A fuller description of this work, listing station terms and tables of P travel times, is in preparation and will be published elsewhere.

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MgSiP2: a New Member of the II IV V2 Family of Semiconducting Compounds

SINCE the first members of the II IV V2 family of compound semiconductors were synthesized by Goodman[1] there has been an increasing interest in these ternary analogues of the III V compound semiconductors, particularly in the USSR[2]. Until recently only fourteen members of the family were known to exist with the diamond-like chalcopyrite or sphalerite structures[2-4] out of a possible total of 125 (ref. 3). In particular only one compound containing magnesium, MgGeP2 (refs. 3 and 5), had been identified. As with the III V compounds, there is a general tendency for an increase of energy gap with decreasing average atomic number and, in consequence, the magnesium compounds would be expected to have higher energy gaps (in excess of 2·0 eV) than many of the other members of the family.

Major difficulties are experienced in the synthesis of those compounds containing phosphorus from stoichiometric mixtures of the elements[6] due to the high phosphorus pressures developed before complete synthesis, and the high dissociation pressures at their melting points. These difficulties can be overcome using the technique of solution synthesis in molten metallic medium at relatively low temperatures. After synthesis, slow cooling of the resultant melt can lead to the growth of large crystals[2,3]. As has been noted elsewhere[2,3] molten tin fulfils the role of solvent admirably for many of these compounds, and one of us (A. J. S.) has reported the synthesis and growth of crystals of nine of them from tin solution[3]. Early attempts to prepare MgSiP2 using the same technique[3,7] led to the formation of orthorhombic SiP2. (This failure was due to a reaction between magnesium and the silica ampoule.) The solution synthesis of MgSiP2 in molten tin has been investigated further using carbon lined ampoules and crystals of the compound have now been obtained.

Since this work was started, Goryunova[8] has indicated, in an oblique reference, that MgSiP2 exists, having the chalcopyrite structure with a tetragonal compression $(2 - c/a)$ of 0·23 (corresponding to a lattice parameter ratio $c/a \sim 1·77$). In common with much of the Russian work in this field, however, no details of preparation were given.

In our method of preparation, stoichiometric quantities of the constituent elements and sufficient tin to form a resultant 10 mole per cent solution were placed inside a 2 mm wall, 2 cm diameter, high purity carbon tube, which was sealed inside an evacuated clear silica tube. This sealed ampoule was then heated in a vertical resistance furnace at 60° C/h to $\sim 1,150°$ C (from $\sim 400°$ C), followed by slow cooling at 6° C/h to $\sim 400°$ C and air quenching. Because MgSiP2 was found to be readily decomposed by water and mineral acids (as is its III V analogue AlP) it was not possible to extract the crystals from the tin matrix using hot concentrated HCl (the technique used for the more inert members of the family[3]), and instead an excess of hot mercury was used[9].

The separated crystals were predominantly extremely brittle, orange-yellow, hexagonal prisms, typically $2 \times 0·5 \times 0·5$ mm³, the prism axis being the [111] axis of the chalcopyrite unit cell. This growth habit is the same as that of tin-solution grown crystals of ZnSiP2 and CdSiP2 (ref. 3). X-ray powder photography confirmed the structure as chalcopyrite with the following lattice parameters: $a = 5·721 \pm 0·001$ Å, $c = 10·095 \pm 0·002$ Å, $c/a = 1·764$. The degree of tetragonal compression of MgSiP2 is thus 0·236, in good agreement with Goryunova's reported value[8], and consequently it has the most highly compressed unit cell of the II IV V2 family.

Optical transmission measurements, carried out on an unpolished as-grown crystal plate, indicated a sharp rise in absorption coefficient in the region of 5500 Å, corresponding to an optical energy gap of $\sim 2·24$ eV at 300° K. The energy gap of MgSiP2 is thus higher than for any of the other members of the family grown from tin solution[3], in agreement with the observed trend to higher energy gap with decreasing average atomic number.

The fragile nature and small size of the crystals have so far prevented meaningful measurement of the electrical properties from being carried out.

Attempts to prepare the other two possible magnesium compounds (MgSiAs2 and MgGeAs2) using the solution synthesis technique have not been successful.

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Surface Self-diffusion of Tungsten

HERE we describe briefly the results of some recent experiments on the diffusion of tungsten atoms over an atomically clean surface of tungsten. The method used was that of following the decay with time of a series of sinusoidal grooves in the surface of the specimen at various temperatures. Mullins[1] has shown that the depth of the grooves