

Growth of ZnSiP_2 from tin solution and temperature composition diagram of the ZnSiP_2 : Sn system

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ZnSiP_2 crystals (1 cm or more in length) have been grown from tin solution on a reproducible basis. The dimensions of the largest crystals obtained were $1.7 \times 0.25 \times 0.03 \text{ cm}^3$ and $2 \times 0.1 \times 0.02 \text{ cm}^3$. The temperature of the reaction region was 1050 to 1080°C and the cooling rate used to form these crystals was 7.5°C h^{-1} .

A practical temperature-composition section of the ZnSiP_2 :Sn phase diagram has been determined by differential thermal analysis, X-ray diffraction measurements and microscopic studies. The resulting information on the liquidus temperature variation with composition served to give better control of ZnSiP_2 growth from tin solution. It was concluded that ZnSiP_2 reacted eutectically with Sn and the eutectic composition was close to 100%.

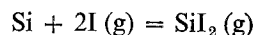
1. Introduction

II-IV-V₂ compounds are iso-electronic analogues of the III-V group of compounds. They have been investigated by many workers and subsequent publications have been reviewed by Borshchevski *et al* [1] and Ray [2]. Various techniques are applied to the preparation of these compounds [1]. The melting point of some of the II-IV-V₂ compounds is higher than the softening point of the silica containers used to prepare them. In ZnSiP_2 , the relatively high melting point (1420°C) and low vapour pressure of silicon set against the highly volatile phosphorus mitigate against preparation from the constituent elements [3]. Solution growth and vapour transport methods (described elsewhere [4]) were selected as most appropriate to meet these conflicting requirements for preparation and crystallization of ZnSiP_2 semiconducting material.

Preparation of ZnSiP_2 from tin solution has been reported previously [1, 5]. Crystallization of the material from 20 mol % ZnSiP_2 in tin at a cooling rate of 20°C h^{-1} was recorded by Borshchevski *et al* [1], while Spring-Thorpe and Pamplin [5] have successfully grown ZnSiP_2 crystals from tin solution at a cooling rate of 1°C h^{-1} in a rocking furnace. The temperature

of the bottom of the ampoule where Sn, Zn and Si were present was thought to be about 100°C below the melting point of the material. Repetition of the above work by vibrating the ampoule instead of using a rocking furnace did not produce similar results. A study of the Sn:Si phase diagram [6] and subsequent introduction of iodine produced ZnSiP_2 crystals as reported earlier [7].

It is necessary for the preparation of ZnSiP_2 from tin solutions that silicon along with zinc and phosphorus is dissolved in the tin. It was observed that silicon floated unreacted on the surface of the molten tin indicating the rate of dissolution of Si is slow. Iodine introduced as an intermediate reactant changes silicon to silicon iodides which are well distributed into the tin and react with zinc and phosphorus to produce ZnSiP_2 . The process is thought to be controlled through the temperature-pressure reversible reaction (with the intermediate formation of SiI_4)



This paper described the improved form of technique for growth of ZnSiP_2 from tin solution and the nature of crystals produced.

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2. Preparation and growth technique for ZnSiP_2

A typical temperature profile across the silica growth ampoule is shown in Fig. 1. The dotted line shows the actual rather than the ideal temperature profile, which is given by the continuous line. A well cleaned quartz ampoule was filled with 6 mol % of overall constituent elements of ZnSiP_2 in tin along with iodine 2.5 mg cm^{-3} . This charge also included 12 to 14% excess of phosphorus by weight, relative to the calculated weight of phosphorus for stoichiometric composition of ZnSiP_2 . This excess of phosphorus was found to be necessary for production of larger and low conductivity crystals. The ampoule was sealed under a pressure of about 10^{-4} Torr and placed in a Kanthal wire basket hung inside a vertical furnace. This basket was attached to a 50 Hz vibrator; amplitudes of vibration of the ampoule ranged from 0.1 to 0.2 mm.

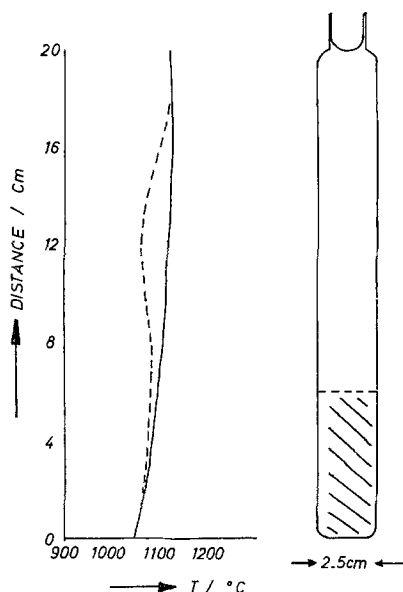


Figure 1 Typical temperature profile of the furnace and the location of the growth ampoule relative to that profile.

The temperature profile of the furnace was selected such that all gaseous materials tended to condense at the bottom of the ampoule being the coldest region. The temperature referred to below is the maximum temperature in the furnace at the top end of the ampoule. The furnace was heated to 500°C in $\frac{1}{2}$ h and then to $1120 \pm 20^\circ\text{C}$ at the rate of 25°C h^{-1} . It was found that

any heating rate below 50°C h^{-1} could be used without causing damage to the growth ampoule. Faster heating rates did not allow phosphorus sufficient time to react and excess pressure developed causing the ampoule to fracture. The furnace was maintained at 1120°C for 36 to 48 h and then cooled at rate of 7.5°C h^{-1} to 680°C . Further cooling from 680 to 400°C was done at 25°C h^{-1} . Then the ampoule was removed from the furnace and as much molten tin as possible was tapped off the ZnSiP_2 to the other end of the ampoule. The ZnSiP_2 -Sn phase diagram indicates the desirability of slow cooling rate down to about 700°C but below this temperature the solubility of ZnSiP_2 in tin is negligible.

The mixture of tin and ZnSiP_2 crystals was treated with warm conc. HCl until the whole of the tin had dissolved. It was observed that a white powder remained trapped in cavities after such treatment. The powder, thought to be tin oxide (soluble in NaOH), was removed by treatment in warm dilute NaOH for 2 h. Further heating in conc. HCl and then distilled water produced clean crystals of ZnSiP_2 apart from occasional tin inclusions inside the crystals.

3. Phase analysis techniques

Differential thermal analysis (DTA) investigations of the ZnSiP_2 :Sn system were made with ZnSiP_2 as prepared above and pure tin (5N) constituent materials and supported by X-ray powder diffraction and microscopic analytical studies. The purpose of these investigations was to provide details of the variation of liquidus temperature with composition.

The experimental form of these instruments was similar to that described by Mughal *et al* [7] and Ray *et al* [9]. A specially designed pyrophyllite tube with a screw seal was used for DTA study of pure ZnSiP_2 .

4. Results and discussion

4.1. Nature and characteristics of crystals

The ZnSiP_2 crystals obtained were ruby red platelets or needles. The useful dimensions of typical crystals were $1.7 \times 0.25 \times 0.03 \text{ cm}^3$ and $2 \times 0.1 \times 0.02 \text{ cm}^3$. Crystals were polished for optical transmission studies with the (111) axis parallel to the polishing plane. Some larger but less uniform prismatic crystals were obtained with numerous out growths and had dimensions of the order of $2.5 \times 0.5 \times 0.2 \text{ cm}^3$. The needle shaped crystals had hexagonal cross-sections and grew along the (111) direction.

Ampoule dimensions influenced the size of the crystals grown, although ampoule diameters larger than 2 cm did not produce an appreciable increase in the crystal sizes. The crystal growth took place from the surface of the solution towards the bottom of the ampoule and was contained in the top 2 to 3 cm of solution.

The temperature in the reaction zone of the ampoule was 1050 to 1080°C and cooling rates of 15 and 7.5°C h⁻¹ were used. The cooling rate of 7.5°C h⁻¹ was found to increase crystal size appreciably and reduce the number of tin inclusions, but these inclusions could not be totally removed from all the crystals. The occurrence of tin inclusions has also been reported by Spring-Thorpe and Pamplin [5]. These inclusions did not show the presence of an intermediate phase which would result in diffused boundaries between ZnSiP_2 and tin on microscopic study. It was possible to select inclusion free specimens of reasonable size for further experimental study.

Mass spectrographic analysis by Mining and Chemical Products Ltd [8] of a random sample of ZnSiP_2 crystals indicated the presence of up to 5% tin in some of the material. However carefully selected, transparent crystals were found to contain 5 ppm Al, 5 ppm Cu and 200 ppm Sn. Iodine which was used in the preparation was not detected in this analysis, copper and aluminium were not intentionally included in the mixture.

Copper-doped material (1000 ppm) was also prepared and formed mostly as six-sided needles of a deeper ruby red colour than the undoped material. These needles had high resistivities at room temperature (of the order of 10⁸ Ωcm) and were found to be *n*-type from thermoelectric measurements.

4.2. ZnSiP_2 -Sn temperature composition studies

It was only possible to obtain DTA results on 0.75, 2 to 5, 10, 15 and 20 mol % of ZnSiP_2 in Sn samples contained in silica ampoules. After numerous attempts it was possible to determine a value for the phase transition temperature of ZnSiP_2 contained in a pyrophyllite ampoule. Leakage from the ampoule resulted in damage to the thermocouple and hence the necessity for repetition of the measurement. The maximum temperature used in the test was 1350°C and the only peak observed was at 1270°C, which it seems is most probably the compound's melting point. It could be the disordering temperature

of ZnSiP_2 although the disordering and melting temperatures are normally only separated by between 25 and 100°C in this class of materials, if a disordering temperature occurs at all.

The results of DTA, as shown in Fig. 2, are similar in character to those of a binary phase system where nearly complete separation of one phase occurs. The liquidus temperature changes

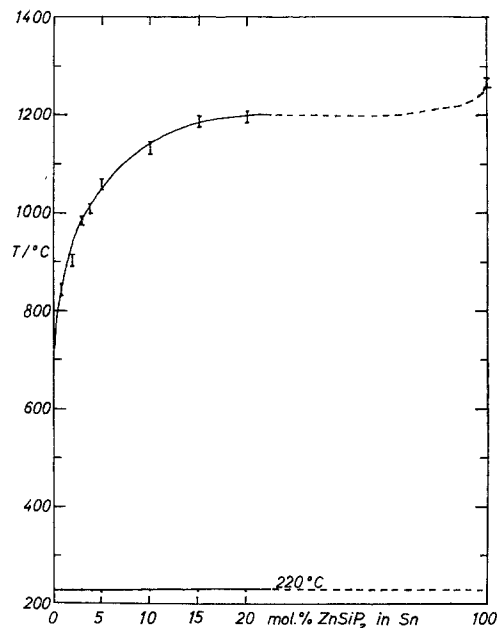


Figure 2 Temperature—composition section of the ZnSiP_2 -Sn phase diagram illustrating the form of the liquidus curve and the eutectic isotherm.

steeply from 0 to 3% Sn then more gradually from 3 to 15% and between 15 and 20% it is almost constant. A eutectic line at 220°C with eutectic composition close to 100% tin was observed. No solid solutions of the type $\text{ZnSi}_{1-x}\text{Sn}_x\text{P}_2$ were observed. The liquidus in the temperature-composition diagram constituted a useful guide as to the starting temperature for growth with a given concentration of the solute and the temperature region over which close temperature control is required for the crystal growth of ZnSiP_2 from tin solution.

X-ray investigations of the ZnSiP_2 - ZnSnP_2 system have indicated that there is no measurable solid solution in the system. Subsequent X-ray studies of ZnSiP_2 crystallites produced from the tin solution have shown a constant lattice parameter (5.407 ± 0.002 Å) for all the concentrations of ZnSiP_2 .

The $\text{ZnSiP}_2\text{:Sn}$ system can reasonably be approximated to a pseudobinary phase system. There is a possibility that tin can replace atoms on both cationic and anionic sublattices of II-IV-V₂ compounds having a diamond type structure. Compounds with such lattice substitutions could still retain their electrical neutrality. Although it was not possible to investigate the middle section of the T - x diagram, there is no evidence of tin substitution for silicon in ZnSiP_2 , such as to invalidate the pseudobinary approach to the ZnSiP_2 -Sn system. The liquidus curve predicted theoretically by Spring-Thorpe and Pamplin [5] for the $\text{ZnSiP}_2\text{:Sn}$ system is in agreement with that observed experimentally up to 7 mol % of ZnSiP_2 . For higher ZnSiP_2 concentrations the experimental curve for the liquidus is higher by as much as 100°C from the theoretical curve.

No measurements were made of vapour pressure over the ZnSiP_2 in tin solution in DTA investigations. It is likely that phosphorus pressure will dominate at all but very high tin concentrations. The phosphorus pressure at the liquidus temperature will vary with solution concentrations. So in fact the T - x section is not a constant pressure region; however, if a constant pressure of one of the constituent elements were used it would not be possible to complete the whole composition range of the T - x section. The pressure conditions for the samples subjected to

DTA measurement would be similar to those used in actually growing ZnSiP_2 from tin solution and as such the results obtained have practical significance.

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References

1. A. S. BORSHCHEVSKI *et al*, *Phys. Stat. Sol.* **21** (1967) 9.
2. B. RAY, *J. Mater. Sci.* **2** (1967) 284.
3. R. E. HONIG, *RCA Rev.* **23** (1962) 567.
4. S. A. MUGHAL, to be published.
5. A. J. SPRING-THORPE and B. R. PAMPLIN, *J. Crystal Growth* **3, 4** (1968) 313.
6. R. P. ELLIOT, in "Constitution of Binary Alloy" (ed. M. Hansen) (McGraw-Hill, New York, 1958), First Supplement (1965) pp. 816-18.
7. S. A. MUGHAL, A. J. PAYNE, and B. RAY, *J. Mater. Sci.* **4** (1969) 895.
8. G. J. BURRELL RAE Farnborough, UK (1970), private communications.
9. B. RAY, S. A. MUGHAL, and A. J. PAYNE, Third International Conference on Thermal Analysis, Davos (1971).

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