

Everett values of n^{σ} in the present investigation are 0.53 and 0.36 millimole for the gel and the ppt respectively. These values are in the ratio of the surface area of the solids. The monolayer values based on 50 \AA^2 as the molecular area of n -hexane are 0.52 and 0.33 millimole. Thus the surface is completely covered during adsorption from this mixture. Possibility of perpendicular orientation of n -hexane is ruled out because 50 \AA^2 is the molecular area in parallel orientation. Schay-Nagy values are slightly smaller. Table II gives the distribution constant K_a for the two solids. Individual adsorption of each component, calculated by the Schay-Nagy and Everett methods over the entire concentration range, is compared in Table III.

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ON $A^{II}B^{IV}C_2^V$ TYPE MATERIALS

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ABSTRACT

Attention is drawn to current developments in the materials technology of chalcopyrite type $A^{II}B^{IV}C_2^V$ compounds. The problems associated with synthesis, characterisation, and crystal growth techniques are discussed in relation to the crystal structure. The tendency of selected compounds of this family to form ternary glasses which crystallise at relatively low temperatures is reviewed. Potential applications in the field of non-linear optics, switching devices, and glassy semi conductors are outlined.

I. INTRODUCTION

THE development of a series of chemical compounds comprising elements of the II-IV-V groups has been at the forefront of technological "action" in the field of Material Science in recent years^{1,2}. This interest has been stimulated by the possibility of several applications in areas such as glassy semiconductors³, non-linear optics^{4,5} and growth of heterojunctions⁶. The successful use of these materials has been hampered, however, because of the lack of readily available high quality single crystals. Single crystals are necessary to perform experiments without the complicating and often uncertain effects of the grain boundaries. With the rapidly emerging potential of these materials, an intensive effort is underway in Materials Research Laboratories around the world to develop techniques of synthesis, characterisation, crystal growth and studies of glass-crystal transformations. It is the intent of this review to outline some of these developments.

II. SYNTHESIS OF MATERIALS

(a) *Direct Fusion*.—The most commonly used method of synthesis is to seal the required amounts of the elements in evacuated quartz ampoules and heat at a relatively slow rate to one to two hundred degrees above the melting point of the compound; this prevents buildup of any high pressure volatile constituents (especially arsenic and phosphorus). To ensure homogenization of the melts, a vibratory rocking furnace may be used. For arsenides it may be necessary to apply a counter pressure of about 2 atmospheres of argon⁷. Following homogenization for several hours, the ampoule with contents is either cooled by shutting off the furnace or quenched directly in ice water. The synthesised materials are often crushed and remelted a number of times to ensure uniformity.

(b) *Glass Preparation*.—Although glass formation is well known in oxides⁸ and chalcogenides⁹, the possibility of the compounds yielding glasses was first explored by Vaipolin *et al.*¹⁰. These workers

prepared glasses in the Cd-Ge-As system and reported properties of CdGeAs₂ glass and crystal materials. Other studies¹¹ have extended the glass forming range in the Cd-Ge-As system and attempts have been made to characterise the glass forming tendencies by thermal techniques¹². CdGeAs₂ and CdGeP₂ are the only known members of the family of compounds that have been prepared as glasses; other compounds may also form glasses but have not been investigated.

(c) *Synthesis from Solutions.*—For compounds that tend to dissociate near the melting point, synthesis is often carried out by crystallizing solutions of the compound in molten metals. A desirable solvent is one which is also a part of the ternary compound. Commonly used solvents are tin and bismuth although indium and antimony have also been used. Many chalcopyrite type phosphides have been synthesised from tin solutions with fair degree of success but the arsenides often yield undesired phases. For example, attempts to crystallise CdGeAs₂ from tin solutions lead to the formation of germanium and a CdGe_{1-x}Sn_xAs₂ phase¹³. As a general rule synthesis from solutions is very attractive for materials with a large temperature gap between the liquidus temperature and the peritectic point; the crystallisation of the solvent must occur below the peritectic.

(d) *Vapour Transport Synthesis.*—Vapour transport is generally used when the constituents have sufficiently high volatility. The transport process is carried out in sealed quartz ampules with a carrier gas (often iodine) in a controlled gradient furnace. The volatile constituents are swept from the hot end to the cold end of the furnace by the carrier gas and deposited under suitable conditions. Pre-synthesised material is often used in this method of synthesis although direct synthesis from elements of the ternary compound is also possible when the vapour pressure is sufficiently high (e.g., Zn, P). The vapour transport method has been successful used to synthesise ZnSiP₂¹⁴.

(e) *Sintering Techniques.*—This is a rarely used method for synthesis although it has special advantages in some cases. For compounds that have a high melting temperature it is often convenient to cold press mixed powders of the constituents and sinter the compact. BeSiN₂ is prepared by this technique by sintering the cold pressed pellets of the nitrides in an ammonia stream using a boron nitride crucible at temperature of 1750 to 1800° C.

III. CRYSTAL STRUCTURE AND MATERIALS CHARACTERISATION

(a) *Crystal Structure.*—Crystallization of the II-IV-V₂ materials occurs in the crystal structure

derived from unit cells of wurtzite and sphalerite by the substitution of one type of atom in the cation sublattice of the initial structure by two different types of atoms. The resulting arrangement is of the "chalcopyrite" type and resembles two unit cells of zinc blende stacked on top of each other. The structure of a representative ternary compound of this family, ZnSnP₂, is shown in Fig. 1, with the random arrangement of Zn and

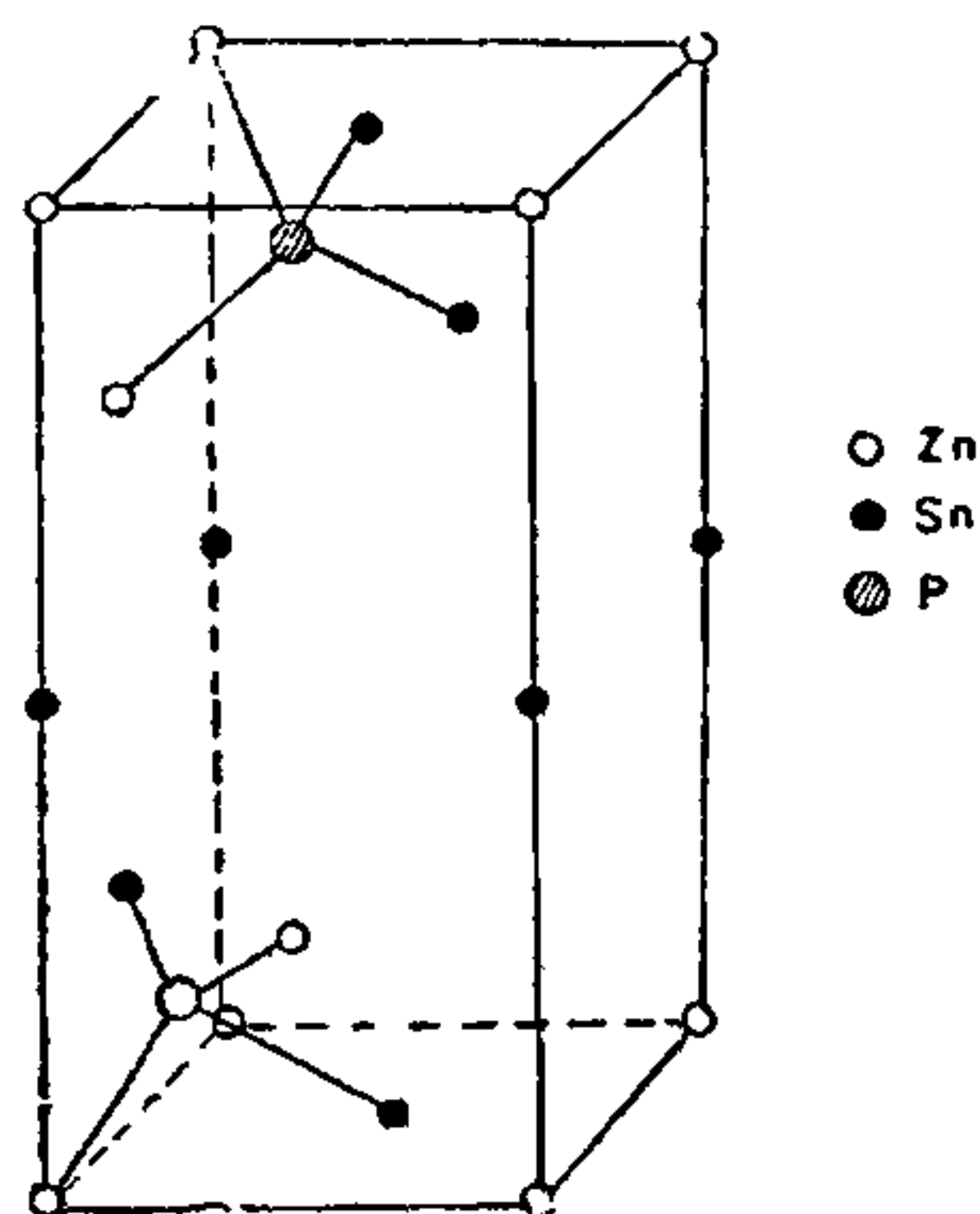


FIG. 1. Crystal Structure of chalcopyrites illustrated by the unit cell of ZnSnP₂.

Sn atoms in the sublattice. The formation of the chalcopyrite structure by tetragonal compression of the sphalerite unit cell introduces a distortion in the lattice characterised by the quantity¹⁵, $\sigma = a-c/a$, where a and c are lattice constants. The larger the σ value the greater is the anisotropy in the thermal properties of the compound. The σ values for a number of compounds are listed in Table I.

TABLE I
Tetragonal distortion value σ in some II-IV-V₂ compounds

Material	Lattice constant a , Å	Lattice constant c , Å	Tetragonal distortion $\sigma = 2 - c/a$
ZnSiP ₂	5.400	10.441	0.067
ZnGeP ₂	5.465	10.771	0.040
ZnSiAs ₂	5.606	10.890	0.057
CdSnP ₂	5.900	11.518	0.050
CdSnAs ₂	6.094	11.918	0.043
CdSiP ₂	5.678	10.431	0.163
CdSiAs ₂	5.884	10.882	0.152
CdGeP ₂	5.741	10.775	0.123
CdGeAs ₂	5.943	11.2172	0.112

(b) *Characterisation of Phases.*—The techniques used to characterise the phases obtained after

synthesis are X-ray diffraction, microscopy and differential thermal analysis (DTA). In some cases the more sophisticated methods of electron microscopy are used for structural studies and differential scanning calorimetry (DSC) for obtaining thermodynamic data. X-ray diffraction is almost always employed to ascertain the presence of crystalline peaks for the material being synthesised. The method is also useful for structure determination and lattice spacing studies. The DTA technique has been used with advantage in studying phase transformations. Being a quantitative technique (due to its dynamic nature) one can derive useful information on kinetics and thermodynamics of the material under observation. For instance, the DTA work on compounds like $ZnGeP_2$ and $CdSiP_2$ have successfully indicated the regions of glass formation and assisted in studies on order-disorder processes¹⁶. Crystallization activation energies for glass-crystal transformations have also been obtained by the DTA technique¹⁷. Optical microscopy with polarised light is a useful characterization tool specially to observe orientation differences in synthesised ingots. Imperfections can also be studied by this technique after suitable etching.

IV. SUMMARY OF CRYSTAL GROWTH TECHNIQUES USED

(a) *Growth from a Melt.*—The first reported attempt to grow single crystals from a melt was on the compound $CdSnAs_2$ ¹⁸. Material sealed in evacuated quartz ampoules was lowered at 2.5 mm/hour into a temperature gradient furnace. This standard method of crystal growth (Bridgman method) yielded polycrystalline ingots with a grain size of about 20 microns. In addition the top of the boules was often found to have two phases. $ZnSnAs_2$ was grown¹⁹ successfully as a single phase crystal by using graphitised quartz ampoules. Directional freezing in horizontal boats has also been attempted with some success for the compounds $ZnSiAs_2$, $ZnGeP_2$ and $ZnSnAs_2$ ²⁰. In cases where the σ value (Table I), which represents the degree of tetragonal distortion in the chalcopyrite structure, is large the growth techniques from melts have very limited success. For instance, $ZnGeP_2$ ($\sigma = 0.040$) was successfully grown from the melt²¹ by the Bridgman technique but the same authors reported highly cracked crystal of $CdGeAs_2$ ($\sigma = 0.112$) when grown from a melt.

(b) *Growth from Solutions.*—The solution growth technique is more time consuming and requires careful temperature control (to prevent spurious nucleation) to get single crystal materials. The method has the following advantages :

- (i) since growth from solutions is carried out well below the normal melting points of the material being grown, no excessive pressure of the volatile constituents is built up ;
- (ii) high temperature phase transitions are avoided ;
- (iii) strain free crystals are obtained with fewer intrinsic defects.

The solution growth technique has been applied to grow a number of small single crystals (mainly phosphides) from tin solvents²². Recently $CdGeAs_2$ has been grown from bismuth solutions in sizes upto 8–10 mm. Accelerated crucible rotation techniques have been suggested to improve quality and size²³.

(c) *Vapour Growth.*—Growth from vapour transport normally yields small platelets with lengths upto 10 mm^{24, 25}. The method is unsuitable when large boules are desired. $ZnSiP_2$ was grown by the vapour transport method²⁶ in an open flow system by mixing $SiCl_4$, PH_3 and zinc in hydrogen gas at 850° C. Vapour grown crystal often tend to be twinned with a capillary in the direction of the crystal axis. A clear understanding of the vapour mechanisms requires often the availability of enthalpies, dissociation free energies and other thermodynamic data. Such an attempt was made for a series of chalcopyrites²⁷ and the crystal growth was analysed.

In a brief review of the kind presented here it is not possible to list all the growth attempts used. The voluminous literature on the subject is summarised in Ref. 28.

V. PROPERTIES AND APPLICATIONS

The ultimate success of the compounds of the II–IV–V₂ will lie in the application of these materials in technological practice. It is gratifying to note that several applications are already known for this family of materials. In Table II are listed the physical properties of a few chalcopyrites and the specific applications reported so far are briefly outlined below.

Applications in infrared (conversion from the 8–12 micron range to below 1 micron) have been suggested for these materials²¹ which makes them useful in advanced imaging detectors. Laser action has been reported in $CdSnP_2$ at a wavelength of 1.01 microns when pumped by an electron beam²⁹. The band gap of this material lies close to the 1.06 micron Nd : YAG laser emission thus making it a potential material for room temperature detectors. In addition possible applications have also been suggested³⁰ in optical devices such as limiters and passive Q-switches. The chalcopyrites have

TABLE II

Physical properties of a few chalcopyrites

Material	c/a ratio	M.Pt. °C	Phase transition temperature °C	Energy bandgap, ev
ZnSiP ₂	1.934	1370	..	1.99 2.30
ZnGeP ₂	1.970	1020	952	2.0 2.4
ZnSiAs ₂	1.943	1038 1096	..	1.64 1.76 2.10
CdGeAs ₂	1.888	670	630	0.53

also been recommended as materials in high frequency oscillators³¹.

VI. CONCLUDING REMARKS AND SUGGESTIONS FOR FUTURE WORK

The applications for the present materials open many challenging areas of research. From a processing point of view, the most urgent problem, perhaps, is development of phase equilibria data on the complex ternary compounds. Such phase studies shall be very useful in applying solution growth techniques of crystal growth and will undoubtedly answer questions related to the existence of high temperature (metastable) phases. In the area of glassy materials, there is dearth of knowledge on crystallization kinetics³², morphology of crystals, and the energetics of the glass-crystal transitions. In addition potential exists for investigating and extending the glass formation areas in the family of II-IV-V₂ compounds. The role of phase separation or unmixing of the glasses in promoting or inhibiting the nucleation and growth kinetics also need exploration.

Much data have been reported on the electronic and physical properties of these materials. The non-availability of single crystals of sufficient size and quality is still a major hurdle, in the work on crystal physics. Many fascinating advances in the study and applications of these materials can be expected to be investigated, as the "art" of the crystal growing continues to be refined by the systematic studies of the Materials Scientist.

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