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Preparation and Characterization of Several II–IV–V_2 Chalcopyrite Single Crystals

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Single crystals of $ZnSiP_2$, $ZnGeP_2$, $ZnGeP_{1.8}As_{0.2}$, and $ZnGeP_{1.6}As_{0.4}$ have been grown by several techniques and their electronic and optical properties were compared. For $ZnSiP_2$ there are marked absorption bands at 10 and 11.5 μm, and at 13 μm for $ZnGeP_2$. Upon substitution of 10 mole% of arsenic for phosphorus, the latter band does not shift to higher wavelengths. Further substitution of arsenic for phosphorus in $ZnGeP_2$ showed a weak second band at 9.8 μm.

Introduction

The ternary compounds $ZnSiP_2$ and $ZnGeP_2$ are semiconductors which crystallize with the chalcopyrite structure (space group $I\bar{4}2d$). An excellent review discussing the formation and properties of this class of compounds was presented by Borshchevskii *et al.* (*1*). $ZnSiP_2$ has been reported to melt at 1250°C (*2*) and single crystals were obtained from a molten zinc or tin flux (*2, 3*) as well as by chemical vapor transport (*3–6*) using Cl_2, CCl_4, $ZnCl_2$, or I_2 as the transport agent. There has been no report of crystal growth from the melt.

Single crystals of $ZnGeP_2$ have been grown from the melt (*4, 6–8*) or from molten metal fluxes (*3, 4, 9–11*). $ZnGeP_2$ has also been grown by chemical vapor transport using excess phosphorus as the transport agent (*8*). These materials show low absorption in the wavelength range from their optical band gap to the IR absorption band (13 μm for $ZnGeP_2$).

Despite the relatively large number of publications describing various properties of these compounds, there has been no comparative study of the crystal growth process and the electronic and optical properties of these phases. Single crystals of members of the solid solution $ZnSiAs_xP_{2-x}$ have been grown by chemical vapor transport using iodine as the transport agent (*3*). However, only the variation of lattice parameters as a function of composition was reported in this study. There have been no reports concerning the substitution of arsenic for phosphorus in $ZnGeP_2$. The extent of arsenic substitution into $ZnGeP_2$, as well as the effect on both the observed optical and electronic properties, is included in this study of these chalcopyrites.

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Experimental

$ZnSiP_2$ Single Crystals

Growth from a zinc flux. Single crystals of $ZnSiP_2$ were grown from a zinc flux. The zinc metal (Gallard and Schlesinger, 99.9995) was prereduced in a Ar/H_2 (85/15) atmosphere at 200°C for 3 hr. Silicon and phosphorus (Gallard and Schlesinger, 99.999) were used without further purification. The molar ratio of the reactants was 60 : 1 : 2 (Zn : Si : P). Approximately 20 g was placed in a silica tube which was then evacuated to 3 μm Hg, sealed, and heated in a furnace at 20°C/hr to 1000°C. After a soaking period of 24 hr at this temperature, the furnace was cooled at a constant rate of 5°C/hr to 500°C. The tube was then allowed to cool to room temperature and opened. Crystals were retrieved by leaching away the solidified flux with hot dilute (2 *M*) hydrochloric acid. The crystals were red and the maximum site was 8 × 2 × 1 mm^3.

Growth by chemical vapor transport. Single crystals of $ZnSiP_2$ were also synthesized by chemical vapor transport using chlorine as the transport agent. Charge compositions in the molar ratio 1 : 1 : 2 were introduced into silica tubes which were then evacuated to 2 μm Hg and 100 Torr of Cl_2 was then added to the transport tube which was then sealed. The transport tube was placed in a three-zone furnace and the charge prereacted at 700°C for 24 hr with the growth zone maintained at 970°C, in order to prevent transport. The furnace was equilibrated to give a constant temperature zone across the reaction tube and was then programmed to give, in 24 hr, the temperature gradient necessary for single crystal growth to take place. Crystals grew in the cooler zone of the furnace with experiments generally running 20 days. A gradient of 1000–970°C was used and polyhedral crystals 5 × 3 × 3 mm^3 were obtained.

$ZnGeP_2$ Single Crystals

Growth by chemical vapor transport. Single crystals of $ZnGeP_2$ were also grown by chemical vapor transport using chlorine as the transport agent. The germanium used was obtained from Cominco (7-9's, resistivity 50 Ω-cm). The growth procedure was similar to that described for $ZnSiP_2$. However, a temperature gradient of 980–950°C was used. Polyhedral crystals 8 × 5 × 3 mm^3 were obtained.

Growth from the melt. $ZnGeP_2$ boules were grown by a modified Bridgman method. The charge which contained 2 g of reactants and 2% excess phosphorus was placed in a graphite Bridgman-shaped crucible and then sealed in a silica tube; the charge was then prereacted in an argon-pressurized furnace. The argon back pressure was maintained at 26 atmospheres and the heating was carried out in three stages. Initially, the temperature was 600°C for 24 hr, then 800°C for 24 hr, and finally 900°C for 24 hr. The tube was transferred to a vertical furnace equipped with a puller/rotor action motor. The motor was used to ensure uniform heating across the growth ampoule during crystal formation. The charge was allowed to reach a temperature of 1070°C. The growth ampoule was maintained at this temperature for 48 hr. The maximum temperature was then lowered to 1040°C and the ampoule was allowed to pass through a temperature gradient of 3°C/cm at the liquid–solid interface at a rate of 0.2 mm/hr for a period of 1 week. The size of the boule was 2.5 cm × 0.7 cm. A 1-mm slice was removed and discarded from both the top and bottom of each boule.

Arsenic-Substituted $ZnGeP_2$ Single Crystals

Arsenic was introduced into the chemical vapor transport tubes and the conditions for crystal growth were maintained the same as for pure $ZnGeP_2$. In addition, boules of $ZnGeP_{1.8}As_{0.2}$ and $ZnGeP_{1.6}As_{0.4}$ were obtained from the melt by a procedure similar to that used for the growth of pure $ZnGeP_2$. However, these boules must be annealed at 700°C for at least 2 days to ensure uniform distribution of the arsenic. Powder diffraction patterns of ground single crystals were obtained with a Norelco diffractometer using monochromatic radiation from a high-intensity copper source (λ-$CuK\alpha_1$ = 1.5405 Å). Cell parameters were determined from slow-scan ($\frac{1}{4}$°/min) diffraction patterns over the range $12° < 2\theta < 72°$. The reflections were indexed on unit cells determined from studies of previous investigations (*12, 13*) and the precise lattice parameters were obtained using a least-squares refinement from these reflections.

Optical and Electrical Measurements

Optical measurements on polished single-crystal slices were performed at room temperature on a Perkin–Elmer 580 single-beam scanning infrared spectrophotometer. The measurements were performed in the transmission mode over the range 2.5–25 μm. Transmission through the sample was normalized to the signal obtained in the absence of sample.

Transmission in the vicinity of the optical band edge was measured with an Oriel Model 1724 monochromater, an Oriel G 772-5400 long-pass filter, and a calibrated silicon diode detector. Optical band gaps were determined from the responses with and without the crystal in the beam.

High-temperature infrared spectra were measured in a high-temperature cell with a Nicolet Model 605X Fourier transform spectrometer having a resolution of four wave numbers.

The van der Pauw (*14*) method was used to measure electrical resistivities and Hall voltages from 77 to 400 K. Contacts were made by the ultrasonic soldering of indium directly onto the samples, and ohmic behavior was established by measuring the current–voltage characteristics. The activation energy of resistivity E_a (defined for semiconductors by $\rho = \rho_0 \exp(E_a/kT)$, where ρ = resistivity, ρ_0 is a constant, T = temperature (K), and k = the Boltzmann constant, was determined by measuring ρ as a function of T.

Results and Discussion

For $ZnSiP_2$, the best crystals were obtained by chemical vapor transport. The relatively high melting point reported (*2*) for $ZnSiP_2$ precluded growing the crystals from the melt in silica tubes. However, pure $ZnGeP_2$ crystals were obtained by Bridgman growth from the melt and these crystals were grown crack-free when the wall of the graphite crucible was thinned sufficiently so as to allow cracking of the crucible on expansion of the product as the melt solidified.

X-ray diffraction analysis confirmed the cell parameters (see Table I) for $ZnSiP_2$ and $ZnGeP_2$ previously reported (*12, 13*). Microhardness measurements (Knoop indenter) were made on $ZnSiP_2$ and $ZnGeP_2$ single crystals with a Kentron microhardness tester. The results using a diamond indenter with a 100-g load gave values of 770 (100) kg/mm^2 for chemical vapor transport grown $ZnSiP_2$. Crystals obtained from a zinc flux gave a much lower value. For both chemical vapor transport and melt-grown crystals of $ZnGeP_2$, the Knoop hardness values were 620 (100) kg/mm^2. The higher value for the relatively pure $ZnSiP_2$ sample is consistent with the tighter bonding present in the silicon chalcopyrite.

The properties for the arsenic-substituted phases $ZnGeP_{1.8}As_{0.2}$ and $ZnGeP_{1.6}As_{0.4}$ are also given in Table I. The principal effects of substitution are on the microhardness and the decrease in resistivity. The properties obtained for crystals of this composition grown by chemical vapor transport

TABLE I

PROPERTIES OF $ZnSiP_2$, $ZnGeP_2$, $ZnGeP_{1.8}As_{0.2}$, AND $ZnGeP_{1.6}As_{0.4}$

Compound	Cell parameter		ρ(R.T.)	E_a	E_g	Hardness[a]
	a	c	(Ω-cm)	(eV)	(eV)	(kg/mm²)
$ZnSiP_2$ (Zn Flux)	5.401(2)	10.443(2)	2.7×10^5	0.26(5)	2.00(2)	640(100)
$ZnSiP_2$ (c.v.t.)	5.401(2)	10.443(2)	1.8×10^6	0.33(5)	2.00(2)	770(100)
$ZnGeP_2$ (c.v.t.)	5.473(2)	10.717(2)	6.9×10^5	0.11(5)[b] 0.58(5)[c]	1.80(2)	620(100)
$ZnGeP_2$ (melt)	5.469(2)	10.718(2)	3.6×10^6	0.58(5)	1.80(2)	620(100)
$ZnGeP_{1.8}As_{0.2}$ (c.v.t.)	5.486(2)	10.753(2)				
$ZnGeP_{1.8}As_{0.2}$ (melt)	5.480(2)	10.742(2)	2.5×10^6	0.51(5)	1.78(2)	510(100)
$ZnGeP_{1.6}As_{0.4}$ (c.v.t.)	5.498(2)	10.775(2)				
$ZnGeP_{1.6}As_{0.4}$ (melt)	5.492(2)	10.772(2)	1.0×10^6	0.50(5)	1.76(2)	490(100)

[a] Knoop indenter at 100 g.
[b] $T < 220$ K.
[c] $T > 220$ K.

were essentially the same as those for melt-grown samples.

The stability of $ZnSiP_2$, $ZnGeP_2$, and $ZnGeP_{1.8}As_{0.2}$ toward oxidation was determined by heating these compounds in a flowing oxygen stream (65 cm³/min) and by determining the change in weight during the heating period. The results are shown in Fig. 1 and indicate that $ZnGeP_2$ is stable up to 740°C. The $ZnSiP_2$ sample also begins to oxidize at approximately 740°C but the rate of its oxidation is much slower than that of $ZnGeP_2$. It can be noted from Fig. 1 that the substitution of 10 mole% of arsenic for phosphorus lowers the decomposition temperature considerably.

The infrared spectral response for $ZnSiP_2$ and $ZnGeP_2$ is given in Fig. 2. There are marked absorption bands for $ZnSiP_2$ at approximately 10 and 11.5 μm and for $ZnGeP_2$ at 13 μm. It has been reported by Isomura and Masumoto (*15*) and Alekperova *et al.* (*16*) that these absorption bands are due to lattice vibrations. In order to demonstrate

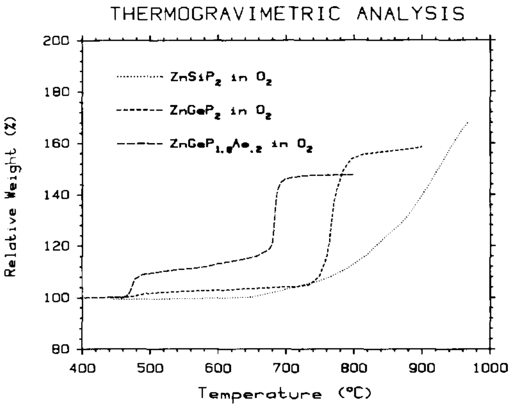

FIG. 1. Relative weight of ground crystals of $ZnSiP_2$, $ZnGeP_2$, and $ZnGeP_{1.8}As_{0.2}$ as a function of increasing temperature in flowing oxygen.

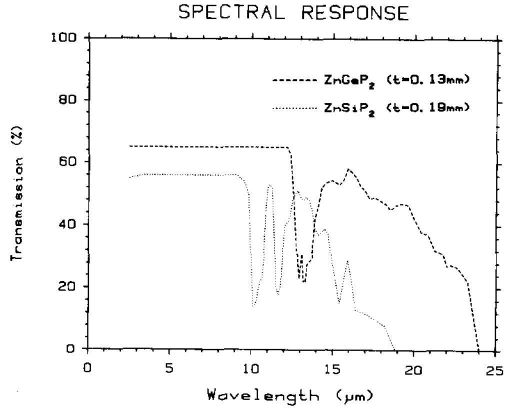

FIG. 2. Percentage of incident radiation transmitted through polished crystals of $ZnGeP_2$ and $ZnSiP_2$.

that these bands were not caused by P–O bonds, $ZnGeP_2$ samples were heated in a flowing oxygen stream at 300°C for 2 hr. The spectrum of the treated samples was exactly the same as the untreated crystals. The indirect optical band gaps for $ZnSiP_2$ and $ZnGeP_2$ were obtained from plots of $(\alpha h \nu)^{1/2}$ vs energy. The values of these gaps were 2.0 and 1.8 eV, respectively. Figure 3 shows a comparison of the spectral response for pure $ZnGeP_2$ taken at room temperature and 400°C. It can be seen that there is very little change in the position

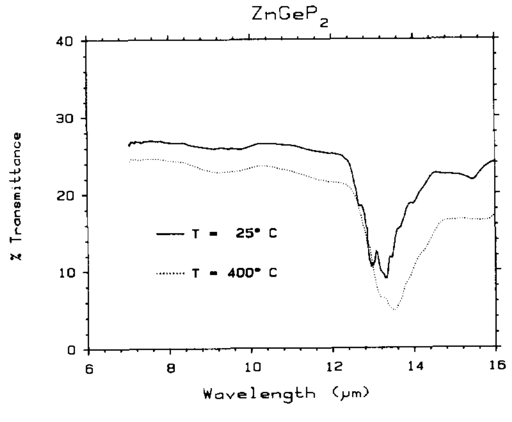

FIG. 3. Transmittance of a polished slice of $ZnGeP_2$ at room temperature and at 400°C.

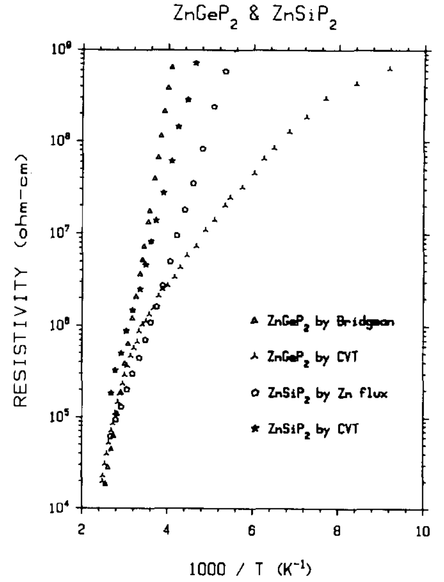

FIG. 4. Resistivity as a function of temperature for crystals of $ZnGeP_2$ and $ZnSiP_2$ grown by various techniques.

and shape of the absorption band as the temperature is increased.

A comparison of the infrared spectra of pure $ZnGeP_2$ and $ZnGeP_{1.8}As_{0.2}$ indicates no appreciable shift in the absorption band. In addition a weak second band appears at 9.8 μm in the transmission spectra of the 20% arsenic-substituted sample. The invariance of the principal absorption band at 13 μm for these compositions suggests that it depends primarily upon vibrations of the cations. For these reasons samples containing higher arsenic substitution were not attempted.

The activation energy of $ZnSiP_2$ single crystals was obtained from log ρ vs $10^3/T$ plots (Fig. 4). Within the reported experimental error, there is little difference in the results obtained from crystals grown from a zinc flux or by chemical vapor transport. For $ZnGeP_2$ (Fig. 4) the melt-grown crystals showed an activation energy of $\sim$ 0.6 eV, which is consistent with the observed optical band gap of $\sim$1.8 eV. The observed activation energy for $ZnSiP_2$ (~0.3 eV) suggests that the material behaves as an extrinsic semiconductor. The substitution of arsenic for phosphorus in $ZnGeP_2$ did not significantly affect the variation of resistance with temperature. In addition, the high values of the resistivity prevented measurement of the Hall effect.

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