305
1-8-80

MASTER

D. 552

DOE/ET/23039-1

**SYNTHESIS, EVALUATION, AND DEFECT COMPENSATION OF
TETRAHEDRAL GLASSES AS POSSIBLE SOLAR CELL MATERIALS**

Quarterly Technical Progress Report No. 1 for February 1—April 30, 1979

By
R. D. Rauh
T. L. Rose
A. N. Scoville

June 1979

Work Performed Under Contract No. AC03-79ET23039

EIC Corporation
Newton, Massachusetts

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

U.S. Department of Energy

Solar Energy

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

This report has been reproduced directly from the best available copy.

Available from the National Technical Information Service, U. S. Department of Commerce, Springfield, Virginia 22161.

Price: Paper Copy \$4.00
Microfiche \$3.00

SYNTHESIS, EVALUATION, AND DEFECT COMPENSATION OF
TETRAHEDRAL GLASSES AS POSSIBLE SOLAR CELL MATERIALS

Quarterly Technical Progress Report No. 1
February 1, 1979 - April 30, 1979

R. D. Rauh, Principal Investigator
T. L. Rose, Senior Scientist
A. N. Scoville, Staff Scientist

ETC Corporation, 55 Chapel Street
Newton, Massachusetts 02158

June, 1979

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Sponsored by DOE Division of Solar Energy
Photovoltaics Program Office
UNDER CONTRACT NO. DE-AC03-79ET23039

ABSTRACT

This report describes the work performed during the first quarter of a new project to synthesize $A^{II}B^{IV}C_2^V$ glasses and evaluate their potential use as solar cell materials. The results of an extensive literature search on the ternary glasses showed that those composed of Zn and Cd as the group two element, Sn, Ge, Si as the group four, and As and P as the group five element comprise the most promising materials on the basis of cost, band gap, and tendency for glass formation. The initial analysis of the defect structure expected in the ternary glasses showed that both radical and ionic defects are possible. The sparse results published in the literature indicate, however, that the former type are not important. The laboratory work was directed towards preparing bulk quantities of the ternary compounds. All the ternary arsenides have been prepared.

DESCRIPTION OF PROJECT

The goal of this project is to evaluate the potential of the $A^{II}B^{IV}C_2^V$ tetrahedral glasses as solar cell materials. The chalcopyrite glasses have structural and electronic properties which allow their chemical modification for ideal photovoltaic characteristics. The research is directed towards four principal tasks.

1. Synthesis and characterization of bulk quantities of $A^{II}B^{IV}C_2^V$ compounds.
2. Production of amorphous thin films of these materials.
3. Evaluation of optical and electrical properties of the amorphous materials.
4. Construction and testing of solar cells.

The work will concentrate on the series $CdMP_2$, $CdMas_2$, $ZnMP_2$ and $ZnMas_2$ where M is Ge, Si or Sn, since these materials are the least expensive and have the most promising band gaps.

I. INTRODUCTION

Use of amorphous materials for solar cells offers a potentially simple and inexpensive method for fabrication of large solar cells. The present research program is directed towards synthesis and evaluation of amorphous materials made up of ternary systems with the general formula $A^{II}B^{IV}C_2^V$. These compounds are attractive for the following reasons:

- They are the structural analogs of $A^{III}B^V$ compounds with rigid tetrahedral bonding which should restrict dopants to fourfold coordination, allowing them to act as donors or acceptors.
- The class is so varied that changes in the ratio of the constituent elements permits adjustment of the band gap for maximum efficiency under solar irradiation using the most economical elements.
- The compounds have demonstrated a strong tendency towards glass formation.
- The materials are inexpensive and plentiful.

This report presents the results of a literature survey on the ternary compounds of Cd and Zn with P and As, which are selected for initial investigation. The physical, electrical, and optical properties of most of the ternaries with Sn, Ge, or Si as the group IV element has been reported for the crystalline state, but the information is much less complete for the amorphous state. The next section presents the beginning of an analysis of the defect structure in the ternary compounds. Understanding of the defect structure is essential for development of methods for their compensation. The last section presents the results for bulk preparation of the ternary compounds synthesized in the laboratory. The x-ray results indicate that they are polycrystalline samples with lattice parameters in good agreement with the literature values.

II. LITERATURE SURVEY ON $A^{II}B^{IV}C_2^V$ TETRAHEDRAL GLASSES

There is a good deal of information about the physical, electrical, and optical properties of the ternary $A^{II}B^{IV}C_2^V$ compounds in the crystalline state. Shay and Wernick have covered the literature prior to 1974 (1). A more recent review was published by Prochukhan and Rud (2). Table 1 lists the Zn and Cd compounds of interest in order of decreasing optical band gaps of the crystal. Also included are the reported ranges of resistivities and carrier concentrations at 300°K.

In the last two years, several papers of interest on $A^{II}B^{IV}C_2^V$ crystals have appeared. Perhaps most relevant to the present study is the work of Littlejohn et al. on the use of crystalline $A^{II}B^{IV}C_2^V$ materials for solar cell applications (3,4). Brudnyi et al. have published several papers on the effect of electron irradiation on the electrical and optical properties of $ZnGeP_2$ (5), $CdGeAs_2$ (6), and $ZnSnAs_2$ (7). Recent work appearing on the much-studied $CdGeAs_2$ system includes new features of the Cd-Ge-As phase diagram (8), and electrical and optical properties of large grain ingots (9). The following subjects were reported for the Zn ternary compounds: Ge doping of $ZnSiP_2$ (10), preparation of $ZnSiP_2$ (11) and $ZnGeP_2$ (12), and optical properties of $ZnGeP_2$ and $ZnGeAs_2$ (13).

The literature on the amorphous $A^{II}B^{IV}C_2^V$ compounds is much less extensive than for the crystalline state. There are short sections in Shay and Wernick's book (1) and in other reviews on semiconducting $A^{II}B^{IV}C_2^V$ compounds (14-16). We have carried out a computer search for all references since 1971 on amorphous Zn and Cd ternary chalcopyrites. Most of the work was done in Russia prior to 1972. Table 2 lists the available information on formation of the glassy compounds. The glasses are formed by rapid quenching of the melt, explosion in vacuum, or sputtering of the polycrystalline material. There are literature references for glass formation for all the materials except $ZnSiAs_2$, $ZnSnP_2$ and $CdSnP_2$. It is not known whether the absence of literature references is due to difficulty in preparation of the amorphous form or merely indicates that no attempts have been made. The tetragonal distortion for the three compounds is very small (1), and may make it difficult to form glasses by cooling of the melt. Uhlmann (17) has presented a model for evaluating the ease of glass formation, but it requires information that is not available for the compounds of interest.

The band gaps observed in the amorphous materials (see Table 2) do not form any systematic relationship when compared with the band gaps for the crystals. Moreover, there is little agreement between the band gap measured by electric measurement and the optical value. An interesting

TABLE 1
PROPERTIES OF TERNARY CHALCOPYRITE CRYSTALS (Ref. 2)

<u>Compound</u>	<u>$E_g^{\min}$ (cry, eV)</u>	<u>Type</u>	<u>ρ (ohm cm)</u>	<u>n (cm⁻³)</u>
ZnSiP ₂	2.07	n	1.4×10^5	10^{13} - 10^{18}
		p	10^9	10^{14}
CdSiP ₂	2.05	n	10^2 - 10^7	10^{10} - 10^{15}
		p	not observed	
ZnGeP ₂	1.99	n	10^4	10^{13} - 10^{15}
		p	10^2 - 10^8	10^{10} - 10^{17}
ZnSiAs ₂	1.74	n	10^9	10^8
		p	3.5×10^3	10^{13} - 10^{17}
CdGeP ₂	1.72	n	10^2 - 2×10^5	10^{11} - 10^{14}
		p	4×10^3 - 10^8	10^{10} - 4×10^{13}
ZnSnP ₂	1.66	n	not observed	
		p	2-10	5×10^{16} - 2×10^{17}
CdSiAs ₂	1.55	n	1	10^{17}
		p	10^{-2} - 10^3	10^{14} - 10^{17}
CdSnP ₂	1.16	n	10^{-3} - 10^5	10^{15} - 10^{18}
		p	10^3 - 10^4	10^{14}
ZnGeAs ₂	1.15	n	not observed	
		p	10^{-1} - 10^{-2}	4×10^{18} - 10^{19}
ZnSnAs ₂	0.73	n	10^2	10^{15}
		p	10^{-1} - 10^{-4}	10^{17} - 10^{21}
CdGeAs ₂	0.57	n	10^{-1} - 10^{-3}	10^{17} - 10^{18}
		p	10^{-1} - 10^2	10^{16} - 10^{18}
CdSnAs ₂	0.27	n	10^{-2} - 10^{-4}	10^{17} - 10^{18}
		p	1 - 50×10^{-2}	10^{17} - 6×10^{18}

TABLE 2
PROPERTIES OF $A^{II}B^{IV}C_2^V$ GLASSES

Compound	m.p. crystal (°C) (Ref. 1)	T_r (°C) ^a	E_g , glass (eV) ^b	Prep. ^c	Ref.
ZnSiP ₂	1370, 1250			f	d
CdSiP ₂	1120		1.1(e)	g	16
ZnGeP ₂	1027		1.1(e)	q	16
ZnSiAs ₂	1096 ^d	No information on glass formation			
CdGeP ₂	778, 795	485	1.1(o), 0.9(e)	q, e	e, f
ZnSnP ₂	930	No information on glass formation			
CdSiAs ₂	850, 715	455	1.05(o), 1.4(e)	q	1
CdSnP ₂	570	No information on glass formation			
ZnGeAs ₂	850, 875			e, s	f, g
ZnSnAs ₂	775			f	h
CdGeAs ₂	667, 645	440	0.73(e), 0.53(o)	q, e	e, f
CdSnAs ₂	595		0.15(e)	q	16

a - T_r = Recrystallization temperature

b - Band gap from (o) or (c) electrical measurements

c - Method of preparation:

f = formed as film, conditions not specified

q = glass made by rapid quenching of melt

e = explosion in vacuum; film not same stoichiometry
as bulk source

s = sputtered film

d - P. Kirsten, V. Kulihauskus, K. S. Shishkin, Tr. Vses Soveshch. Fiz. Vzaimodeistviya Zaryazhennykh Chastits Monokist., 6th (1975), p. 433; CA 87, 172949v.

e - N. A. Goryunova, G. S. Kuzmenko and E. O. Osmanov, Nat. Sci. Enq., 7, 54 (1971).

f - V. G. Baryshev, N. S. Boltivets, A. S. Borshchevskii, N. A. Goryunova and P. T. Oreshkin, Sov. Phys. Semi., 4, 308 (1970).

g - W. Braun and M. Cardona, Phys. Stat. Sol. B, 76, 251 (1976).

h - R. Grigorovici in Amorphous and Liquid Semiconductors, J. Tauc, ed., (New York: Plenum Press, 1974), p. 45.

relationship has been proposed relating the recrystallization temperature to the band gap for materials of similar coordination number (18,19). For the limited data on the Cd ternaries, the relationship seems to hold. It will be of value, therefore, to determine the recrystallization temperatures for the other amorphous materials not only to prevent recrystallization during annealing and formation of glasses but also to indicate the band gap of the material.

The vast majority of the work on amorphous $A^{II}B^{IV}C_2^V$ materials has been done on $CdGe_xM_{1-x}As_2$ where M is a group III, IV, or V metal atom and x ranges from 1 to 0. The simple ternary, x = 1, is the only $A^{II}B^{IV}C_2^V$ glass for which any electrical properties have been reported (20-22). Generally, the samples were n-type with resistances of $\approx 1 \times 10^6$ ohm-cm at room temperature. The Seebeck coefficient became positive at reduced temperature and was a strong function of the fraction of Ge in the sample. The range of values obtained indicates the sensitivity of the material to the preparation conditions and impurity levels.

Recent work by Uemura on the four-element system with M = Si, Sn, and Pb and x = 1, 0.9 and 0.8 has shown ready glass formation with quenching of the melt (23,24). A study with M = Sb has also been reported (25). The results indicate that substitution of Pb and Sb reduce the band gap of the material. Si and Sn substitution, however, have much less effect on the amorphous material. These results are consistent with the substantial electrical and optical effects on CdM_xAs_2 glasses when M = Tl or Sb up to x = 0.8 (20).

Early reports of magnetic susceptibility measurements on amorphous CdM_xAs_2 , where M = Ge, Si, Th, Sb, indicated that there were paramagnetic centers in concentrations as high as $4 \times 10^{19} \text{cm}^{-3}$ (20,26). Later measurements, however, have shown that the levels must be less than 10^{17}cm^{-3} in $CdGeAs_2$ (27). Uemura's results also show no temperature dependence of the magnetic susceptibility indicating that paramagnetic centers are not introduced by substitution of up to 0.2 mole fraction of Si or Sn in place of Ge (23). Modeling of the structure of glassy $CdGeAs_2$ is also consistent with a lack of homonuclear "wrong bonds" in the compounds (28).

III. BONDING DEFECTS IN $A^{II}B^{IV}C_2^V$ GLASSES

Bonding defects in semiconducting materials can be generally categorized into those forming radical species and those leading to ionic defects (29). The first type arise from the dangling bonds as in α -Si whereas the latter have been proposed in the chalcogenides and $A^{III}B^V$ systems (30). Analyses of the $A^{II}B^{IV}C_2^V$ glasses of interest in this research shows that both types of defects are possible.

The structure for the simple $A^{II}C_2^V$ compounds is shown in Figure 1 using $CdAs_2$ as the example. The top picture gives a perspective view of the atom locations while the bottom is a schematic representation of the bonding around the tetrahedrally coordinated A^{II} atom. Two of the bonds to Cd are covalent and two are coordinate covalent (dative). Each arsenic forms a covalent bond, donates a pair of electrons for the dative bond, and has a lone pair. The addition of the group IV element results in the structure shown in Figure 2 for $CdGeAs_2$ (31). The bonding around the Cd remains unaltered but the lone pair of As in the binary compound is now utilized to form two covalent bonds with Ge making the As tetrahedrally bonded.

Four defect structures can arise from breaking the Cd-As and Ge-As bonds. If the bonds are broken heterolytically with the electrons remaining on the more electronegative As atom, the structure shown in Figure 3(b) arises. The As has a lone pair which results in either a $-1/2$ or -1 charge depending on whether the As-Cd or As-Ge bond, respectively, is broken. The result is an ionic defect in which the electrons are paired; no electron spin signal is expected. Homolytic bond rupture (Figure 3(c)) results in charge formation from the Cd-As bond, but forms a neutral defect for the Ge-As bond. Both bond fragmentations, however, lead to unpaired electrons. Results of previous magnetic susceptibility experiments on glassy $CdGeAs_2$ (27) indicate that the density of such spin states is low (see Section II).

The bond defect pattern for the ternary compounds is analogous to that for the $A^{III}B^V$ compounds. For $GeAs$, it has been proposed that the defects are self-compensated by formation of homopolar bonds, i.e., Ge-Ge and As-As (29). A similar situation is possible for the ternary glasses as shown in Figure 3(d). Such compensation would reduce the spin density but may introduce new states in the gap because of the low energy of the homonuclear bonds.

A more detailed investigation of the energetics associated with the defect formation of the ternary systems is in progress.

Fig. 1: Diagram of structure and bonding for binary $\text{A}^{\text{II}}\text{C}_2^{\text{V}}$ compound CdAs_2 .
 a) Perspective view showing the spacial orientation of the atoms.
 b) Schematic representation of the bonding.

a)

b)

Fig. 2: Diagram of structure and bonding of ternary $\text{A}^{\text{II}}\text{B}^{\text{IV}}\text{C}_2^{\text{V}}$ compound CdGeAs_2 . a) Perspective view showing the tetrahedral bonding of Ge within the CdAs_2 lattice. b) Schematic diagram of the bonding.

(a) Bonding of ternary system without defects.

(b) Defect structure resulting from heterolytic Cd-As and Ge-As bond rupture.

(c) Defect structure resulting from homolytic Cd-As and Ge-As bond rupture.

(d) Partial compensation of defect by formation of homonuclear bonds.

Fig. 3: Defect structures proposed for CdGeAs_2 .

IV. SYNTHESIS OF BULK QUANTITIES OF $A^{II}B^{IV}C_2^V$ COMPOUNDS

None of the ternary chalcopyrite compounds of interest in this study are available commercially. Most of the laboratory work this quarter, therefore, was directed towards preparation of bulk quantities of the Cd and Zn ternary compounds. Our initial efforts showed the need for developing careful preparative procedures for each compound. Many of the literature reports on the syntheses were too vague to be useful. We have now succeeded in preparing bulk quantities of all the ternary arsenides whose crystalline band gaps are in the useful region for solar energy photovoltaic application. The phosphides have proven more difficult to make; procedures are still being developed to make them using the binary phosphide compounds as starting materials.

Preparation of Ternary Arsenides. All the arsenides have been prepared using the method described by Masumoto (32) for $ZnSiAs_2$. In this procedure the constituent elements (99.999% purity) are mixed in stoichiometric amounts and sealed in an evacuated, thin-walled, quartz tube which has been coated with pyrolyzed graphite. The tube is placed in an oven and heated at a rate of 75°C/hr to a temperature less than 40°C above the melting point of the ternary product (see Table 2). Those mixtures with Sn were held at this temperature for only 3 hours before air cooling. The other samples were held at the elevated temperature overnight (≈ 15 hours) and then allowed to cool slowly in the oven. The samples yielded silver-gray ingots several millimeters in length (see Figure 4).

One sample of Cd, Ge, and As was heated to 800°C and held at that temperature overnight. The sample was removed from the oven and quenched in oil. The resulting material was a polycrystalline ingot of $CdGeAs_2$ rather than a glass. Apparently the relatively slow cooling that occurred between the time of removal of the sample from the oven and the quenching permitted crystallization. A smaller sample of Cd-Ge-As melted in a quartz tube without the graphite coating yielded an amorphous material when quenched in water.

Preparation of Ternary Phosphides. Preparation of the ternary phosphides by simple fusion of the constituent elements is generally not possible. All attempts resulted in explosion or lack of reaction. The explosion is due to the pressure built up as the phosphorus vaporizes. At temperatures low enough to prevent explosion, the reaction did not occur.

An attempt was made to prepare $CdSnP_2$ by a two-step procedure using a single zone furnace. First, stoichiometric quantities of Cd,

Magnification 8X

Magnification 16X

Fig. 4: ZnSnAs₂ polycrystalline ignot produced from fusion of stoichiometric amounts of the elements.

Sn, and red P were mixed in an evacuated, thin-walled quartz tube (i.d. 4 mm). The inside of the tube was not coated with graphite. The tube was brought to 500°C, maintained there for 20 hours, and then quenched in cold water. The tube was then reheated to 650°C over a period of 6 hours and held at that temperature for 6 hours before rapid quenching. This procedure yielded a blood-red ingot approximately 15 mm long. While the x-ray spectra gave lattice parameters in reasonably good agreement with those in the literature for CdSnP_2 , subsequent elemental analysis using atomic emission spectroscopy showed that the compound was Cd_3P_2 .

An alternative method for producing the phosphides is melting the ZnP_2 or CdP_2 in the presence of the group IV element (33). The binary phosphides were prepared by the method of Rubenstein and Dean (34). The components are sealed in an evacuated quartz tube with the red phosphorus at one end and the metal (Zn or Cd) at the other. The tube is placed in a 3-zone furnace which is tilted about 20° to raise the phosphorus end. First the phosphorus end is heated to 350°C, and then the metal end is raised to a temperature slightly below the boiling point of the metal. The equilibrium temperature of the middle zone is about 500°C. After 12-36 hours the furnace is shut off, and the tube is allowed to cool slowly. Preparation of ZnP_2 in this manner resulted in a 50% yield. Approximately half of the material was formed as the monoclinic (black) modification. The remainder was the red, tetragonal form. CdP_2 was prepared in a similar manner, except that the tube was backfilled with nitrogen to a pressure of 1 atm. A small yield of the red tetragonal CdP_2 was obtained.

In order to increase the yield of CdP_2 production, the dissociation of Cd_3P_2 (Cerac, 99.5%) in an excess of phosphorus was attempted (35). The Cd_3P_2 was placed in one end of the tube and red phosphorus in the other. The phosphorus end was raised to 460-480°C and the Cd_3P_2 to 700°C. An orange-red ring of CdP_2 formed in the middle zone held at 600-640°C. While the yield was increased, it was still far below the 50% value obtained for ZnP_2 production.

X-Ray Analysis. X-ray diffraction powder analyses were made on the binary and ternary compounds that were synthesized in the laboratory. The crystalline state of the compounds is confirmed by the x-rays. The lattice dimensions calculated from the diffraction angles are given in Table 3 along with the literature values. The lattice parameters agree quite well with the literature values.

TABLE 3

X-RAY ANALYSIS OF $\text{AIIIC}_2^{\text{V}}$ AND $\text{AIIIVC}_2^{\text{V}}$ COMPOUNDS PREPARED IN THE LABORATORY^a

Compound	$a(\text{\AA})$		$c(\text{\AA})$		c/a	
	This Work	Literature	This Work	Literature	This Work	Literature
CdP_2	5.3	5.29	20.59	19.74	3.88	3.73
ZnP_2	5.18	5.08	17.85	18.59	3.46	3.66
CdGeAs_2	5.73	5.943	11.62	11.217	1.92	1.88
CdSnAs_2	6.05	6.093	11.73	11.92	-	1.96
CdSiAs_2	5.82	5.884	10.79	10.882	-	1.85
ZnSnAs_2	5.82	5.851	12.16	11.710	2.09	2.00
ZnSiAs_2	5.73	5.612	10.71	10.878	1.87	1.94

^aThe precision of x-ray lattice parameters determined in this work is estimated as $\pm 0.10\text{\AA}$. The literature values are taken from the compilation in J. L. Shay and J. W. Wernick, Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties, and Applications (New York: Pergamon Press, 1975), p. 7.

V. SUMMARY

Our efforts during this first quarter were directed towards (1) a literature search to determine the state-of-the-art of amorphous $A^{II}B^{IV}C_2^V$ compounds; (2) beginning development of a chemical model from the defect structure expected in the ternary glasses; (3) synthesis of bulk amounts of the compounds. The survey of the literature showed that while there is fragmentary information on the preparation of the glassy $A^{II}B^{IV}C_2^V$ compounds, with the exception of $CdGeAs_2$ and its alloys with other metals, almost nothing has been reported about their optical and electrical properties. The analysis of the defect structure follows that used for GaAs. The presence of a third element in a ternary system increases the number of different possible defect structures. Both radical and ionic defects are possible. The failure to observe significant temperature-dependent paramagnetism in $CdGeAs_2$ glasses, however, indicates that at least for that system there is not a significant density of radical defect states. Bulk quantities of all of the ternary arsenides have been prepared and characterized by x-ray analysis.

VI. REFERENCES

1. J. L. Shay and J. H. Wernick, Ternary Chalcopyrite Semiconductors: Growth, Electronic Properties and Applications (New York: Pergamon Press, 1975).
2. V. D. Prochukhan and Yu.V. Rud, Fiz. Takh. Poluprovodn., 12, 209 (1978).
3. M. A. Littlejohn, "Study of II-IV-V₂ Compound Semiconductors for Solar Cell Applications," Proceedings of Photovoltaics Advanced Materials Review Meeting, October 24-26, 1978, Vail, Colorado, p. 505.
4. S. M. Bedair and M. A. Littlejohn, J. Electrochem. Soc., 125, 952 (1978).
5. V. N. Brudnyi, D. L. Budnitskii, M. A. Krivov, R. V. Masagutova, V. D. Prochukhan and Yu.V. Rud, Phys. Stat. Sol. A, 50, 379 (1978).
6. V. N. Brudnyi, M. A. Krivov, A. I. Potapov, I. K. Polushina, V. D. Prochukhan and Yu.V. Rud, ibid., 49, 761 (1978).
7. V. N. Brudnyi, D. L. Budnitskii, M. A. Krivov and V. G. Melev, ibid., 35, 425 (1976).
8. B. R. Pamplin and R. S. Feigelson, Mat. Res. Bull., 14, 263 (1979).
9. G. W. Isler, H. Kildal and N. Menyuk, J. Electron. Mat., 7, 737 (1978).
10. E. Ziegler, W. Siegel, G. Kühnel and E. Buhrig, Phys. Stat. Sol. A, 48, K63 (1978).
11. K. Winkler, U. Schulz and K. Hein, Krist. Teck., 13, 137 (1978).
12. A. Horak, I. Mitotkowski and J. Wieszka, ibid., 13, K65 (1978).
13. J. C. Rife, R. N. Dexter, P. M. Bridenbaugh and B. W. Veal, Phys. Rev. B, 16, 4491 (1977).
14. A. S. Borshchevskii, N. A. Goryunova, F. P. Kesamanly and D. W. Nasledov, Phys. Stat. Sol., 21, 9 (1967).
15. N. A. Goryunova, Proceedings of Ninth International Conference on Physics of Semiconductors (Leningrad: Nauka, 1978), Vol. 2, p. 1198.

16. H. Fritzsche in Amorphous and Liquid Semiconductors, J. Tauc, ed. (New York: Plenum Press, 1974), p. 241.
17. D. R. Uhlmann, J. Non-Cryst. Solids, 7, 337 (1972).
18. D. D. Thornburg, Thin Solid Films, 45, 95 (1977).
19. J. P. DeNeufville and H. K. Rockstad, Proceedings of Fifth International Conference on Amorphous and Liquid Semiconductors (London: Taylor and Francis, 1974), p. 419.
20. L. Cervinka, A. Hruby, M. Matyas, T. Simecek, J. Skacha, L. Stourac, J. Tauc and V. Vorlicek, J. Non-Cryst. Solids, 4, 258 (1970).
21. J. Tauc, L. Stourac, V. Vorlicek and M. Zavetova, Proceedings of Ninth International Conference on Physics of Semiconductors (Leningrad: Nauka, 1978), Vol. 2, p. 1251.
22. R. Callaerts, M. Denayer, F. H. Hashmi and P. Nagels, Discuss. Faraday Soc., 50, 27 (1970).
23. T. Satow, O. Uemura and S. Watanabe, Phys. Stat. Sol. A, 44, 731 (1977).
24. O. Uemura and T. Satow, ibid., 44, 303 (1977).
25. N. Van Dong, T. H. Danh, B. Auguin and A. Defresne, ibid., 33, 295 (1976).
26. M. Matyas, J. Non-Cryst. Solids, 8-10, 592 (1972).
27. F. J. DiSalvo, B. G. Bagley, J. Tauc and J. V. Waszczak, Proceedings of Fifth International Conference on Amorphous and Liquid Semiconductors (London: Taylor and Francis, 1974), p. 1043.
28. M. Popescu, R. Manaila and R. Grigorovici, J. Non-Cryst. Solids, 23, 229 (1977).
29. S. Ovshinsky and D. Adler, Contemp. Phys., 19, 109 (1978).
30. M. Kastner, D. Adler and H. Fritzsche, Phys. Rev. Letters, 37, 1504 (1976).
31. L. Cervinka, R. Hosemann and W. Vogel, J. Non-Cryst. Solids, 3, 294 (1970).
32. K. Masumoto, S. Isomura and W. Goto, J. Phys. Chem. Solids, 27, 1939 (1966).
33. S. A. Mughal, A. J. Payne and B. Ray, J. Mat. Sci., 4, 895 (1969); B. Ray, A. J. Payne and G. J. Burrell, Phys. Stat. Sol., 35, 197 (1969).
34. M. Rubenstein and P. J. Dean, J. Appl. Phys., 41, 1777 (1970).
35. W. Zdanowicz and A. Wajakowski, Phys. Stat. Sol., 10, K93 (1965)