In the introduction, some of the applications of the \( A^{IV}B^{VI}C^{II} \) compounds are indicated. Their limitations are mentioned and two possibilities are suggested for overcoming these. In view of the \( A^{IV}B^{VI}C^{II} \) compounds' outstanding contribution in recent years, the investigation of their isoelectric analogues, the \( A^{IV}B^{IV}C^{II} \) 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 \( A^{IV}B^{IV}C^{II} \) compounds is given.

1. Introduction

The investigation of group IV elements, \( A^{III}B^{V} \) and \( A^{IV}B^{VI} \) 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 \( A^{IV}B^{IV} \) group of compounds has proved to be of great interest, and it seems natural to extend investigations to their isoelectronic analogues, the \( A^{III}B^{IV}C^{II} \) compounds, the subject of this bibliography.

The \( A^{III}B^{IV}C^{II} \) compounds have received only limited investigations but, nevertheless, have shown interesting possibilities. The arsenides and phosphides appear to be the only \( A^{III}B^{IV}C^{II} \) 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 \( A^{III}B^{IV}C^{II} \) compounds fall into this category. Obviously, too, the compound must be obtain-
able 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 ZnSnP₂, ZnGeP₂, ZnSiP₂, CdGeP₂, and CdSiP₂; and it is possible that MgSiAs₂, MgSiP₂, and MgGeP₂ might also fall into this category.

It is with this view of the growing importance of the AIIBIVCV₂ 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

   “A New Group of Compounds with Diamond-Type (Chalcopryte) Structure”

Seven compounds are observed with the chalcopryte structure: ZnSiAs₂, ZnGeP₂, CdGeP₂, ZnGeAs₂, CdGeAs₂, ZnSnAs₂, ZnSnP₂ and CdSnP₂ have unidentified crystal structures. Incomplete reactions occurred with CdSiP₂, CdSiAs₂, the antimonides, and the bismuthides. Absorption measurements indicate energy gaps as follows: CdGeP₂, 1.8 eV; ZnGeP₂, 2.0 to 2.4 eV; ZnSiP₂, 2.1 eV; ZnGeAs₂, 0.6 eV; ZnSnP₂, 2.1 eV; CdSnP₂, 1.5 eV.

   “New Semiconducting Compounds with Chalcopryte Structure”

The Debye-Scherrer X-ray photographs of ZnGeAs₂, GaAs, and Ge are compared. The chalcopryte structure is illustrated; the a lattice parameter and the c/a ratio are reported as follows: ZnSiP₂, 5.398 Å, 1.934; ZnGeP₂, 5.46 Å, 1.97; ZnGeAs₂, 5.670 Å, 1.967; CdGeAs₂, 5.942 Å, 1.889; CdSnAs₂, 6.092 Å, 1.957.

   “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 AIIBIVCV₂ and AIIBV compounds. The nonformation of the ternary antimonides is suggested in terms of reduced stability compared with the equivalent binaries.

   “Crystal Structure of Ternary Compounds of the Type AIIBIVCV₂”

This is a fuller version of reference 2. The additional information concerns the comparison of unit cell volumes of the isoelectronic analogues in the AIIBIVCV₂ and AIIBV compounds.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Ve = (a²c)/a³</th>
<th>Compound</th>
<th>2Ve = (2a²)/a³</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnGeP₂</td>
<td>320.5</td>
<td>GaP</td>
<td>323.9</td>
</tr>
<tr>
<td>ZnGeAs₂</td>
<td>358.6</td>
<td>GaAs</td>
<td>361.4</td>
</tr>
<tr>
<td>CdSnAs₂</td>
<td>442.4</td>
<td>InAs</td>
<td>444.8</td>
</tr>
</tbody>
</table>

   “The Existence of Tetrahedral Phases”

The Grimm-Sommerfeld rule, which pertains to tetra-
hedral 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 AIIBIVCV₂ group of ternary compounds.

   “The Crystal Structure of ZnSnAs₂”

The zinc blende structure is suggested as the stable structure for ZnSnAs₂ 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 AIIBIVCV₂ 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.

   “Solid Solutions of Quaternary Systems Based on InAs and InSb”

Solid solutions of the systems InAs-CdSnAs₂ and InSb-CdSnSb₂ have been investigated. In the former system, the chalcopryte structure was extended as far as 50 mol % In₂As₂ in CdSnAs₂. The microhardness reaches a maximum of 414 kg/mm² at 25 mol % In₂As₂. CdSnAs₂ melts at 615°C and the maximum melting point in the phase diagram is 852°C for 90 mol % In₂As₂. In the latter system, single-phase alloys with zinc blende structure are obtained up to 50 mol % CdSnSb₂ in InSb₂ (melting point for this extreme alloy is 424°C). The maximum microhardness occurs for 20 mol % CdSnSb₂ in InSb₂ with a value of 273 kg/mm². CdSnSb₂ itself is observed to be unstable.

   “Some Electrical Properties of Quaternary Alloys Based on InAs”

The electrical properties of the InAs-CdSnAs₂ system have been studied from 80 to 900° K. In the temperature