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Abstract

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PHYSICS

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OPTICAL AND PHOTOELECTRIC PROPERTIES OF SINGLE CRYSTALS OF $ZnSiP_2$

(Presented by Academician L. A. Artsimovich on 29 I 1965)

The chemical compound $ZnSiP_2$ belongs to compounds of the type $A^{II}B^{IV}C_2^{V}$, which are electronic analogues of $A^{III}B^{V}$ (^{1,2}). According to preliminary data (^{3}), the forbidden-band width at room temperature is 2.3 eV and the electron mobility is 1000 cm/V · sec. The physical properties of $ZnSiP_2$ have not been investigated in any detail, which is apparently explained by the difficulty of obtaining this compound in the form of relatively pure single crystals.

1. Characterization of $ZnSiP_2$ single crystals. In the present work, the photoelectric and optical properties are considered for *n*-type single crystals obtained from the gas phase by the method of gas-transport reactions. The grown single crystals had the form of trigonal and tetragonal prisms, whose length often exceeded 10 mm, while the large faces reached a width of 0.5–0.6 mm. Plate-like crystals were also obtained, the area of whose basal faces (112) amounted to several square millimeters. The crystals were transparent and had a red coloration. X-ray diffraction analysis showed that the preferential growth of prismatic crystals occurs in the (111) direction, and that their most developed faces correspond to the crystallographic planes (112). The compound crystallizes in the chalcopyrite structure with unit-cell parameters $a = 5.400 \pm 0.001$ Å and $c = 10.441 \pm 0.002$ Å, in agreement with the data of work (^{3}).

The $ZnSiP_2$ crystals were studied under a polarizing microscope. The overwhelming majority of the crystals exhibit extinction, indicating that the tetragonal c axis (or its projection) lies in the plane of the crystal. For a crystal of prismatic form it was found that the direction of the c axis coincides with the direction of elongation of the crystal. In crystals having the form of plates, the angle was determined between the crystal c axis and some distinctly expressed growth feature (a blunted edge, faceting, etc.). In this way two groups of crystals were revealed: in some the c axis lay parallel to the edge, while in others it was at an angle of 24° to it.

2. Measurement procedure. To study the photoelectric properties, ohmic contacts were made on the (111) plane of the crystal by fusing indium in a hydrogen atmosphere. The absence of a barrier at the metal-semiconductor contact was checked from the current-voltage characteristics and from the absence of a photo-emf.

The spectral sensitivity of the photoconductivity was investigated at 77 and 300° K on an apparatus consisting of a tungsten incandescent lamp, a light-beam chopper, an IKS-21 monochromator, a V2-6 amplifier, a synchronous detector, and an EPP-09 electronic potentiometer. The use of synchronous detection of the electrical signal from the crystal made it possible to study the photosensitivity of $ZnSiP_2$ in the region of photon energies smaller than the forbidden-band width. The absorption spectrum was studied

on an ISP-51 spectrograph with an $F = 800$ camera at temperatures of 300, 77, and 4.2° K. In addition, the influence of the polarization of the incident light on both the optical and the photoelectric properties was studied. To investigate the dependence of the photosensitivity on the direction of polarization of the light, a film polaroid was used.

3. **Experimental results.** Photoconductivity was detected in the energy range of incident photons $h\nu = 0.5$–2.5 eV (Fig. 1). At $T = 300°$ K, on the spectral photoconductivity curve reduced to one incident photon, a pronounced maximum is observed at $h\nu = 2.14$ eV, as well as two maxima at 1.0 and 0.8 eV. At $T = 77°$ K, the photoconductivity curve shifts toward higher energy values and the maxima occupy positions at 2.19, 1.04, and 0.84 eV, respectively (Fig. 1). In addition to these maxima, three bends are outlined on the spectral photoconductivity curve near $h\nu = 1.3$, 1.6, and 1.9 eV (in the form of two steps), after which a sharp increase in the photocurrent begins, apparently caused by direct transitions of electrons from the valence band to the conduction band.

[Figure 1 graph]

Fig. 1. Photoconductivity spectra of $ZnSiP_2$.
1 $-T = 300°$ K; 2 $-T = 77°$ K

The influence of the polarization of the exciting radiation on the photoconductivity was also studied. The photoconductivity did not depend on the polarization of the incident radiation at photon energies $h\nu < 2$ eV. At $h\nu > 2$ eV, which corresponds to the photoconductivity maximum with $h\nu_{\text{max}} = 2.14$ eV (300° K), a rather sharp dependence of the photosensitivity on the direction of the vector $\mathbf{E}$ relative to the crystal c axis was found (Fig. 2). The directions of the vector $\mathbf{E}$ at which the maximum and minimum of the photosensitivity are attained are at an angle of 90° to one another.

[Figure 2 graph]

Fig. 2. Microphotogram of the absorption edge of $ZnSiP_2$ at $T = 300°$ K (a) and $T = 77°$ K (b, b'). Curves b, b' correspond to the perpendicular (b)

and parallel (b') relative arrangement of the vector **E** of the polarized exciting radiation and the crystal c axis

From the measurements it was found that not all crystals have a sharp absorption edge. This is probably connected with structural defects in some crystals. For optical and photoelectric investigations, the most perfect crystals, about $100\,\mu$ thick, with a natural surface and proper faceting, were selected. It was found that the absorption edge depends on temperature and polarization. At $T = 300^\circ$ K, the absorption edge is located near 2.13 eV (Fig. 2a), and it is sharper for $\mathbf{E} \perp c$. At $T = 77^\circ$ K, the edge shifts to the short-wavelength side (2.22 eV), revealing structure–two absorption bands at 2.23 and 2.27 eV (Fig. 2b). At $T = 4.2^\circ$ K the edge

absorption has the same two bands as at $T = 77^\circ$ K, while the shift of the edge (10–15 Å) and the narrowing of the bands are very slight. At $T = 77^\circ$ K and $T = 4.2^\circ$ K the absorption edge is also sharper for $\mathbf{E} \perp c$ (Fig. 2b, b′).

4. Discussion of results. Comparison of the results of optical and photoelectric measurements gives good agreement between the position of the main maximum of the spectral photoconductivity curve E_{phot} and the onset of the sharp rise of absorption E_{opt} (Table 1).

Table 1

Photon energy, °K	300	77
E_{phot}, eV	2.14	2.19
E_{opt}, eV	2.13	2.22

The sharp edge of photoconductivity and absorption makes it possible to assume the presence of direct electron transitions band–band in $ZnSiP_2$.

From the optical and photoelectric measurements it may be concluded that the forbidden-band width at $T = 77^\circ$ K lies between 2.2 and 2.25 eV. At $T = 300^\circ$ K the forbidden-band width is about 2.13 eV.

As mentioned in Section 3, crystals having an imperfect structure exhibit a very blurred absorption edge. This explains the discrepancy between our data and the data of work ([3]), in which the measurements were carried out on less perfect crystals.

The origin of the two absorption bands at 2.23 and 2.27 eV, appearing at T equal to 77 and 4.2° K, is as yet unclear. The small absorption coefficient in them and the insufficient narrowing with decreasing temperature do not allow one to assume an exciton character of their origin.

The temperature coefficient of the forbidden band in the temperature interval $77 \div 300^\circ$ K is $\alpha = \Delta E_g/\Delta T = -(4 \pm 1) \cdot 10^{-4}$ eV/deg. At temperatures below 77° K, α is evidently smaller.

As already mentioned above, in the long-wavelength region two more maxima of the photoeffect are observed, independent of the polarization of the exciting radiation. One may assume an impurity origin of these levels, the depths of the impurity levels being 0.8 and 1.0 eV below the bottom of the conduction band.

The dependence of the photocurrent and of the absorption edge on the polarization angle at $h\nu \geq 2$ eV is connected with the anisotropy of the crystal.

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Note: Figure translations are in progress. See original paper for figures.