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Preparation and Phase Studies of the Ternary Semiconducting Compounds $ZnSnP_2$, $ZnGeP_2$, $ZnSiP_2$, $CdGeP_2$, and $CdSiP_2$

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$ZnSnP_2$, $ZnGeP_2$, $ZnSiP_2$, $CdGeP_2$ and $CdSiP_2$ have been prepared in single or polycrystalline form by direct synthesis from the elements, combination of the group IV element with the II-V_2 phosphide, vapour transport or solution growth. Differential thermal analysis and X-ray powder diffraction studies have been used to determine the temperatures of phase transitions in each of these compounds. Of particular interest is the observation of a phase transition in $CdSiP_2$ at 1098° C some 22° C below the melting point. The thermal analysis studies of $ZnSnP_2$ indicate a peak, the cause of which is uncertain, at 720° C which is well separated from the melting temperature of 930° C; further $ZnSnP_2$ does not appear to be congruently melting and has a freezing point at 970° C. *c/a* ratios have been determined for all five compounds to 1 part in 2000.

1. Introduction

The general subject of $A^{II}B^{IV}C^{V}_2$ compounds has been reviewed extensively by Borshchevskii *et al* [1] and Ray [2]. $A^{II}B^{IV}C^{V}_2$ compounds may be considered as isoelectronic analogues of the $A^{III}B^{V}$ compounds in which the group III anion element is replaced by equal proportions of group II and group IV elements to give, on average, the same total number of bonding electrons per atom. The $A^{II}B^{IV}C^{V}_2$ phosphides which are to be discussed below are of particular interest as visible emitting semiconductors and chemically are considerably more stable than their $A^{III}B^{V}$ phosphide counterparts.

An increasing number of experimental techniques has been applied to the preparation and crystal growth of the $A^{II}B^{IV}C^{V}_2$ phosphides. It is significant perhaps, that compounds such as $ZnSnP_2$ and $CdSnP_2$ which in early investigations were thought not to form, have now been produced in single crystal form by solution growth [3–5]. Tin solution growth has proved particularly useful in preparing the phosphides which could not easily be melt grown because of their high melting points and dissociation pressures. In this context Spring-Thorpe and Pamplin [6] have recently produced single crystals of $ZnSiP_2$ and $ZnGeP_2$ of 1 cm length and 1 to 5 mm lateral dimensions.

The work of the present investigation incorporates the basic ideas given above and applies them to the preparation and crystal growth of $ZnSnP_2$, $ZnGeP_2$, $ZnSiP_2$, $CdGeP_2$ and $CdSiP_2$. The polycrystalline and single crystal material thus obtained has been subjected to thermal analysis, X-ray powder diffraction analysis and microscopic studies.

2. Synthesis and Single Crystal Preparation

It is difficult to distinguish between synthesis and single crystal preparation, since all the preparation techniques used, if subjected to sufficiently accurate temperature control, will produce single crystal material. It is therefore proposed to treat the two topics together and to point out the particular conditions necessary for single crystal preparation where appropriate.

The synthesis of the $A^{II}B^{IV}C^{V}_2$ phosphides may be divided into four principal methods:

1. Direct synthesis from the constituent elements.
2. Direct combination of the B^{IV} element with the $A^{II}C^{V}_2$ phosphide.
3. Vapour transport of the constituent elements.

4. Solution growth.

A general feature of all these techniques is that encapsulation in an evacuated quartz tube is necessary and that carbonisation of the quartz tube prevents attack by the constituent elements when prolonged heating is required. The vitreous carbon layer formed on the walls of the quartz tube also has the effect of conducting the heat of solidification away as the sample freezes and thus reduces the problem of surface bubble formation.

2.1. Direct Synthesis from the Constituent Elements

Ideally, synthesis and single crystal growth from the constituent elements represents the simplest approach to compound preparation. The $A^{II}B^{IV}C^{V}_2$ phosphides as a group, however, suffer from too high phosphorus pressures and dissociation pressures at their melting points for a complete reaction of their constituent elements.

It has nevertheless been possible in this investigation to prepare $ZnGeP_2$ from the elements by careful control of the heating cycle. Thermal analysis experiments had previously indicated that considerable reaction of the constituent elements occurred at temperatures in excess of 500° C and that at 850° C a further reaction occurred. The interpretation placed on these observations is that at 500° C zinc and phosphorus react to form phosphides of zinc and at 850° C zinc diphosphide (ZnP_2) reacts with germanium to form zinc germanium phosphide.

The appropriate atomic proportions of zinc, germanium and phosphorus were sealed off in a 10 cm long, 10 mm bore, quartz ampoule which was set in a vertical furnace. There existed a temperature gradient along the ampoule of 5° C/cm and the base of the ampoule was at the lowest temperature. The form of the temperature gradient forced the phosphorus to the bottom of the tube and assisted in the reaction with zinc. The lowest temperature point of the quartz tube was raised at 50° C/h to 530° C (free phosphorus pressure of 15 atm), where reaction took place over a period of 48 h. The temperature was further raised to 900° C at 20° C/h and left at this value for 16 h. Finally the heating to 1100° C was at 20° C/h. After several hours at this elevated temperature cooling at 20° C/h produced uniform polycrystalline $ZnGeP_2$ which had the chalcopyrite structure. The cooling rate used was sufficiently slow to avoid any rapid differential contractions which might crack the quartz tube.

At a cooling rate of 20° C/h the formation of cracks as suggested by other workers [1] was not observed, although in preparations at considerably slower cooling rates cracks did appear. The cracking is thought to result from the anisotropy of the thermal expansion coefficients in the chalcopyrite structure.

If heating from the reaction temperature at 530° C was continued either at a much faster rate than 20° C/h or beyond 900° C without allowing time for reaction, then explosion of the quartz ampoule frequently occurred between 850 and 950° C. It is thought that over-rapid heating causes the zinc phosphides to decompose at too fast a rate for the germanium to react and form the relatively stable ternary compound. This suggestion is supported by the observations of Ray and Burnet [7] that at least one of the phosphides, monoclinic zinc diphosphide, starts to decompose at temperatures in excess of 700° C.

Extremely slow cooling techniques (4° C/h) have been successful in producing single crystal sections within large ingots of $ZnGeP_2$. As mentioned above the cracks were observed in the ingot as a whole, although the single crystal sections appeared to be free of cracks. The same furnace and sample temperature conditions were used as for the synthesis of polycrystalline material. The tube, however, containing the $ZnGeP_2$ had a shaped tip to help promote crystal growth. The single crystal chunks were of the order of 10 mm^3 volume.

2.2. Direct Combination of the B^{IV} Element with the $A^{II}C^{V}_2$ Phosphide

Combination of the group IV element with the $A^{II}C^{V}_2$ phosphide represents a slight variation on the theme of direct synthesis. The time for preparation of $ZnGeP_2$ was reduced considerably with this method, a faster heating rate being used and no waiting time at 530° C being required. The zinc diphosphide used in this method of preparation of $ZnGeP_2$ was of the red, tetragonal kind, which is considerably more stable than the black, monoclinic variety. Similar conditions applied to the preparation of $CdGeP_2$ and $CdSiP_2$.

Both ZnP_2 and CdP_2 have been prepared by heating the constituent elements in a quartz tube along which there is an appreciable temperature gradient. A zinc and phosphorus mixture when so heated gives rise to the formation of both Zn_3P_2 and ZnP_2, which two compounds are formed in different temperature sections of the quartz tube and are thus easily separated. As mentioned above the ZnP_2 forms as small red crystalline platelets with a tetragonal structure. A cadmium and phosphorus mixture when heated, generally resulted in the formation of CdP_2; such CdP_2 was homogenised by heating in a uniform temperature, short, quartz ampoule at 800° C for some 6 h. The CdP_2 produced had a bright, metallic lustre and a crystal structure similar to that of the ZnP_2 discussed immediately above.

$ZnGeP_2$ has been prepared by heating stoichiometric proportions of ZnP_2 and Ge at a uniform rate of 50° C/h to 1050° C. The whole of the quartz encapsulating ampoule was maintained at the same temperature. After 24 h at 1050° C the sample was cooled at 20° C/h to room temperature and polycrystalline $ZnGeP_2$ was obtained, very similar in character to that produced by direct synthesis from the elements.

Both $CdGeP_2$ and $CdSiP_2$ have been prepared by heating CdP_2 and the appropriate group IV element to 1000 and 1200° C respectively. The heating rate and ampoule conditions were the same as for $ZnGeP_2$. Reaction takes place at the elevated temperatures within 12 h and thereafter slow cooling (20° C/h) to room temperature produces the homogeneous ternary compound. $CdGeP_2$ and $CdSiP_2$ both have a metallic, lustrous appearance and $CdSiP_2$ when finely powdered is yellow-orange in colour. The chalcopyrite structure was always observed for these two compounds.

2.3. Vapour Transport of the Constituent Elements

Vapour transport techniques have been applied to the synthesis and crystal growth of materials which have high melting points and permit the use of considerably lower preparation temperatures. In many instances it is possible to transport all the constituent elements of a compound and recombine them at an appropriate temperature as polycrystalline or single crystal material. Valov and Ushakova [8] have shown that silicon is a non-volatile component in the decomposition of $ZnSiP_2$ even at temperatures as high as 1170° C. Consequently a carrier gas such as iodine or chlorine has to be used in order to transport silicon; both $ZnSiP_2$ and $CdSiP_2$ have been successfully synthesised with such a carrier gas transport system [8, 9].

Several experimental arrangements have been used in this investigation of the preparation of $ZnSiP_2$ and $CdSiP_2$ by iodine carrier transport. Initially an evacuated 12 to 15 mm bore quartz tube of length 25 to 30 cm containing the constituent elements and approximately 10 mg/cm^3 of iodine, was placed in a furnace with a linear temperature gradient. The temperature was raised slowly at first to prevent sudden pressure build up and to drive the volatile constituents to the cold end of the ampoule. Thereafter the ampoule was heated at 50° C/h to the maximum temperature, when the low and high temperature end of the ampoule were at 1025 ($ZnSiP_2$) or 1000 ($CdSiP_2$) and 520° C respectively. After 4 days, the starting material had been transported to give a crystalline deposit of the ternary phosphide. Small crystallite agglomerates of $ZnSiP_2$ or $CdSiP_2$ were formed in the central region of the ampoule at temperatures between 950 and 980° C. However, the small size of the separated crystallites did not permit any useful optical or electrical measurements to be made. This method of processing has been used to produce large quantities of $ZnSiP_2$ to act as a base material for other methods of crystal growth.

A second stage in the experimental development was to take the already formed $ZnSiP_2$ with a further addition of iodine (10 mg/cm^3). The charge was placed at one end of a quartz ampoule similar to that described above except that a 12 mm diameter, 15 cm long graphite rod had been inserted at the opposite end of the tube to the charge. The purpose of the graphite rod was to conduct away the heat of crystallisation and also to provide nucleation sites for crystallisation. The temperatures of the extremities of the quartz ampoule were 1020 and 680° C and it is estimated that the hot end of the graphite rod was at 920° C. Nucleation of crystal growth occurred in the gap between the graphite rod and the quartz container, to give single crystals of $3 \times 1 \times 0.5$ mm dimensions after a period of 4 days. An extension of this method has been to polish the end surface of the graphite rod with 10 μm particle size abrasive before its insertion into the growth ampoule. Homogeneous, reddish-brown, crystalline layers of $ZnSiP_2$ have been grown on the polished surface with thicknesses up to 300 μm.

One final variation on the theme of iodine carrier transport growth is an experimental system used to prepare large volume, polycrystalline $ZnSiP_2$. In the arrangement, illustrated in fig. 1, growth of polycrystalline $ZnSiP_2$ occurs at the hot end of a 30 cm long quartz ampoule. A graphite rod is again used to conduct the heat of crystallisation away and is in this instance located 5 cm from the hot tip of the quartz ampoule. Thus crystallisation occurs on the hot side of the graphite rod where the temperature gradient is very shallow and growth extends over a large area. The period required for growth is 2 days in which time uniform, polycrystalline $ZnSiP_2$ ingots of dimensions up to $4 \times 1 \times 0.5$ cm have been obtained. $ZnSiP_2$ produced in this manner without any added impurities apart from the iodine carrier had resistivities in the 0.05 to 30 Ω cm range which is lower by a factor of between 10^4 and 10^6 than that for the $ZnSiP_2$ single crystals discussed above.

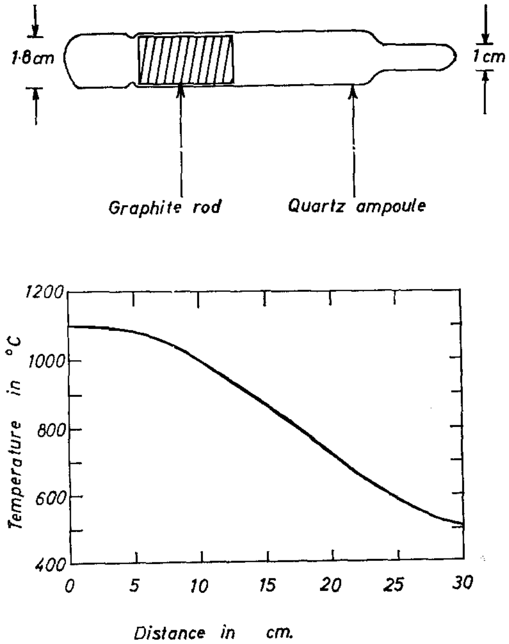

Figure 1 Experimental arrangement and temperature profile used in the preparation of large volume polycrystalline $ZnSiP_2$.

Single crystal platelets of $ZnGeP_2$ of several mm^2 surface area have been grown by vapour transport from a $ZnGeP_2$ charge under an applied phosphorus pressure. The $ZnGeP_2$ charge at one end of the tube was maintained at 1050° C and some 5 cm from that end a maximum temperature of 1150° C existed while a phosphorus reservoir at the other end of the tube was at 450° C. Dark red single crystal platelets of $ZnGeP_2$ grew in the region at 700° C, while red transparent platelets of ZnP_2 formed at 800° C.

2.4. Solution Growth

Several previous studies [3–6] have indicated that it is possible to prepare the $A^{II}B^{IV}C^{V}{}_2$ phosphides from tin solutions. The following ternary phosphides have been prepared from tin solution in the present study: $ZnSnP_2$, $ZnGeP_2$, $ZnSiP_2$ and $CdSiP_2$.

$ZnSnP_2$ was crystallised from a 50 mol % solution of $ZnSnP_2$ in tin. The solution was heated at 910° C for 7 days with a continuously applied 50 Hz vibration. It was then cooled to 350° C at 60° C/h and finally allowed to cool freely to room temperature. The container ampoule was held throughout the processing in a vertical furnace with a uniform temperature region over the length of the ampoule. The resultant mixture was composed of black crystallites of $ZnSnP_2$ and tin. The tin was removed with a mixture of HCl and HNO_3. The $ZnSnP_2$ crystallites obtained were too small to be of any great use other than for the determination of crystal structure and of phase changes.

More dilute solutions of the ternary phosphide (20 mol %) in tin have been used to prepare $ZnGeP_2$, $ZnSiP_2$ and $CdSiP_2$. For these three phosphides the four elements concerned have been placed in a quartz ampoule and heated at 50° C/h to 1100° C ($ZnGeP_2$ and $ZnSiP_2$) or 1200° C ($CdSiP_2$). Reaction for 20 to 30 h at these elevated temperatures with a continuous 50 Hz vibration was necessary to produce a homogeneous melt. Thereafter slow cooling of the melt (4 to 16° C/h) resulted in the growth of crystals of the appropriate ternary phosphide. At around 600° C the tin solution had become very dilute and the quartz ampoule was inverted in order to decant the tin from the crystals. The tin that remained on the surface of the crystals was removed with a particular cleaning cycle. The crystals were first treated with dilute HNO_3, rinsed (distilled water), boiled in hot concentrated HCl, rinsed, treated in hot 30% NaOH solution, rinsed, further heated in concentrated HCl, rinsed and dried. The appropriately cleaned crystal had plane surface faces and the thinner crystals were transparent at the long wavelength end of the visible spectrum.

$ZnGeP_2$ formed as an interpenetrant mass of single crystal polyhedra of volume, 10 to 50 mm^3, which were difficult to separate. $ZnSiP_2$

occurred as red transparent, single crystal platelets of dimensions 5 × 3 × 0.5 mm^3 and also as larger and less uniform prismatic growths (up to 25 × 5 × 2 mm^3) with numerous outgrowths. $CdSiP_2$ grew as small yellow-brown platelets (2 × 1 × 0.1 mm^3) and as an aggregate of thin fibrous needles up to 3 cm in length. Fig. 2 illustrates some of the crystals of the ternary phosphides grown from tin solution. It is interesting to compare $ZnSiP_2$ grown at different freezing rates as seen in fig. 2b and c. Much more uniform growth occurs at the slower rate (7.5° C/h), but the overall crystal size is slightly smaller. Freezing rates between 4 and 16° C/h do not significantly change the form of crystal growth for the other two compounds, $ZnGeP_2$ and $CdSiP_2$.

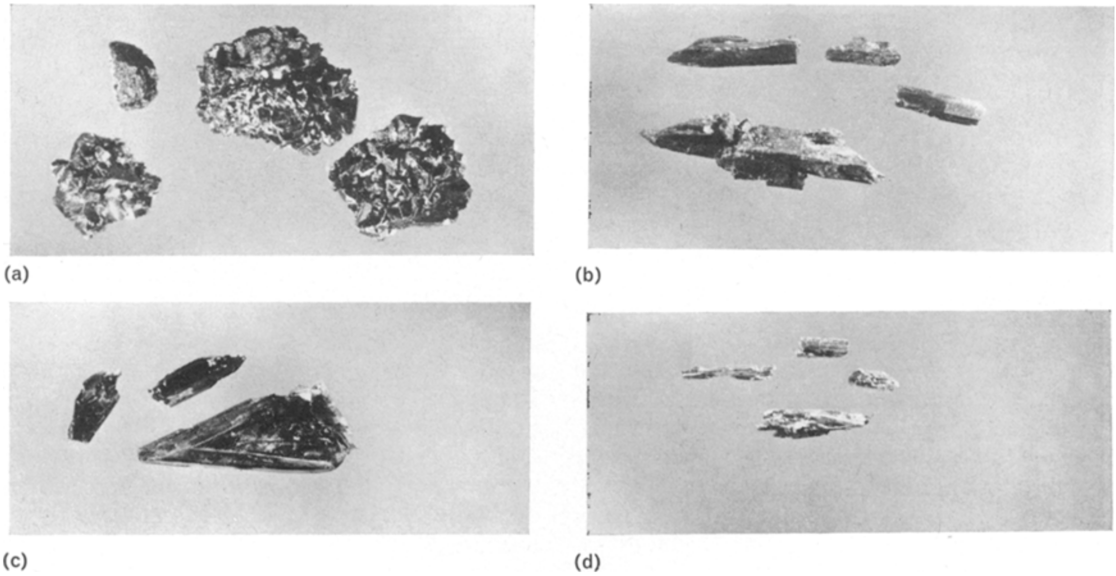

Figure 2 Photographs of crystals of the $A^{II}B^{IV}C^{V}_2$ compounds grown from tin solution (×1.65). (a) $ZnGeP_2$, mass of polyhedra. Cooling rate 15° C/h. (b) $ZnSiP_2$, needles and prisms. Cooling rate 15° C/h. (c) $ZnSiP_2$, plates and prisms. Cooling rate 7.5° C/h. (d) $CdSiP_2$, fibres and platelets. Cooling rate 15° C/h.

3. Phase Analysis

Differential thermal analysis, X-ray powder diffraction analysis and microscopic analysis have been used to study the compounds.

3.1. Experimental Techniques

A Standata 6.25 differential thermal analyser (D T A) manufactured by Stanton Instruments Ltd was used to study phase change temperatures. The instrument employs platinum-rhodium thermometry and can operate up to 1500° C. The temperature differential, sensitive to changes of 1/50° C, and the sample temperature are recorded simultaneously on a calibrated chart. The usual practice in these investigations was to use a heating rate of 4° C/min, and then phase change temperatures could be estimated to within ± 2° C.

X-ray diffraction studies have been made with a Philips PW 1008 X-ray generator (Cu anode) and a Debye-Scherrer powder camera (114.83 mm diameter and Straumanis mounting). With this arrangement it was possible to measure the lattice spacing to 1 part in 5000. All the compounds studied have the chalcopyrite structure with the space group $I\bar{4}2d$. A computer program has been set up to draw out an enlarged version of the Bjurstrom chart for the c/a ratios of interest and the allowed planar reflections in the space group. Line intensities can also be determined with this program for a given compound and comparison can be made with the identified line intensities.

A Nikon Stereozoom microscope with magnifications between × 20 and × 125 has been used for the microscopic analysis. The crystalline habit of small crystallites and imperfections on larger single crystals have been studied with the microscope.

3.2. Experimental Results

Table I summarises the results obtained from the phase analysis of the five ternary compounds, $ZnSnP_2$, $ZnGeP_2$, $ZnSiP_2$, $CdGeP_2$ and $CdSiP_2$.

In the DTA investigations of three of the compounds, $ZnSnP_2$, $ZnGeP_2$ and $CdSiP_2$, an additional peak below the melting peak was observed. It is thought that this lower temperature peak is associated with a disordering of the chalcopyrite structure to give the zinc blende structure. Certainly the observation by Goryunova [10, 11] of the zinc blende structure in rapidly cooled $ZnSnP_2$ lends support to the occurrence of a disordering process.

TABLE I

	$ZnSnP_2$	$ZnGeP_2$	$ZnSiP_2$	$CdGeP_2$	$CdSiP_2$
a Å	5.651	5.466	5.407	5.743	5.671
c Å	11.303	10.722	10.451	10.774	10.423
c/a	2.000	1.961	1.933	1.876	1.838
Disorder temperature ° C	720	952			1098
MP ° C	930–970	1025	1250	779	1120

High temperature X-ray powder investigations of $ZnGeP_2$ have indicated that the c/a ratio increases from 1.961 to 2.000 between room temperature and 950° C. The c/a ratio at 950° C was derived with the greatest difficulty since crystallisation of the vitreous silica container tube created additional diffraction lines and recrystallisation of $ZnGeP_2$ led to the chalcopyrite diffraction lines having a broken character. It is hoped to surmount these difficulties by the use of a microfocus X-ray beam which will reduce the exposure time and hence the time available for crystallisation processes. Modification of the furnace arrangement will also permit the ordering temperature for $ZnGeP_2$ of 952° C, to be exceeded and the question of the zinc blende structure at the high temperatures to be clarified. The change in c/a ratio in $ZnGeP_2$ with increase of temperature would seem to add further support for a disordering process to occur below the melting point.

Contrary to the evidence of other investigators [3, 4], in the present investigation it has been found that $ZnSnP_2$ prepared by solution growth does not melt congruently. As shown in table I there is a temperature difference of 40° C between the melting and freezing points of $ZnSnP_2$.

The studies of $ZnSiP_2$ have given no indication of thermal effects up to 1250° C. Such a result is perhaps a little surprising in the light of Valov and Ushakova's observations [8] of the decomposition of $ZnSiP_2$ at temperatures well below 1250° C. However, the silica ampoules used in the thermal studies were short (4 cm) and probably had insufficient overall temperature difference to permit appreciable decomposition.

In the $CdSiP_2$ grown from tin, solution elevation of the congruent melting point to 1136° C and depression of the disordering temperature to 1070° C occurred. A possible explanation for these changes may be that a phosphorus deficiency in $CdSiP_2$ exists because of the solubility of phosphorus in tin. Such a deficiency would make $CdSiP_2$ effectively silicon rich, so as to raise the melting point and lower the disordering temperature. The alternative explanation involving the substitution of tin or silicon lattice sites is unlikely since it should depress the melting temperature as well as the disordering temperature. X-ray studies did not distinguish between the iodine carrier, and tin solution grown $CdSiP_2$.

$CdGeP_2$ does not exhibit a disordering peak below the melting temperature but it does take on a vitreous character in addition to its crystalline behaviour. If $CdGeP_2$ is sealed into thin walled, 3 mm bore, silica tubing and quenched from the melt at 850° C, the vitreous form of the compound is obtained. Quench rates of the order of 200° C/sec are necessary to produce single-phase, amorphous $CdGeP_2$. A combination of slow cooling rates and thicker walled silica tubes gives rise to two-phase mixtures of vitreous and crystalline $CdGeP_2$. Thermal analysis of the glassy material indicated that a transition from the vitreous to the crystalline state occurs at 520° C. The transition is observed both as a free energy change and a change in specific heat.

4. General Comment and Other Observations

No general pattern can be fitted to the occurrence of additional peaks below the melting peak in some of the five compounds investigated. $ZnGeP_2$ ($c/a = 1.961$) and $CdSiP_2$ ($c/a = 1.838$) both exhibit such peaks and although high temperature X-ray measurements on $ZnGeP_2$ show a change in c/a ratio towards 2, it is unlikely that a change in c/a ratio to that extent would occur in $CdSiP_2$. Further X-ray investigation of these compounds in the region of their melting points would help to elucidate this point and also decide whether one is justified in describing the additional peak as a disordering peak. It is perhaps significant that $CdGeP_2$ which does not exhibit an additional peak is the only one of the compounds investigated which is obtained in the vitreous state.

Electrical resistivity measurements of $ZnGeP_2$ and $ZnSiP_2$ indicate that low resistivities are generally obtained in solution grown, undoped materials. It is possible that excesses of tin in the compound could give rise to low resistivities and Spring-Thorpe [12] has shown that in extreme instances tin inclusions can occur in both $ZnSiP_2$ and $ZnGeP_2$. Electrical resistivities as low as 0.05 Ω cm and hole mobilities of 2 cm^2/V sec at 300° K have been observed in the polycrystalline, iodine-carrier grown $ZnSiP_2$. The grain-boundaries in the polycrystalline $ZnSiP_2$ are not observable under the microscope at magnifications of × 125 and suggest that the material is extremely homogeneous. The growth technique used to produce polycrystalline $ZnSiP_2$ when further developed should be capable of producing large volume single crystal material.

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