* **48** (1965) 9.
3. K. TSUSHIMA, *J. Appl. Phys.* **37** (1966) 443.
4. ASTM Powder Diffraction File No. 5-672.
5. ASTM Powder Diffraction File No. 13-255.
6. B. M. WANKLYN, *J. Crystal. Growth* **5** (1969) 323.
7. L. A. HARRIS and C. B. FINCH, *Amer. Min.* **50** (1965) 1493.
8. J. FELSCHE, "The Crystal Chemistry of the Rare-Earth Silicates, in Structure and Bonding", Vol. 13 (Springer-Verlag, New York, 1973) p. 113.
9. ASTM Powder Diffraction File No. 20-1364.
10. ASTM Powder Diffraction File No. 17-734.
11. ASTM Powder Diffraction File No. 9-71.
12. ASTM Powder Diffraction File No. 17-735.

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Pre-precipitation phenomena in Zn—Cd alloys

It has been known for many years that pre-precipitation phenomena are present in some binary alloys: the aluminium-based alloys, especially Al–Cu, Al–Ag and Al–Zn, are the most well studied examples of them [1-3]. In all these alloys, before true precipitation there is a formation of small clusters of solute atoms whose size is normally in the order of 20 to 30 Å, and which are characterized by the coherence with the host lattice. These are called Guinier-Preston zones. Until now this kind of phenomena has not been observed in hexagonal close-packed metals and in particular in zinc-based alloys. Therefore, it is of interest that we have observed phenomena in Zn–Cd alloy which may be interpreted in this way.

The solubility of Cd in Zn is very poor at room temperature (in the order of 0.01 at. % or less) and maximum solubility is attained at about 350° C (1.5 at. %) [4]. Of course a certain amount of Cd may be maintained in solution at room temperature, at least for some time, by rapid quenching from high temperature. The alloys studied were obtained from high purity Zn and Cd (99.999 and 99.9% respectively) and contained 0.6 at. % (1 wt %) Cd and 0.2 at. % (0.36 wt %) Cd.

First precise lattice parameter measurements were obtained by the Debye-Scherrer powder method, taking three photographs (Cu$K\alpha$ radiation, 114.6 mm diameter camera and 3.5 h exposure) of each sample: the first (A) before thermal treatments, the second (B) immediately after annealing at 350° C in inert Helium atmosphere and quenching in water at 0° C (beginning the exposure 20 min after quenching) and the third (C) a few days after quenching. Typical results found for two of the alloys examined are shown in Table I.

It is important to note that before thermal treatment and some time after quenching the alloys exhibit equal lattice constants which are coincident with those of pure Zn, clearly indicating that the solute Cd is totally precipitated. The observation made shortly after quenching, shows a marked increase especially in the c value, related to the complete dissolution

TABLE I

	0.2 at. % Cd			0.6 at. % Cd		
	a (± 0.0004 Å)	c (± 0.0008 Å)	c/a (± 0.0006)	a (± 0.0004 Å)	c (± 0.0008 Å)	c/a (± 0.0006)
A	2.6648	4.9468	1.8563	2.6650	4.9465	1.8561
B	2.6649	4.9488	1.8570	2.6649	4.9522	1.8583
C	2.6650	4.9470	1.8563	2.6649	4.9467	1.8562