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PREPARATION AND CHARACTERIZATION OF ZNSIP2 AND ZNGEP2
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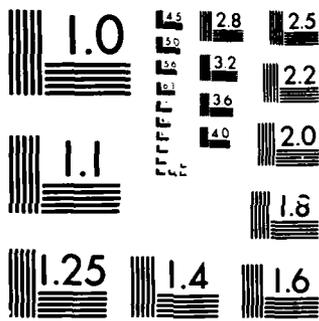
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Preparation and Characterization of
ZnSiP₂ and ZnGeP₂ Single Crystals

by

Guang-Qing Yao, He-Sheng Shen, Robert Kershaw, Kirby Dwight and Aaron Wold

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ABSTRACT

Single crystals of ZnSiP₂ and ZnGeP₂ have been grown by several techniques and their electronic and optical properties were compared. It was found that Fe(III) could not be substituted for equal amounts of Zn(II) and Ge(IV) in the II-IV-V₂ chalcopyrites. However, 0.5 atomic percent of Mn(II) was successfully substituted in the structure for Zn(II).

MATERIALS INDEX: Stable, Infrared, Transmitting, Chalcopyrite

Introduction

The ternary compounds ZnSiP₂ and ZnGeP₂ are semiconductors which crystallize with the chalcopyrite structure (space group I $\bar{4}$ 2d). ZnSiP₂ has been reported to melt at 1250°C (1) and single crystals were obtained from a molten zinc or tin flux (1, 2) as well as by chemical vapor transport (2-5) using Cl₂, CCl₄, ZnCl₂ or I₂ as the transport agent. There has been no report of crystal growth from the melt.

Single crystals of ZnGeP₂ have been grown from the melt (3, 5-7) or from molten metal fluxes (2, 3, 8-10). ZnGeP₂ has also been grown by chemical vapor transport using excess phosphorus as the transport agent (7). These materials show low absorption in the wave length range from their optical band gap to the IR absorption band (12 μ m for ZnGeP₂).

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. There have been reports concerning the substitution of Fe(II) and Mn(II) into I-III-VI₂ semiconductors with the chalcopyrite structure (11-14). However, there has been no study concerning the extent of substitution of Fe(III) or Mn(II) into the II-IV-V₂ chalcopyrites. The extent of such substitutions and their effect on both the observed optical and electronic properties is included in this study of these chalcopyrites.

Experimental

ZnSiP₂ Single Crystals

(1) Growth from a Zinc Flux

Single crystals of ZnSiP₂ were grown from a zinc flux. The zinc metal (Gallard and Schlesinger 99.9995) was prereduced in a Ar/H₂ (85/15) atmosphere at 200°C for 3 hours. 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 grams were placed in a silica tube which was then evacuated to 3 microns, sealed, and heated in a furnace at 20°C/hr to 1000°C. After a soaking period of 24 hours 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 (2M) hydrochloric acid. The crystals were red and the maximum size was 8 x 2 x 1 mm³.

(2) Growth by Chemical Vapor Transport

Single crystals of ZnSiP₂ 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 2μm Hg and 100 torr of Cl₂ 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 hours 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 hours, 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 x 3 x 3 mm³ were obtained.

ZnGeP₂ Single Crystals

(1) Growth by Chemical Vapor Transport

Single crystals of ZnGeP₂ 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 ZnSiP₂. However, a temperature gradient of 980-950°C was used. Polyhedral crystals 8 x 5 x 3 mm³ were obtained.

(2) Growth from the Melt

ZnGeP₂ boules were grown by a modified Bridgman method. The charge which contained 2 g of reactants and 2% excess phosphorous 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 hours, then 800°C for 24 hours, and finally 900°C for 24 hours. 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 hours. 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 one week. The size of the boule was 2.5 cm x .7 cm. A 1 mm slice was removed and discarded from both the top and bottom of each boule.

(3) Doped ZnGeP₂ Single Crystals

Iron and manganese were introduced into the chemical vapor transport tubes in an attempt to substitute Zn(II) by Mn(II) or Zn(II) and Ge(IV) by Fe(III). The conditions for crystal growth were maintained the same as for pure ZnGeP₂. Powder diffraction patterns of ground single crystals were obtained with a Norelco diffractometer using monochromatic radiation from a high-intensity copper source (λ -CuK α_1 = 1.5405Å). Cell parameters were determined from slow-scan (1/4°/min) diffraction patterns over the range 12° < 2 θ < 72°. The reflections were indexed on unit cells determined from studies of previous investigations (15, 16) and the precise lattice parameters were obtained using a least-squares refinement from these reflections.

Magnetic, Optical and Electrical Measurements

Magnetic measurements were performed using the Faraday balance previously described by Morris and Wold (17). The magnetic susceptibilities were measured as a function of temperature from 77 to 300 K at a field strength of 10.3 kOe.

Optical measurements on polished single-crystal slices were performed at room temperature on a Perkins-Elmer 580 single-beam scanning Infrared Spectrophotometer. The measurements were performed in the transmission mode over the range 2.5 μ m - 25 μ m. Transmission through the sample was normalized to the signal obtained in the absence of sample.

Measurement of the absorption coefficient was made with an Oriel Model 1724 monochromator, an Oriel G 772-5400 long pass filter, and a calibrated silicon diode detector. Absorption values were calculated from the responses with and without the crystal in the beam.

The van der Pauw (18) method was used to measure electrical resistivities and Hall voltages from 77K to 400K. 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 $\rho = \rho_0 e^{(E_a/kT)}$, 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 ZnSiP₂, best crystals were obtained by chemical vapor transport. The relatively high melting point reported (1) for ZnSiP₂ precluded growing the crystals from the melt in silica tubes. However, pure ZnGeP₂ 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. Manganese-doped ZnGeP₂ crystals were obtained from chemical vapor transport and these crystals grew more readily than the pure ZnGeP₂.

X-ray diffraction analysis confirmed the cell parameters (see Table 1) for ZnSiP_2 and ZnGeP_2 previously reported (15, 16). Microhardness measurements (Knoop Indenter) were made on both ZnSiP_2 and ZnGeP_2 single crystals with a Kentron Microhardness Tester. The results using a diamond indenter with a 100g load gave values of $770(100)\text{kg/mm}^2$ 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 $620(100)\text{kg/mm}^2$. The higher value for the relatively pure ZnSiP_2 sample is consistent with the tighter bonding present in the silicon chalcopyrite.

TABLE I
PROPERTIES OF ZnSiP_2 AND ZnGeP_2

Compound	Cell Parameters		ρ (R.T.) ($\Omega\text{-cm}$)	E_a (e.V.)	E_g (e.V.)	Hardness* kg/mm^2
	a	c				
ZnSiP_2 (Zn Flux)	5.401(1)	10.443(1)	2.7×10^5	0.26(5)	2.0(1)	640(100)
ZnSiP_2 (c.v.t.)	5.401(1)	10.443(1)	1.8×10^6	0.33(5)	2.0(1)	770(100)
ZnGeP_2 (c.v.t.)	5.473(1)	10.717(1)	6.9×10^5	0.11(L.T.) ^a 0.58(H.T.) ^b	1.8(1)	620(100)
ZnGeP_2 (Melt)	5.469(1)	10.718(1)	3.6×10^6	0.58	1.8(1)	620(100)

*Knoop indenter at 100 g

a) $T < 220\text{K}$

b) $T > 220\text{K}$

The stability of ZnSiP_2 and ZnGeP_2 towards oxidation was determined by heating these compounds in a flowing oxygen stream (65cc/min) and 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 .

The infrared spectral response for both compounds 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 (19) and Alekperova et al. (20), that these absorption bands are due to lattice vibrations. In order to demonstrate that these bands were not caused by P-O

THERMOGRAVIMETRIC ANALYSIS

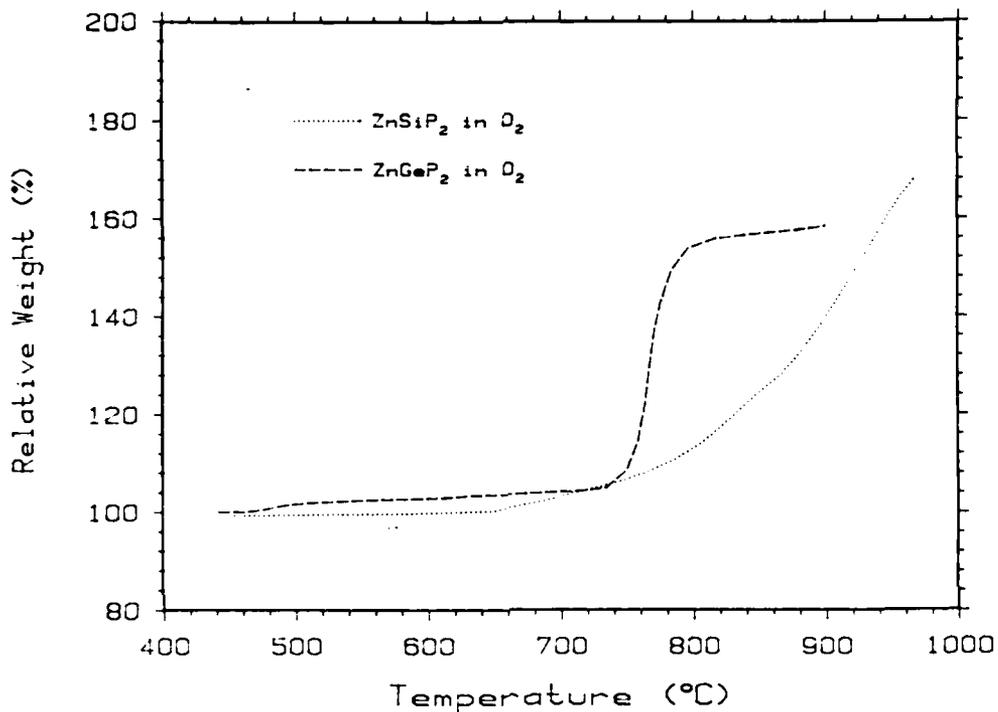


FIG. 1
Relative weight of ground crystals of ZnGeP₂ and ZnSiP₂ as a function of increasing temperature in flowing oxygen.

bonds, ZnGeP₂ samples were heated in a flowing oxygen stream at 300°C for 2 hours. The spectrum of the treated samples was exactly the same as the untreated crystals. The indirect optical band gaps for ZnSiP₂ and ZnGeP₂ were obtained from plots of $(\alpha h\nu)^{1/2}$ vs energy. The values of these gaps were 2.0 and 1.8eV, respectively.

The activation energy of ZnSiP₂ single crystals was obtained from log vs $10^3/T$ plots (Fig. 3). Within the reported experimental error, there is little difference in the results obtained from crystals grown from a zinc flux or by

SPECTRAL RESPONSE

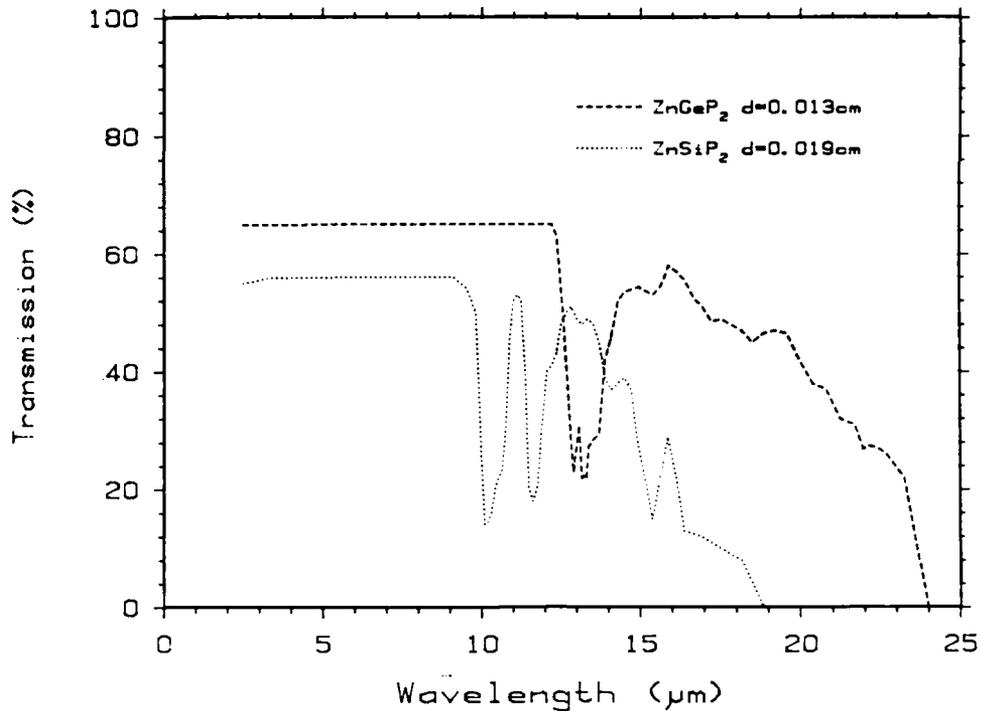


FIG. 2
Percent of incident radiation transmitted through polished crystals
of ZnGeP₂ and ZnSiP₂

chemical vapor transport. For ZnGeP₂ (Fig. 3) the melt-grown crystals showed an activation energy of ~ 0.6 eV which is consistent with the observed optical band gap of ~ 1.8 eV. The observed activation energy for ZnSiP₂ (~ 0.3 eV) suggests that the material behaves as an extrinsic semiconductor. Attempts to substitute Fe(III) for equal amounts of Zn(II) and Ge(IV) were unsuccessful. Under various conditions of crystal growth by chemical vapor transport, only crystals of ZnGeP₂ free of iron were obtained.

However, crystals of ZnGeP₂ grown by chemical vapor transport, in which Mn(II) is substituted for Zn(II) resulted in much larger, better formed crystals than those grown without manganese. When a nominal charge composition of Zn_{0.9}Mn_{0.1}GeP₂ is used, crystals were obtained containing 0.5 atomic percent of manganese. The concentration of manganese was established from both susceptibility measurements and chemical analysis by atomic absorption. At this concentration of Mn manganese, no change was observed in the optical spectrum or the electrical activation energy.

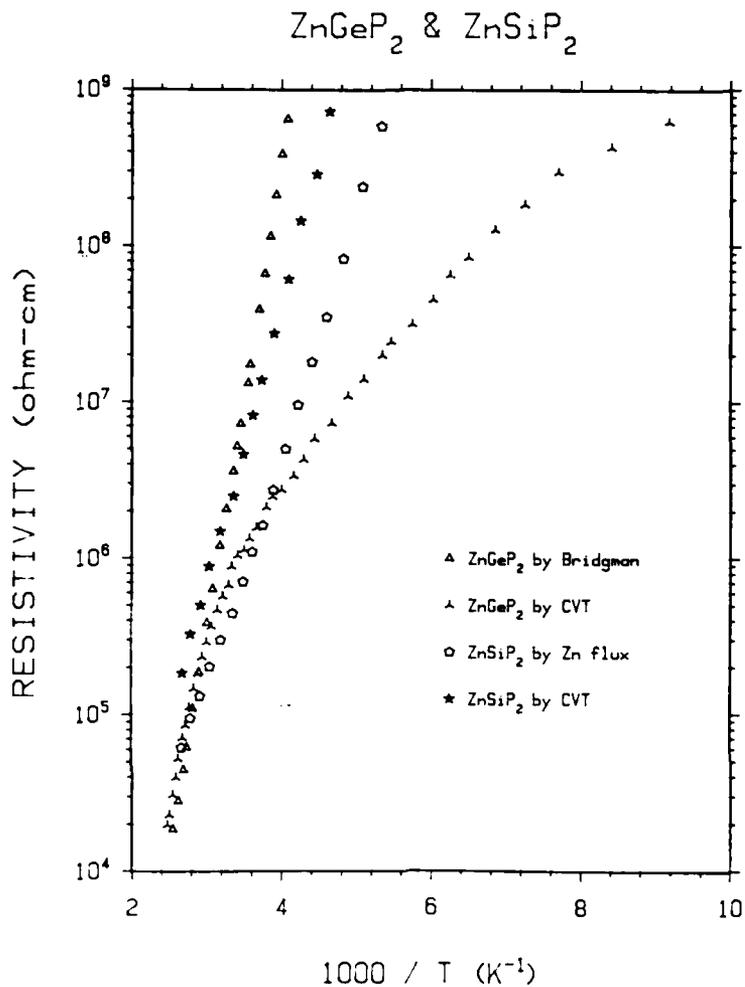


FIG. 3
Resistivity as a function of increasing temperature for crystals of ZnGeP_2 and ZnSiP_2 grown by various techniques

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