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Bibliography on $A^{II}B^{IV}C^{V}_2$ Ternary Compounds

Annotated References 1957 to 1966

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In the introduction, some of the applications of the $A^{III}B^{V}$ compounds are indicated. Their limitations are mentioned and two possibilities are suggested for overcoming these. In view of the $A^{III}B^{V}$ compounds' outstanding contribution in recent years, the investigation of their isoelectric analogues, the $A^{II}B^{IV}C^{V}_2$ compounds, is suggested as a logical step. $CdSnAs_2$ is shown to be the most investigated compound in this group, although several phosphides have potentialities as materials with energy gaps in the visible region of the spectrum. A comprehensive bibliography of the published work on $A^{II}B^{IV}C^{V}_2$ compounds is given.

1. Introduction

The investigation of group IV elements, $A^{III}B^{V}$ and $A^{II}B^{VI}$ compounds has been quite extensive over the last generation. The work on the group IV elements and the $A^{III}B^{V}$ compounds has produced many exciting new developments. Three materials, silicon, gallium arsenide, and indium antimonide, have in particular found outstanding applications, in the microelectronic field, as p-n junction lasers, and as infrared detectors, respectively; this is to mention but a few of their applications. As with all semiconductors, their optical and electrical properties set limits to their application, e.g. the energy gap will determine the energy of emission of a p-n junction laser. Thus there exist two obvious possibilities for reducing these limits: (i) employ compounds which form substantial solid solution to give a continuous variation of properties; (ii) investigate other materials which contain three or more constituents. The former approach is certainly possible in some cases; however, it is frequently the case that alloys cannot be obtained with the same purity, from an electrical standpoint, as their constituent compounds. In these circumstances, the investigation of other compounds becomes necessary; such compounds should have the minimum number of elements and be easily prepared in a stoichiometric form. The $A^{III}B^{V}$ group of compounds has proved to be of great interest, and it seems natural to extend investigations to their isoelectronic analogues, the $A^{II}B^{IV}C^{V}_2$ compounds, the subject of this bibliography.

The $A^{II}B^{IV}C^{V}_2$ compounds have received only limited investigations but, nevertheless, have shown interesting possibilities. The arsenides and phosphides appear to be the only $A^{II}B^{IV}C^{V}_2$ compounds to form. Most of these compounds take a chalcopyrite structure, a tetragonal form based on two zinc blende cells, in which the group II and IV elements order on one sublattice. At temperatures in the region of 100° C of the melting point, the chalcopyrite structure, in most cases, disorders to give a zinc blende structure. $ZnSnP_2$ and $CdSnP_2$ have unidentified structures, while $MgGeP_2$ takes the zinc blende structure at all temperatures.

$CdSnAs_2$ is the most well documented of this class of material. It is obtained in both n- and p-type form and has an optical energy gap, which is thought to be direct, of 0.26 eV at room temperature. It is prepared by zone melting and directional freeze techniques and has a melting point of 615° C.

In this class of materials, there also exist several compounds with energy gaps in the visible region of the spectrum. This is a region of particular interest at present for p-n junction lasers, in which there are very stringent materials' requirements. Direct energy gaps are essential, and there is good evidence to suggest that $A^{II}B^{IV}C^{V}_2$ compounds fall into this category. Obviously, too, the compound must be obtainable in both p- and n-type form; there is a lack of information on this condition, which results mainly from the limited experimental investigations to-date. The compounds which are reported to have energy gaps in the region 1.8 to 2.4 eV are $ZnSnP_2$, $ZnGeP_2$, $ZnSiP_2$, $CdGeP_2$, and $CdSiP_2$; and it is possible that $MgSiAs_2$, $MgSiP_2$, and $MgGeP_2$ might also fall into this category.

It is with this view of the growing importance of the $A^{II}B^{IV}C^{V}_2$ class of compounds that a comprehensive bibliography has been compiled. The bibliography contains both predicative and experimental investigations. The papers are listed for each year, with the authors' names in alphabetical order, and are accompanied by their full title and a brief abstract. A summary table of the main physical properties is given on page 291.

2. Bibliography

1. C. H. L. GOODMAN, *Nature* **179** (1957) 828-9.
"A New Group of Compounds with Diamond-Type (Chalcopyrite) Structure"

Seven compounds are observed with the chalcopyrite structure: $ZnSiAs_2$, $ZnGeP_2$, $CdGeP_2$, $ZnGeAs_2$, $CdGeAs_2$, $ZnSnAs_2$, $CdSnAs_2$. $ZnSnP_2$ and $CdSnP_2$ have unidentified crystal structures. Incomplete reactions occurred with $CdSiP_2$, $CdSiAs_2$, the antimonides, and the bismuthides. Absorption measurements indicate energy gaps as follows: $CdGeP_2$, 1.8 eV; $ZnGeP_2$, 2.0 to 2.4 eV; $ZnSiP_2$, 2.1 eV; $ZnGeAs_2$, 0.6 eV; $ZnSnP_2$, 2.1 eV; $CdSnP_2$, 1.5 eV.

2. O. G. FOLBERTH and H. PFISTER, *Halbleiter and Phosphore* (Vieweg, Braunschweig, 1958) 474-6.
"New Semiconducting Compounds with Chalcopyrite Structure"

The Debye-Scherrer X-ray photographs of $ZnGeAs_2$, GaAs, and Ge are compared. The chalcopyrite structure is illustrated; the a lattice parameter and the c/a ratio are reported as follows: $ZnSiP_2$, 5.398 Å, 1.934; $ZnGeP_2$, 5.46 Å, 1.97; $ZnGeAs_2$, 5.670 Å, 1.967; $CdGeAs_2$, 5.942 Å, 1.889; $CdSnAs_2$, 6.092 Å, 1.957.

3. C. H. L. GOODMAN, *J. Phys. Chem. Solids* **6** (1958) 305-14.
"The Prediction of Semiconducting Properties of Inorganic Compounds"

Various criteria are presented for the prediction of semiconducting behaviour. This includes mixed covalent-ionic character in the bonds and the consideration of valency in the formation of bonds. Phase diagrams are used to indicate that congruently melting, line phases, coupled with the above considerations, lead to compounds ideally suited for preparation in high-purity form. The data given include a table comparing energy gaps of $A^{II}B^{IV}C^{V}_2$ and $A^{III}B^{V}$ compounds. The non-formation of the ternary antimonides is suggested in terms of reduced stability compared with the equivalent binaries.

4. H. PFISTER, *Acta Cryst.* **11** (1958) 221-4.
"Crystal Structure of Ternary Compounds of the Type $A^{II}B^{IV}C^{V}_2$"

This is a fuller version of reference 2. The additional information concerns the comparison of unit cell volumes of the isoelectronic analogues in the $A^{II}B^{IV}C^{V}_2$ and $A^{III}B^{V}$ compounds.

Compound	$V_E = (a^2c)$ Å^3	*Compound*	$2V_E = (2a^3)$ Å^3
$ZnGeP_2$	320.5	GaP	323.9
$ZnGeAs_2$	358.6	GaAs	361.4
$CdSnAs_2$	442.4	InAs	444.8

5. O. G. FOLBERTH, *Z. Naturforsch* **149** (1959) 94-6.
"The Existence of Tetrahedral Phases"

The Grimm-Sommerfeld rule, which pertains to tetrahedral structures when an average of four electrons per atom exists, is applied in the case of repeated cross-substitution. This reveals a large number of possible, ternary, tetrahedral phases. The tetrahedral phases include the $A^{II}B^{IV}C^{V}_2$ group of ternary compounds.

6. O. G. FOLBERTH and H. PFISTER, *Acta Cryst.* **13** (1960) 199-201.
"The Crystal Structure of $ZnSnAs_2$"

The zinc blende structure is suggested as the stable structure for $ZnSnAs_2$ on the grounds of the similarity of the polarisability of the Zn-As and Sn-As bonds in contrast to the bonds in the other $A^{II}B^{IV}C^{V}_2$ compounds. This leads to a random distribution of Zn and Sn on one sublattice leading to a zinc blende structure with a lattice parameter of 5.851 Å.

7. N. A. GORYUNOVA and V. D. PROCHUKHAN, *Soviet Phys. Sol. State* **2** (1960) 161-3.
"Solid Solutions of Quaternary Systems Based on InAs and InSb"

Solid solutions of the systems InAs-$CdSnAs_2$ and InSb-$CdSnSb_2$ have been investigated. In the former system, the chalcopyrite structure was extended as far as 50 mol % In_2As_2 in $CdSnAs_2$. The microhardness reaches a maximum of 414 kg/mm^2 at 25 mol % In_2As_2. $CdSnAs_2$ melts at 615° C and the maximum melting point in the phase diagram is 852° C for 90 mol % In_2As_2. In the latter system, single-phase alloys with zinc blende structure are obtained up to 50 mol % $CdSnSb_2$ in In_2Sb_2 (melting point for this extreme alloy is 424° C). The maximum microhardness occurs for 20 mol % $CdSnSb_2$ in In_2Sb_2 with a value of 273 kg/mm^2. $CdSnSb_2$ itself is observed to be unstable.

8. S. MAMAEV, *Izvest. Akad. Nauk Turk. Ser. fiz.* **6** (1960) 7-12.
"Some Electrical Properties of Quaternary Alloys Based on InAs"

The electrical properties of the InAs-$CdSnAs_2$ system have been studied from 80 to 900° K. In the temperature interval 80 to 268° K, the electrical conductivity is found to depend on the composition and not on the temperature. The conductivity, σ, decreases as the InAs in the system is increased to 25 mol % In_2As_2 in $CdSnAs_2$. Above 268° K, ln σ increases linearly with decreasing $1/T$. The conductivity at all temperatures is electronic in character.

9. A. J. ROSENBERG and A. J. STRAUSS, *Bull. Amer. Phys. Soc.* **5** (1960) 83.
"Properties of $CdSnAs_2$"

It is observed that directional freeze of a stoichiometric melt of $CdSnAs_2$ leads to single-phase material with the chalcopyrite structure: $a = 6.084$ Å, $c/a = 1.957$. $\mu_e = 5600$ cm²/V sec for $n = 2.7 \times 10^{18}/\text{cm}^3$.

10. A. J. STRAUSS and A. J. ROSENBERG, *Lincoln Lab. Quart. Report Sol. State* (April 1960) 23-4.
"Preparation and Properties of $CdSnAs_2$"

Room-temperature electron mobilities of 1.2×10^4 cm²/V sec are observed for $n = 5.5 \times 10^{17}/\text{cm}^3$. Infrared transmission measurements give $E_G = 0.23$ eV (300° K). The compound is synthesised by melting stoichiometric quantities in an evacuated quartz tube. Although cooling rates of 1° C/min produce fractured ingots, single crystals up to 1 cm in length can be selected from the remains. Melting point 590 to 600° C. The samples appear to be extrinsic and degenerate at 300° K. Thermoelectric power data suggest an electron effective mass $m_e^* = 0.01$ to $0.06\ m_0$.

11. O. G. FOLBERTH and H. PFISTER, *Acta Cryst.* **14** (1961) 325-6.
"New Ternary Semiconducting Phosphides $MgGeP_2$, $CuSi_2P_3$, and $CuGe_2P_3$"

$MgGeP_2$ takes a zinc blende structure rather than the ordered chalcopyrite structure of most other $A^{II}B^{IV}C^{V}_2$ compounds. The lattice parameter value, $a = 5.652$ Å, is compared with values for other members of the same family. The relation of bond character to the structure is discussed with reference to ionic and covalent radii.

12. G. GIESECKE and H. PFISTER, *Acta Cryst.* **14** (1961) 1289.
"Mixed Crystals of $ZnSnAs_2$-InAs and $ZnGeAs_2$-InAs Systems"

The variation of lattice parameter with composition is given for these systems. In the $ZnGeAs_2$-InAs system, the zinc blende structure is obtained for all compositions with 90 mol % $ZnGeAs_2$ in In_2As_2 or less. Vegard's law is obeyed to a reasonable approximation in both systems.

13. W. G. SPITZER, J. H. WERNICK, and R. WOLFE, *Sol. State Electron.* **2** (1961) 96-9.
"Electrical and Optical Properties of $CdSnAs_2$"

n-type samples with carrier concentrations of 1×10^{18} to $3 \times 10^{18}/\text{cm}^3$ give electron mobilities of 6200 to 5500 cm²/V sec. Degenerate behaviour is observed between 4.2 and 300° K, but, for $T > 300°$ K, intrinsic behaviour occurs with an approximate energy gap of 0.3 eV, the lattice thermal conductivity = 0.071 W/cm °K. Thermoelectric power measurements suggest that alloying with InAs could produce a high thermoelectric figure of merit. Reflectivity data give an electron effective mass of $0.04\ m_0$ to $0.06\ m_0$ and a lattice dielectric constant of 12.1

14. A. J. STRAUSS and A. J. ROSENBERG, *J. Phys. Chem. Solids* **17** (1961) 278-83.
"Preparation and Properties of $CdSnAs_2$"

Repeats information in reference 10. The shift of the absorption edge with increasing carrier concentration to shorter wavelengths is reported. Comparisons are made between $CdSnAs_2$ and InSb, InAs and HgSe, for varying carrier concentrations.

15. D. B. GASSON *et al*, *J. Phys. Chem. Solids* **23** (1962) 129-302.
"The Properties of $ZnSnAs_2$ and $CdSnAs_2$"

DTA and X-ray powder-diffraction measurements indicate that $ZnSnAs_2$ transforms from chalcopyrite to zinc blende structure at 650° C and melts at 775° C. The lattice thermal conductivity at 300° K is 0.070 W/cm ° K for the disordered structure, and 0.115 W/cm ° K for the ordered structure. $ZnSnAs_2$ is always observed p-type with hole concentrations from 2×10^{19} to $3 \times 10^{21}/\text{cm}^3$ and the highest value obtained for the hole mobility is 22 cm²/V sec at 300° K. A hole effective mass of $0.5\ m_0$ is suggested from thermoelectric measurements and an optical energy gap of 0.6 eV.

The experiments on $CdSnAs_2$ confirm the previous results. A phase diagram for the Zn_3As_2-Sn_3As_4 is proposed and indicates the behaviour of the $ZnSnAs_2$ phase. $ZnSnAs_2$, $a = 5.852$ Å, $c/a = 2.000$.

16. N. A. GORYUNOVA, S. MAMAEV, and V. D. PROCHUKHAN, *Doklady Akad. Nauk SSSR* **142** (1962) 623-6.
"Certain Properties of the Semiconductor $CdSnAs_2$, an Electronic Analogue of InAs"

The following experimental values were obtained for $CdSnAs_2$: energy gap, 0.26 eV; $\mu_e = 2.2 \times 10^4$ cm²/V sec, with $n = 10^{17}/\text{cm}^3$; melting point 615° C; and $a = 6.092$ Å, $c/a = 1.957$. The electron mobility is observed to exceed that of its isoelectronic analogue InAs. The electrical conductivity has been measured over the range 77 to 840° K.

17. P. LEROUX-HUGON, *Compt. rend. Acad. Sci.* **255** (1962) 662-4.
"Study of InAs-$CdSnAs_2$ Alloys"

The ordered structure of $CdSnAs_2$ is maintained in alloys which contain more than 75 mol % $CdSnAs_2$ in In_2As_2. The thermoelectric power measurements give an electron effective mass of $0.037\ m_0$ for $CdSnAs_2$. A comparison of carrier concentrations, energy gaps, and effective masses in $CdSnAs_2$ and InAs samples is made.

18. S. MAMAEV, D. N. NASLEDOV, and V. V. GALANOV, *Soviet Phys. Sol. State* **3** (1962) 2473-8.
"Electrical Properties of Semiconducting Solid Solutions $x$$CdSnAs_2$-$y$$In_2As_2$"

The conductivity and Hall coefficient are determined as a function of temperature from 77 to 950° K. For $x = 1$, $y = 0$: $\mu_e = 5800$ cm²/V sec, with $n = 4.4 \times 10^{17}/\text{cm}^3$. All solid solutions exhibit carrier concentrations in excess of $10^{18}/\text{cm}^3$. When $y/x \leqslant 3$, specimens are n-type, but above this value all samples are p-type, and, except for those compositions close to InAs, they show no inversion to n-type when heated.

19. M. MATYAS and P. HÖSCHL, *Czech. J. Phys.* **12** (1962) 788-95.

"The Semiconducting Properties of $CdSnAs_2$"

The electrical conductivity, Hall effect, and magnetic susceptibility have been studied as a function of temperature in n-type $CdSnAs_2$. An electron effective mass of 0.02 m_0 has been determined from these dependencies and is independent of temperature. $\chi_{\text{mole}} = 112 \times 10^{-6}$ emu, μ_e (500° K) $= 2.5 \times 10^4$ cm²/V sec and varies as $T^{-1.67}$.

20. H. BORCHERS and G. MAIER, *Metall* **17** (1963) 775-80.

"The Ternary Semiconducting Crystal $ZnSnAs_2$ and the Structure of the Three-Component System Zn-Sn-As"

Several sections of the Zn-Sn-As ternary diagram have been studied to understand the formation of $ZnSnAs_2$. DTA and dilatometry measurements were made on $ZnSnAs_2$ samples during both heating and cooling. $ZnSnAs_2$ is thought to lie on the pseudo-binary section Sn-$ZnAs_2$ and is formed by a peritectic reaction with Sn. A change from chalcopyrite to zinc blende structure at 645° C occurs. The melting region is rather complex and two decompositions occur.

21. H. BORCHERS and R. G. MAIER, *Metall* **17** (1963) 1006-10.

"Pseudo-binary Phase Diagrams of the Semiconducting Crystal InAs with $ZnSnAs_2$, $ZnGeAs_2$ and $CdGeAs_2$"

Includes results of thermal analysis, dilatometry measurements, and X-ray analysis on the systems 2InAs-$ZnSnAs_2$, 2InAs-$ZnGeAs_2$, and 2InAs-$CdGeAs_2$. In the case of the 2InAs-$ZnSnAs_2$ system, solid solution is obtained across the whole range of compositions at high temperatures when the two compounds have the same crystal structure. For the 2InAs-$ZnGeAs_2$ system, solid solution is extensive with a small, two-phase region separating the structurally different phases. InAs-$CdGeAs_2$ is a system in which only limited solid solution occurs at the InAs end of the diagram, which is basically a eutectic form.

22. F. M. GASHIMZADE, *Soviet Phys. Sol. State* **5** (1963) 875-6.

"Band Structure of Semiconducting Compounds of $A^{II}B^{IV}C^{V}_2$ Type with Chalcopyrite Structure"

Theoretical calculations indicate that the conduction band is nonparabolic although the energy surfaces are spherically symmetrical. The band extrema are located at (000). In the case of $CdSnAs_2$, the valence band is triply degenerate with spin orbit splitting of 0.45 eV and crystalline field splitting of 0.01 to 0.03 eV. $E_G = 0.23$ eV (300° K) and $m_e^* = 0.014\ m_0$.

23. N. A. GORYUNOVA, V. I. SOKOLOVA, and T. BIN-SI, *Doklady Akad. Nauk SSSR* **152** (1963) 363-6.

"The Solubility of Germanium in Some Ternary Semiconducting Compounds"

The solubility of Ge in $ZnGeAs_2$ is investigated by X-ray and thermal analysis techniques. The amphoteric role of Ge in the solution is discussed.

24. P. LEROUX-HUGON, *Compt. rend. Acad. Sci.* **256** (1963) 118-20.

"Properties of Several Ternary Compound Semiconductors"

DTA measurements indicate that the chalcopyrite structure disorders at a range of temperatures T_D below the melting point T_M of each ternary compound. Thermoelectric power, Hall effect, thermal and electrical conductivity measurements have been made for these compounds.

	Carrier type	μ(cm²/V sec) 300° K	m^*/m_0	K_L(W/cm °K)
$CdGeAs_2$	n	30 to 70	0.02	0.04
$CdSnAs_2$	n	4100	0.05	0.07
$ZnGeAs_2$	p	4 to 8	0.7	0.11
$ZnSnAs_2$	p	25	0.3 to 0.6	0.07

25. P. LEROUX-HUGON, *Compt. rend. Acad. Sci.* **256** (1963) 3991-4.

"Thermal Conductivity of the Compounds $CdSnAs_2$, $CdGeAs_2$, $ZnSnAs_2$, and $ZnGeAs_2$"

The thermal conductivity of these compounds is measured in the temperature range 100 to 700° K. The possible conductive mechanisms are discussed and, in particular, a quantitative explanation of the thermal conductivity change is given at the order transition for $ZnSnAs_2$.

26. D. N. NASLEDOV, S. MAMAEV, and O. V. EMELYANENKO, *Soviet Phys. Sol. State* **5** (1963) 104-7.

"Investigation of the Thermoelectric power and Magnetothermal Effects of Alloys in the $CdSnAs_2$-2InAs System"

The longitudinal and transverse Nernst and Ettinghausen coefficients and the thermoelectric power have been measured from 100 to 600° K in $CdSnAs_2$, and $CdSnAs_2$-2InAs solid solutions. The scattering of electronic carriers in the compounds is related to phonons and impurity ions, while the predominant scattering source in the solid solution is the disordered structure lattice defects. The electron effective mass takes a value of 0.045 m_0 for most compositions in the solid solution.

27. H. PFISTER, *Acta Cryst.* **16** (1963) 153.

"Crystal Structure of $ZnSnAs_2$"

The ordered structure of $ZnSnAs_2$ is reported with $a = 5.851$ Å and $c/a = 2$ at 300° K. Disordering is observed at 635° C to zinc blende structure, with $a = 5.880$ Å at 640° C.

28. S. S. BATSANOV, *Russ. J. Struct. Chem.* **5** (1964) 862-4.
"A New Method for Calculating the Width of the Forbidden Zone"

A calculation of the band gap is made in terms of electronegativity difference and interatomic distances, frequencies, refractions, and other crystal characteristics. Deviations from the pure covalent bond are allowed for, although the actual calculations are not clearly shown. Comparison of the predicted and observed band gaps are made for $ZnGeP_2$, $ZnGeAs_2$, $ZnSiAs_2$, and $CdGeP_2$.

29. N. A. GORYUNOVA, F. P. KESAMANLY, and E. O. OSMANOV, *Soviet Phys. Sol. State* **5** (1964) 1484-5.
"Preparation and Some Properties of $CdGeAs_2$ Single Crystals"

$CdGeAs_2$ crystallises in the chalcopyrite structure with $a = 5.9425$ Å and $c/a = 1.8875$, with a microhardness of 471 kg/mm^2. No details are given of a special technique, which is mentioned in the paper, to prepare single crystals. Optical measurements give a band gap at 300° K of 0.53 eV; n- and p-type samples with carrier densities of the order of 10^{17}/cm^3 exhibit high-resistance contacts. Low-resistance contacts are produced if holes are drilled in the crystal, and indium is dropped into them. At 300° K, $\mu_p = 20$ to 25 cm^2/V sec, $\mu_n = 800$ to 1000 cm^2/V sec. An electron effective mass of 0.27 m_0 is erroneously described as being small for a band gap of 0.53 eV.

30. N. A. GORYUNOVA *et al*, *Soviet Phys. Sol. State* **6** (1964) 89-91.
"Electrical Properties of p-type $ZnSnAs_2$ Crystals"

Single crystals of p-type $ZnSnAs_2$ have been prepared with dimensions 8 × 15 × 50 mm. Hole concentrations in the range 2×10^{18} to 3×10^{18}/cm^3 are obtained at 300° K. A maximum in the curve of Hall coefficient versus temperature is taken to indicate degenerate splitting of the valence band into two bands.

31. P. LEROUX-HUGON and G. WEILL, *7th Int. Conf. Phys. Semicond. (Radiation Damage)* (Dunod, Paris) **3** (1965) 73-7.
"Effect of Fast Neutron Irradiation on Thermal Conductivity in the Ternary Arsenides"

The influence of irradiation with fast neutrons on the thermal conductivity has been studied in $CdSnAs_2$ and $ZnSnAs_2$. The interpretation of the results is made in terms of point defects and clusters. Annealing experiments indicate that the recovery may be accounted for in $CdSnAs_2$ by a second-order mechanism with an activation energy of 0.65 eV.

32. A. A. VAIPOLIN *et al*, *Izvest. Akad. Nauk SSSR Ser. fiz.* **28** (1964) 1085-9.
"Investigation of the Physicochemical and Electrical Properties of Crystals of Some Ternary Semiconductor Compounds of the $A^{II}B^{IV}C^{V}_2$ Type"

Single crystals of $CdGeAs_2$, $ZnSnAs_2$, $ZnSiAs_2$, $CdSiP_2$, and $ZnSiP_2$ have been investigated and are all observed to take a chalcopyrite structure. The lattice parameter, melting point, microhardness, density, colour, and Hall mobility have been compared for these materials in tabular form. The temperature dependence of the Hall coefficient and electrical conductivity are shown and a band structure is proposed for $A^{II}B^{IV}C^{V}_2$ compounds.

33. A. A. VAIPOLIN *et al*, *Doklady Akad. Nauk SSSR* **154** (1964) 1116-9.
"$ZnSiP_2$, $CdSiP_2$, and $ZnSiAs_2$ Crystals"

The crystal habit of the phosphides takes on three forms which depend on the lateral edge, either hexagonal, pentagonal, or trigonal. Electron mobilities as high as 1000 cm^2/V sec are observed in $ZnSiP_2$, with carrier concentrations of 10^{17}/cm^3, and lead to an effective mass of 0.08 m_0. Tabular comparison is again made of the main physical properties of the $A^{II}B^{IV}C^{V}_2$ phosphides and arsenides.

34. B. V. BARANOV, V. D. PROCHUKHAN, and N. A. GORYUNOVA, *Latvijas Zin. Akad. Vestis* **3** (1965) 301-8.
"Thermal Analysis of Some Solid Solutions"

The solid solution of $CdSnAs_2$ in InAs is investigated by a DTA technique. Each alloy sample has its homogeneity tested by microstructural and X-ray analyses, microhardness, and electrical measurements.

35. A. G. BYCHKOV *et al*, *Ukrain. fiz. Zhur. (USSR)* **10** (1965) 867-72.
"Electric and Photoeletric Properties of $ZnSiP_2$"

$ZnSiP_2$ crystals have been produced with electron concentrations of 1×10^{17} to 2×10^{17}/cm^3 and mobilities of 70 to 100 cm^2/V sec at 300° K. $dE_G/dT = -(7$ to $8) \times 10^{-4}$ eV/° K in the range 350 to 670° K. Donor levels at $E_1 = 0.08$ eV and acceptor levels at $E_2 = 0.32$ eV are indicated.

36. N. A. GORYUNOVA, "The Chemistry of Diamond-like Semiconductors" (Chapman and Hall, London, 1965), pp. 142-4.

Tabulated data of energy gaps in most $A^{II}B^{IV}C^{V}_2$ compounds is given plus fairly full information on $CdSnAs_2$.

37. N. A. GORYUNOVA, V. I. SOKOLOVA, and P. H. CHIANG, *Zhur. priklad. Khim.* **38** (1965) 771-8.
"Synthesis and Some Properties of the Compound $ZnGeAs_2$"

Zn and As react to form $ZnAs_2$ only after all the Zn has melted. $ZnGeAs_2$ in turn starts to form as $ZnAs_2$ melts at 771° C. A two-zone, vertical furnace is used to crystallise out $ZnGeAs_2$ at 1000° C. Thermal analysis measurements indicate that $ZnGeAs_2$ is congruently melting. The energy gap of $ZnGeAs_2$ is intermediate between its two isoelectronic analogues Ge and GaAs.

38. N. A. GORYUNOVA *et al*, *Soviet Phys. Sol. State* **7** (1965) 1060-2.
"Electric and Photoelectric Properties of $ZnSiP_2$"

Single-crystal n-type $ZnSiP_2$ has been prepared with

$n = 1 \times 10^{17}$ to $2 \times 10^{17}/\text{cm}^3$ and Hall mobilities of 70 to 100 cm²/V sec. Impurity compensation is suggested as the reason for the sharp fall in conductivity and the rise in the Hall coefficient over the temperature range which has been studied. $dE_G/dT = -(7 \text{ to } 8) \times 10^{-4}$ eV/° K with $E_G = 1.99$ eV at 300° K. The existence of a recombination centre 0.32 eV above the valence band is proposed from the photoelectric spectrum.

39. N. A. GORYUNOVA *et al*, *Izvest. Akad. Nauk SSSR Neorg. Matls.* **1** (1965) 885-9.
"Some Properties of $CdGeAs_2$"

In $CdGeAs_2$: $a = 5.9427$ Å, $c = 11.2172$ Å; the microhardness is 471 kg/mm²; absorption edge at 300° K is 2.0 to 2.3 μm; disordering temperature is 630° C, and melting point is 665° C. Both n- and p-type samples have been obtained. Electron mobility at 300° K is 1000 cm²/V sec, and the mobility varies as $T^{0.4}$ to 400° K then as $T^{1.5}$ for higher temperatures. Electrical conductivity versus temperature gives $E_G = 0.73$ eV. The electron effective mass determined from thermoelectric power measurements has a value of 0.027 m_0.

40. F. P. KESAMANLY, D. N. NASLEDOV, and YU. V. RUD, *Phys. Stat. Sol.* **8** (1965) K159-62.
"Electrical Properties of p-type $ZnSnAs_2$ Crystals at Low Temperatures"

In p-type $ZnSnAs_2$ with a carrier concentration of $1.3 \times 10^{19}/\text{cm}^3$, a hole effective mass of 0.6 m_0 is obtained. Light and heavy hole valence bands are separated by a very small amount.

41. F. P. KESAMANLY, YU. V. RUD, and S. V. SLOBODCHEKOV, *Soviet Phys. Doklady* **10** (1965) 336-7.
"On Photoelectric Properties of p-$ZnSiAs_2$ and p-$CdGeAs_2$ Crystals"

p-type $ZnSiAs_2$ at 300° K with $p = 4 \times 10^{14}/\text{cm}^3$ has a hole mobility of 45 cm²/V sec. Photosensitive peaks are found at 2.29 eV (300° K) and 2.33 eV (200° K). $dE_G/dT = -4.2 \times 10^{-4}$ eV/° K. Band gaps calculated from half peak value are 2.10 eV (300° K) and 2.14 eV (200° K). Similar investigations on p-type $CdGeAs_2$ give $E_G = 0.50$ eV (300° K) and 0.54 eV (80° K) and $dE_G/dT = -1.9 \times 10^{-4}$ eV/° K.

42. F. P. KESAMANLY, D. N. NASLEDOV, and YU. V. RUD, *Soviet Phys. Sol. State* **6** (1965) 1727-9.
"The Thermo-emf and Transverse Nernst-Ettinghausen Effect in p-$ZnSnAs_2$ Crystals"

The intrinsic absorption edge at 300° K gives $E_G = 0.65$ eV. The hole mobility varies with carrier concentration as follows.

Hole mobility (cm²/V sec)	*Carrier concentration* (cm⁻³)
190	9.5×10^{17}
52	8.6×10^{18}
7	1.8×10^{20}

43. P. LEROUX-HUGON and J. J. VEYSSIE, *Phys. Stat. Sol.* **8** (1965) 561-8.
"Thermal Properties of the Ternary Compounds $CdSnAs_2$ and $ZnSnAs_2$"

The low values for the lattice thermal conductivity in $CdSnAs_2$ and $ZnSnAs_2$ are obtained from specific heat measurements below 4.2° K. A detailed account of the scattering by acoustical phonons is given.

Compound	*Debye temperature* θ_D (° K)	*K* (W/cm ° K)	*Specific heat* (mJ/mole ° K)
$CdSnAs_2$	234	0.082	$0.60T^3 + 0.006T^5$
$ZnSnAs_2$	271	0.153	$0.39\,T^3$

44. S. MAMAEV and A. ALLANAZAROV, *Izvest. Akad. Nauk Turk. SSSR* **3** (1965) 98-9.
"Unusual Temperature Dependence of the Hall Coefficient in Solid Solutions $CdSnAs_2$-$2InAs$"

A maximum is observed in the plot of Hall coefficient versus temperature for all of the alloys, which are always p-type. An interpretation is discussed in terms of defect centres which act as acceptors at low temperatures.

45. K. MASUMOTO and S. ISOMURA, *J. Phys. Chem. Solids* **26** (1965) 163-72.
"The Preparation and Semiconducting Properties of Single Crystals of $ZnSnAs_2$ Compound B"

Large single crystals of $ZnSnAs_2$ have been prepared by the vertical Bridgman technique. 100 c/sec mechanical vibrator is used at 820° C to remove gas bubbles from the melt and the crystals are grown at a rate of 3 mm/h. The single crystals are p-type and cleave along (110) planes. A hole mobility of 130 cm²/V sec is found at 300° K for $p = 1.2 \times 10^{18}/\text{cm}^3$. Conductivity versus temperature gives $E_G = 0.59$ eV at 0° K, while infrared absorption measurements indicate E_G for a direct transition at 0° K is 0.74 eV. The hole effective masses from thermoelectric power measurements are $0.43m_0$ (300° K) and $0.59m_0$ (550° K).

46. B. R. PAMPLIN, J. S. SHAH, and R. A. L. SULLIVAN, *J. Electrochem. Soc.* **112** (1965) 1249-50.
"The $Zn_xCd_{1-x}SnAs_2$ Semiconducting Alloy System"

These alloys are prepared by the reaction of the elements in evacuated quartz tubes and followed by annealing at above 600° C. Continuous solid solution is found from $ZnSnAs_2$ to $CdSnAs_2$. The unit cell size is plotted against composition and shows an almost linear relationship.

47. M. RODOT, "Les Materiaux Semiconducteurs" (Dunod, Paris, 1965), p. 266.

Brief details are given of the physical properties of the $A^{II}B^{IV}C^{V}_2$ compounds.

48. J. RUPPRECHT and R. G. MAIER, *Phys. Stat. Sol.* **8** (1965) 3-39.

"New Investigation of Semiconducting Mixed Crystals with Special Reference to Phase Diagrams"

A review is presented of the previous work done on alloy systems of interest. The phase diagrams of InAs with $CdSnAs_2$, $ZnSnAs_2$, $CdGeAs_2$, and $ZnGeAs_2$ have been investigated. Thermoelectric power is represented as a function of composition in the InAs-$CdSnAs_2$ system.

49. A. A. VAIPOLIN *et al, Doklady Akad. Nauk SSSR* **160** (1965) 633-4.

"New Glass-like Compounds"

$CdGeAs_2$, which normally takes a chalcopyrite structure melting at 700° C, has been produced in a glassy form by quenching the melt. The density is slightly lower, the hardness is considerably less, and the electrical resistivity is very much higher than in the crystalline modification. Recrystallisation commences at 410° C and becomes rapid at 460° C.

50. I. KH. AKOPYAN and L. B. ZLATKIN, *Doklady Akad. Nauk SSSR* **168** (1966) 547-9.

"Optical Reflection Spectrum of $ZnSiP_2$"

High-quality crystals have been grown by vapour transport technique and require no polishing or etching. Measurements of the reflection spectrum for $ZnSiP_2$ are made in the ultraviolet beyond the intrinsic absorption edge. The individual peaks are related to the Brillouin zone.

51. M. L. BELLE *et al, Soviet Phys. Doklady* **10** (1966) 641-3.

"Optical and Photoelectric Properties of $ZnSiP_2$ Single Crystals"

The crystals grown from the vapour transport technique are red and transparent, with lattice parameters $a = 5.400$ Å and $c = 10.441$ Å. Optical transmission and photoconduction measurements are in agreement and suggest $E_G = 2.2$ to 2.25 eV (300° K) and 2.3 eV (77° K). $dE_G/dT = -4 \times 10^{-4}$ eV/° K.

52. V. V. GALAVANOV *et al, Soviet Phys. Sol. State* **7** (1966) 2949-50.

"Some Properties of p-type $CdSnAs_2$"

p-type $CdSnAs_2$ crystals have been grown by zone melting and have carrier concentration of $3 \times 10^{17}/cm^3$ at 100° K. The Hall coefficient changes sign at 300° K, while the conductivity varies as $T^{-0.575}$ up to 300° K. $E_G = 0.254$ eV (0° K) from Hall coefficient measurements and $b = 83$ from Hall coefficient maximum.

53. N. A. GORYUNOVA *et al, Izvest. Akad. Nauk Turk. SSSR* **3** (1966) 29-32.

"Solid Solutions in the $CdGeAs_2$ System"

Continuous solid solution across the whole range of compositions is reported. The solid solutions have been investigated by X-ray, microstructural, thermal analysis, and microhardness techniques. The chalcopyrite structure is taken for all compositions and the a lattice parameter follows Vegard's law. The physical properties of the alloys are presented in tabular form.

54. F. P. KESAMANLY *et al, Soviet Phys. Doklady* **10** (1966) 743-4.

"Energy Band Structure of Some Crystals of the $A^{II}B^{IV}C^{V}_2$ Group"

The valence and conduction band extrema are taken to be located at $K = 0$. The uppermost valence band is triply split owing to the crystalline field anisotropy and spin/orbit interaction. Crystalline field effects are small for the compounds considered, $CdSnAs_2$, $ZnSnAs_2$, $ZnSiAs_2$, $ZnSiP_2$, while the spin/orbit interaction decreases with decreasing molecular weight from 0.45 to less than 0.1 eV.

55. P. LEROUX-HUGON, *J. Phys. Chem. Solids* **27** (1966) 1205-18.

"Experimental Study of the Band Structure of the Compound $CdSnAs_2$"

Optical absorption and reflectivity, magnetoresistance and Hall effect measurements have been used to study single-crystal n-type $CdSnAs_2$ with carrier concentrations between 1.9×10^{17} and $8 \times 10^{18}/cm^3$. Crystalline field splitting of the valence band is observed with energy 0.032 eV. A non-parabolic structure for the conduction band is found and this is described in terms of Kane's model. An electron effective mass of 0.034 m_0 is determined from plasma edge measurements.

56. K. MASUMOTO, S. ISOMURA, and W. GOTO, *J. Phys. Chem. Solids* **27** (1966) 1939-47.

"The Preparation and Properties of $ZnSiAs_2$, $ZnGeP_2$, and $CdGeP_2$ Semiconducting Compounds"

Good crystals of $ZnSiAs_2$, $ZnGeP_2$, and $CdGeP_2$ have been grown by the vertical Bridgman or slow cooling methods. $ZnSiAs_2$ and $ZnGeP_2$ are p-type and $CdGeP_2$ is n-type. The melting points are 1096, 1025, and 800° C, for $ZnSiAs_2$, $ZnGeP_2$, and $CdGeP_2$, respectively. $ZnGeP_2$ disorders at 952° C. Thermal conductivity, microhardness, Seebeck coefficient, resistivity, and Hall coefficient have all been measured as a function of temperature.

57. T. A. POLJANSKAYA *et al, Fiz. Tverdogo. Tela* **8** (1966) 1851-8.

"Galvanomagnetic Properties of $CdSnAs_2$"

The galvanomagnetic properties of n-type and p-type $CdSnAs_2$ have been investigated in the temperature range 1.3 to 450° K. Optical phonon scattering of carriers predominates for temperatures in excess of 300° K. The hole effective mass is approximately 0.1 m_0 and the mobility ratio is 25 at 300° K.

58. B. RAY, *RAE Tech. Memo. Rad.* 777 (1966) 1-17.

"Preliminary Study of IIIA-VB and $A^{II}B^{IV}C^{V}_2$ Compounds"

The $A^{II}B^{IV}C^{V}_2$ compounds are studied from the point of view of electronegativity, ionic and covalent radii. The information has been collected together to predict compounds not already formed with energy gaps in the visible

Comparison of some physical properties of the $A^{II}B^{IV}C^{V}_2$ compounds.

	Lattice parameter a (Å)	c/a	$(a^2c/2)^{1/3}$ (Å)	a from covalent radii (Å)	Energy gap E_G(eV)	m^*/m_0	Carrier type	Mobility at 300° K (cm²/V sec)		Melting point (°C)	Phase change temperature (°C)	Microhardness (kg/mm²)	Thermal conductivity K_L (W/cm °K)
								μ_e	μ_h				
$ZnGeP_2$	5.46^{2}	1.97	5.43	5.46	2.2^{32} 2.0 – 2.4^{1}	—	p^{56}	—	—	1020^{32} 1025^{56}	952^{56}	980^{32}	—
$ZnGeAs_2$	5.670^{2}	1.967	5.64	5.65	0.6^{1} 0.65^{32}	0.7^{24}	p^{22}	—	—	875^{24} 850^{29}	812^{24}	700^{32}	0.11^{24}
$ZnSiP_2$	5.398$^{2,\ 51}$	1.934	5.34	5.41	1.99^{38} 2.3$^{32,\ 51}$	0.096^{32}	n$^{38,\ 51}$	1000^{51} 100^{38}	—	< 1500^{32}	—	1100^{32}	—
$ZnSiAs_2$	5.606^{32}	1.943	5.55	5.59	1.76^{32} 2.1^{1}	0.071^{32}	p$^{41,\ 56}$	—	45^{41}	1096^{56} 1038^{32}	—	920^{32}	—
$ZnSnP_2$	—	—	—	5.67	2.1^{1}	—	—	—	—	—	—	860^{58}	—
$ZnSnAs_2$	5.851^{15}	2.00	5.85	5.86	0.6^{32} 0.65^{42}	0.43^{45} 0.5^{15}	p^{22}	—	120^{29} 190^{42}	775$^{24,\ 32}$	650^{15} 700^{24}	455^{32}	0.153^{48} 0.070^{24}
$CdGeP_2$	5.740^{56}	1.876	5.63	5.66	1.8$^{1,\ 32}$	—	n^{56}	—	—	800^{56} 776^{32}	—	850^{32}	0.1 – 0.2^{56}
$CdGeAs_2$	5.942^{2}	1.889	5.83	5.85	0.53^{29} 0.54^{32}	0.027$^{32,\ 39}$	n^{29}p$^{29,\ 41}$	1000^{39}	25$^{29,\ 32}$	670^{24} 665$^{32,\ 39}$	630^{24}	471$^{29,\ 39}$ 453^{32}	0.04$^{24,\ 39}$
$CdSiP_2$	5.678^{32}	1.837	5.52	5.61	2.2^{32}	0.092^{32}	—	—	—	< 1000^{32}	—	—	—
$CdSiAs_2$	—	—	—	5.78	—	—	—	—	—	—	—	—	—
$CdSnP_2$	—	—	—	5.87	1.5^{9}	—	—	—	—	—	—	—	—
$CdSnAs_2$	6.093$^{2,\ 14}$	1.959	6.05	6.05	0.26$^{16,\ 19,\ 32}$ 0.23$^{14,\ 22}$	0.034^{55} 0.02^{19} 0.014^{22}	n$^{22,\ 52}$—p^{52}	12 000^{19}	150^{52}	615^{16} 595^{24}	554^{24}	395^{32}	0.071$^{13,\ 24}$ 0.082^{43}
$MgGeP_2$	5.652^{11}	—	—	5.56	—	—	—	—	—	—	—	—	—
$MgSiP_2$	—	—	—	5.51	—	—	—	—	—	—	—	—	—
$MgSnP_2$	—	—	—	5.78	—	—	—	—	—	—	—	—	—
$MgSiAs_2$	—	—	—	5.70	—	—	—	—	—	—	—	—	—

The superscript numbers refer to references in the bibliography.

and infrared regions of the spectrum. The magnesium and mercury $A^{II}B^{IV}C^{V}_2$ phosphides and arsenides are included in the final discussion.

59. G. A. SIKHARULIDZE *et al*, *Soviet Phys. Sol. State* **8** (1966) 924-8.
"Optical and Magneto-optical phenomena in $CdSnAs_2$"

Reflection and absorbtion spectra, opitical activity, and birefringence have been studied in the infrared from 3 to 20 μm for n- and p-type samples of $CdSnAs_2$. The measurements have been made at 130 and 295° K with zero and 25 kG applied magnetic field. E_G (300° K) = 0.25 eV, lattice permittivity = 13.7, and the average value of electron effective mass near the Fermi level is 0.042 m_0.

60. A. A. VAIPOLIN, E. O. OSMANOV, and YU. V. RUD, *Soviet Phys. Sol. State* 7 (1966) 1833-4.
"Diamond-like Semiconductors in the Glassy State"

$CdGeAs_2$ and $CdGeP_2$ are the compounds obtained in the glassy form. The glassy structure occupies compositions of 20 mol % along the line Ge-$CdAs_2$ on either side of $CdGeAs_2$. Glassy $CdGeAs_2$ has n-type conduction with $\rho = 10^6$ Ω cm (300° K). For T greater than 200° K, $\rho = \rho_0 \exp(E_\rho/2kT)$. Which gives E_ρ values from 1.1 eV downwards. Absorption edge measurements give the same band gap 0.6 eV (300° K) as for the crystalline sample.

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