A. A. VAIPOLIN, N. A. GORYUNOVA, E. O. OSMANOV, Yu. V. RUD' ,

D. N. TRETYAKOV

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Abstract

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A. A. VAIPOLIN, N. A. GORYUNOVA, E. O. OSMANOV, Yu. V. RUD' ,
D. N. TRETYAKOV

STUDY OF $ZnSiP_2$, $CdSiP_2$, AND $ZnSiAs_2$ CRYSTALS

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Crystals of $ZnSiP_2$, $CdSiP_2$, and $ZnSiAs_2$ belong to the almost unstudied representatives of compounds of the type $A^{II}B^{IV}C_2^V$, which is explained by the technological difficulties of obtaining them. A special feature of these three high-melting compounds is the large width of the forbidden band. The positions of the constituent elements in the periodic system, the type of bond, and the structure of the crystals make it possible to expect high mobility of current carriers in them.

There are very few data on the crystal structure of these compounds. Gudmen (1) indicates only the possible affiliation of $CdSiP_2$ with the chalcopyrite structure. As for $ZnSiP_2$ and $ZnSiAs_2$, works (1,2) give values of interplanar spacings obtained from Debye diagrams. The present work presents x-ray and electrical measurements carried out on single crystals of these compounds obtained for the first time.

Crystallizing in the chalcopyrite structure, the compounds have the following parameters:

$$\begin{array}{rll} ZnSiP_2 & a = 5.400 \pm 0.001\ \text{Å} & c = 10.441 \pm 0.002\ \text{Å} \\ CdSiP_2 & a = 5.678 \pm 0.001\ \text{Å} & c = 10.431 \pm 0.002\ \text{Å} \\ ZnSiAs_2 & a = 5.606 \pm 0.001\ \text{Å} & c = 10.890 \pm 0.002\ \text{Å} \end{array}$$

The lattice periods of $ZnSiP_2$ and $ZnSiAs_2$ measured by us agree, within the limits of error, with those available in the literature (1,2).

The phosphide crystals are transparent, but have different coloration: $ZnSiP_2$ —ruby-colored, $CdSiP_2$—light red. Crystals of these compounds often grow together into aggregates that are easily separated. The dimensions of the main mass of crystals vary from $3 \times 1 \times 0.6$ to $7 \times 2 \times 1$ mm^3; correspondingly the color darkens and the transparency decreases. The crystals usually have the form of a straight prism elongated in the [111] direction.

The anisotropy of the internal structure of the crystals is manifested in their external form. According to the number of lateral faces, the phosphide crystals

Fig. 1. Section of a $ZnSiP_2$ crystal perpendicular to [111]

Figure 1: Fig. 1. Section of a $ZnSiP_2$ crystal perpendicular to [111]

were of three types: six-sided (A), five-sided (B), and three-sided (V). The crystals are bounded by planes:

type A — $(\bar{1}\bar{1}2)$, (112), $(\bar{1}0\bar{1})$, $(0\bar{1}1)$, (011), (101);
type B — $(\bar{1}\bar{1}2)$, —, $(\bar{1}0\bar{1})$, $(0\bar{1}1)$, (011), (101);
type V — $(\bar{1}\bar{1}2)$, —, —, —, (011), (101) (see Fig. 1).

The broad faces of the crystals are crystallographic planes $(\bar{1}\bar{1}2)$, (101), (011). In crystals of type A a tendency was found toward narrowing of the face (112). Along with predominant growth in the [111] direction, the transverse growth of the crystals apparently occurs by spreading of the face $(\bar{1}\bar{1}2)$ in the directions $[\bar{1}10]$, $[1\bar{1}0]$, by superposition of layers (112) in the direction of the normal to the plane (112), and by more weakly manifested growth in the directions of the normals to $(0\bar{1}1)$ and $(\bar{1}0\bar{1})$, which is clearly confirmed by the disappearance of the faces (112) in crystals of type B and $(0\bar{1}1)$, $(\bar{1}0\bar{1})$ in crystals of type V. The main mass of crystals belongs to type A; the number of crystals of type V is considerably smaller than the others. The ends of the crystals, as a rule, have imperfect faceting.

To judge the single-crystal character and the degree of perfection of the samples, we used the method of X-ray diffraction (the Laue method), investigated the macrostructure and microstructure of the surfaces and transverse sections of the crystals, as well as the volume of the crystal in polarized light and in a "dark" field; the microhardness was determined.

For the surface characterization of the crystallographic planes, their etchability was studied. We used a number of etching media. Acid etchants proved to be more effective. It should be noted that there are no data in the literature on the etching of crystals of ternary compounds with the chalcopyrite structure and on the revelation of dislocations in them. Upon etching, hexagonal pits were found only on one of the {112} faces. The {112} faces may be formed either by P atoms or by Zn (Cd) and Si atoms. In studies on the etching of $A^{\mathrm{III}}B^{\mathrm{V}}$ ($^{3-5}$) it is asserted that dislocations are revealed only on surfaces formed by metal atoms. Drawing an analogy with $A^{\mathrm{III}}B^{\mathrm{V}}$, we assume that the etch pits are caused by Zn (Cd) and Si atoms located on the face. On this basis we assign to this face the index (112). Several dark spots observed on the $(\bar{1}\bar{1}2)$ surface may be a product of the etching reaction. With prolonged etching on (112), together with strongly dissolved pits, characteristic growth figures appear (Fig. 2).

Fig. 1. Section of a $ZnSiP_2$ crystal perpendicular to [111]

Fig. 3

Figure 2: Fig. 3

In contrast to the phosphides, the $ZnSiAs_2$ crystals are not faceted, which is a consequence of the difference in preparation methods. Their color is dark gray with a bluish tint. The phosphide crystals are stable with respect to various acids and alkalis. Common to the crystals of all three compounds is thermal stability: heating in air of the three compounds is thermally stable; heating in air to 400°C is not reflected in their properties.

Fig. 3

Optical measurements made it possible to determine the band-gap width of the compounds studied*. These parameters for $ZnSiP_2$ and $CdSiP_2$ were determined for the first time. The value of the band gap of $ZnSiAs_2$ proved to be lower than the value of 2.1 eV given in (^{1}) (Table 1).

$ZnSiAs_2$ samples for electrical measurements had the form of parallelepipeds with dimensions $12 \times 3.5 \times 1.5$ mm^3. The largest crystals were selected from $ZnSiP_2$ crystals. The electrical contacts in all samples were high-resistance. The method for obtaining low-resistance contacts in $ZnSiAs_2$ and $ZnSiP_2$ samples is similar to that described in (^{6},^{7}).

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Figure 3 presents curves of the dependence of the logarithm of the conductivity ($\lg \sigma$) and of the Hall coefficient ($\lg R$) on reciprocal temperature in the interval from 265 to 620°K for $ZnSiAs_2$. The $ZnSiAs_2$ samples have hole conductivity, and $ZnSiP_2$ electron conductivity. The carrier concentration in $ZnSiP_2$ crystals was $\sim 10^{17}$ cm^{-3}. At room temperature the Hall mobility of electrons in $ZnSiP_2$ reaches 1000 cm^2/V·s. For the purest samples, higher values of carrier mobility were obtained.

Table 1

	Melting temp., °C	Microhardness, kg/mm^2	Density, g/cm^3 (X-ray)	Density, g/cm^3 (pycnom.)	$E_{optical}$, eV (77°K)	$E_{optical}$, eV (300°K)
$ZnSiP_2$	<1500	1100$±100\|3.39\|3.35\|2.5\|2.3\|\|CdSiP_{2}$	[illegible]		[illegible]	3.97
$ZnSiAs_2$	1038	920$±$20	4.720	4.69	1.76	1.64

Using the model for the band spectrum of compounds of type $A^{II}B^{IV}C_2^V$ with the chalcopyrite structure $^{(8)}$, the value of the effective electron mass in $ZnSiP_2$ was estimated by Kane' s formula: $m^* \simeq 0.08\,m_0$. If it is assumed that the ionicity of the bond in $A^{II}B^{IV}C_2^V$ is either smaller than, or the same as, that in the corresponding analogs $A^{III}B^V$, then the lattice mobility in $ZnSiP_2$ should be of the same order as the electron mobility in GaAs.

It is very interesting to compare the properties of the ternary compounds studied in our laboratory and their isoelectronic analogs (9).

As is seen from the data of Table 2, the combinations of properties in ternary compounds of this type differ noticeably from the combinations of properties in compounds of type $A^{III}B^V$. All ternary compounds are characterized by a considerably lower melting temperature.

The microhardness of the phosphides is somewhat higher than the microhardness of their binary analogs, while the width of the forbidden band is of the same order.

As for the arsenides, their microhardness is of the same order as that of the binary analogs, while the width of the forbidden band is lower.

Table 2

	Melting temp., °C	Microhardness, kg/mm^2	Forbidden-band width, eV
$ZnSiP_2$	<1500	1100	2.3
GaP+AlP	( )1500+?	940+?	2.2+3.0
$CdSiP_2$	<1000	–	2.2
InP+AlP	1070+?	435+?	1.3+3.0
$ZnGeP_2$	1020	980	2.2
GaP	( )1500	940	2.2
$CdGeP_2$	776	850	1.8
InP + GaP	1070+(( )1500)	435+940	1.3+2.2
$ZnSiAs_2$	1038	920	1.6
GaAs + AlAs	1237+(>1600)	700+500	1.4+2.2
$ZnGeAs_2$	850	700	0.6–0.7
GaAs	1237	700	1.4
$ZnSnAs_2$	775	455	0.6
InAs+GaAs	942+1237	330+700	0.4+1.4
$CdGeAs_2$	665	453	0.54
InAs + GaAs	1070+1237	330+700	0.4+1.4
$CdSnAs_2$	615	395	0.26
InAs	942	330	0.36

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Fig. 2

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c

Fig. 2. Microstructure of alloys: *a*—with 10 at.% boron and 87.5 at.% nickel (400×); *b*—with 33 at.% boron and 60 at.% nickel (500×); *c*—with 15 at.% boron and 20 at.% nickel.

Since we associate an increase in microhardness, as well as a decrease in the forbidden-band width in isoelectronic series, with an increase in the fraction of covalent bonding, there is reason to suppose that ternary compounds of the type $A^2B^4C^5_2$ possess combinations of properties valuable for practical use.

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Institute of Physics
Academy of Sciences of the AzSSR

Physicotechnical Institute named after A. F. Ioffe
Academy of Sciences of the USSR

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REFERENCES

1. C. H. L. Goodman, *Nature*, **179**, 828 (1957).
2. O. G. Folberth, H. Pfister, *Halbleiter und Phosphore*, Braunschweig, 1958, p. 474.
3. H. C. Gatos, M. C. Lavine, *J. Electrochem. Soc.*, **107**, No. 5, 427 (1960).
4. H. C. Gatos, P. Z. Moody, M. C. Lavine, *J. Appl. Phys.*, **31**, No. 1, 212 (1960).
5. G. Ellis, *J. Appl. Phys.*, **30**, No. 6, 947 (1959).
6. N. A. Goryunova, F. P. Kesamanly, E. O. Osmanov, *Fiz. tverd. tela*, **5**, 2039 (1963).
7. D. N. Nasledov, S. V. Slobodchikov, *Fiz. tverd. tela*, **4**, 2755 (1962).
8. F. M. Gashimzade, *Fiz. tverd. tela*, **5**, 1199 (1963).
9. Tszyan Bin-sai, I. I. Tychina et al., *Dokl. XXI nauchn. konfer. Leningr. inzhenerno-stroit. inst.* Scientific Conference, 21st, 1963, Reports, L., 1963, p. 8.