

Temperature Dependence of the Optical Properties of ZnGeP₂ Semiconductor Compound

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ABSTRACT. The temperature dependence of the optical properties was investigated for the chalcopyrite ternary semiconducting compound ZnGeP₂. The energy gaps were found to be pseudodirect allowed transitions with gaps of 1.87 eV and 1.94 eV for the two investigated samples. The temperature coefficient of the energy gap was also determined in the temperature range (300-400) K and are found to be -5.18×10^{-4} eV/K and -4.99×10^{-4} eV/K for the above mentioned samples.

The ternary semiconductor compounds II-IV-V₂ (ABC₂) which crystalize in the chalcopyrite structure and with a point group 42m are closest isoelectronics and their structures analogous to III-V zincblend compounds (Shay and Wernick 1975). These compounds are covalently bonded with a tetragonal coordinate sp³ hybrid bonds, although some ionic character is present which is due to the two different bonds A-C and B-C. The tetragonal unitcell is compressed along the tetragonal axis, and the anions are displaced from their ideal tetrahedral positions (Cordts *et al.* 1979). The ionic bond component tends to increase the forbidden energy gap and to raise the melting point. This makes the material thermally more stable but too difficult to prepare (Mughal 1971).

The compound ZnGeP₂ belongs to the group II-IV-V₂. Its energy gap, at room temperature is (1.99-2.0) eV (Shay *et al.* 1973) which is termed as a pseudodirect gap relative to that of the indirect gap of its binary analog GaP (Zakharov and Chaldysher 1986). In this work the results of an investigation of the fundamental optical absorption edge of single crystals of this compound are presented.

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Experimental Technique

The ZnGeP₂ crystals have been prepared by Pb solution growth. The optical samples were prepared by polishing the crystals into thin plates up to 2.5 μm. The sample thickness was measured by the optical interference method (Omar 1993).

The tungsten filament lamp powered by a stabilized power supply was placed at the monochromator entrance slit. This monochromator (type MP-1018B) covers the fundamental absorption edge and is automatically scanned with various speeds as required. The output monochromatic light was focussed onto the sample surface and the transmitted portion was detected by a Bausch and Lomb spectrophotometer. This system consists of a sensitive detector with a chopper, an amplifier and a lock-in amplifier after bypassing its own monochromator. The output signal was applied to an XT⁻ chart recorder (Lambros *et al.* 1974 and Goodchild *et al.* 1982).

The optical measurements were made at several temperatures ranging from 290 to 400 K. The samples were mounted between two thin plates (sample holder) which were fitted into a beam path. The temperature is controlled with a heater made from insulated Cu wire wound around the sample. A copper constantan thermocouple was used to measure the sample temperature. One thermocouple junction is fixed on the sample surface while the other was kept in ice. The sample, the heater and the thermocouple were enclosed by two copper plates with a small hole which allows the beam to pass through the sample. The block diagram of the setup is shown in Fig. 1.

Theory of Optical Absorption

Measurements are often given in terms of the absorption coefficient α , reflectivity R and complex refractive index, where α gives the power attenuation per unit length of path in the specimen (Lark - Horowitz and Johnson 1959), it describes the fractional decrease in intensity with distance which determines the attenuation of the amplitude of the electromagnetic wave in the medium (Wolf 1976). It is related directly to the absorption index (extinction coefficient) k which is the imaginary part of the complex refractive index given by (Lark - Horowitz and Johnson 1959).

$$\alpha = (4\pi k / \lambda) \dots\dots\dots (1)$$

For normal incidence of monochromatic radiation, the ratio of the transmitted to the incident portion for a uniform sample thickness is given by (Lark - Horowitz and Johnson 1959).

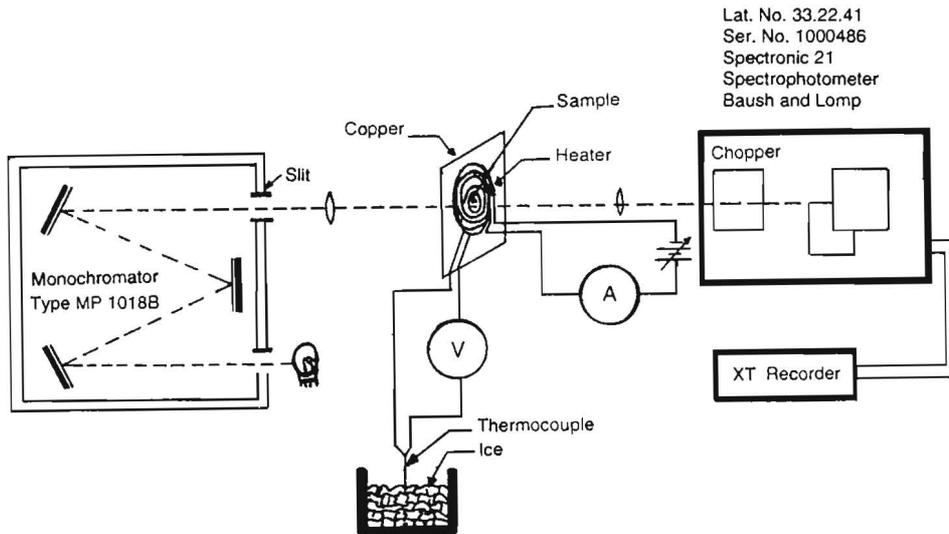


Fig. 1. Block diagram of the experimental setup.

$$T = (I/I_0) = \frac{(1-R)^2 \exp(-\alpha d)}{1-R^2 \exp(-2\alpha d)} \dots\dots\dots (2)$$

where $R = 0.2605$ (Babonas *et al.* 1986) and is assumed to be constant with respect to the wavelength (Madelon *et al.* 1986). However, at room temperature its value for the compound $ZnGeP_2$ does not change by more than 2% within the energy range of the absorption edge. Therefore, it may be considered constant and can be evaluated from the refractive index (Kou. and Seehra 1978). The value of $R^2 \exp(-2\alpha d)$ is much less than unity for all cases, thus Eq. 2 reduces to:

$$T = (1-R)^2 \exp(-\alpha d) \dots\dots\dots (3)$$

The absorption coefficient (α) can also be obtained by reducing Eq. 3 further to $T = (I/I_0) = \exp(-\alpha d)$ by neglecting R from the surface of the sample (Zakharov *et al.* 1986).

The absorption spectrum of a semiconductor can be divided into two regions: $E < BE$ and $E \geq BE$, where BE is the band edge energy, with the absorption wavelength is directly transformed to energy relation:

$$E(\text{eV}) = \frac{1240.6}{\lambda(\text{nm})} \dots\dots\dots (4)$$

The first part of the absorption spectrum is due to free carriers, lattice, impurities and defects, in which the low energy tail (Urbach tail) exhibits an exponential spectrum dependence given by (Sandersheshu and Kendelewicz 1982, Street *et al.* 1974, Omar 1975).

$$\alpha = \alpha_0 \exp [\delta(h\nu - E_g)/kT] \dots\dots\dots (5)$$

Hence the presence of the delta function δ indicates that the absorption will exhibit the characteristic features of the density of spin wavelstates.

The second area of the optical absorption spectrum in the band gap region of many semiconductors consists of two overlapping parts. The photon energy $h\nu \approx E_g$ which is related to the fundamental absorption edge of semiconductor corresponds to the threshold energy of electronic transitions from the highest nearly filled state of the valence band (VB) to the lowest nearly empty state of the conduction band (CB). This corresponds to a rapid rise of α with increasing photon energy. This last region is due to carriers being raised from the VB to the CB band in which the absorption follows the power law:

$$(\alpha h\nu) = A (h\nu - E_g)^n \dots\dots\dots (6)$$

where E_g is the optical band gap energy and A is a constant characteristic of the properties of the bands (Goodchild *et al.* 1982 and Omar 1975), n is a number which characterizes the transition process and is equal to $1/2$ for direct allowed transitions. This occurs when the minimum energy of two states related to different bands have to the same k . n is equal to $3/2$ for forbidden transitions with different k -values, while it is equal to 2 and 3 for indirect allowed and forbidden transitions, respectively (Callaway 1974).

Results

Optical absorption measurements were made for two single crystal samples (S1, S2) of ZnGeP_2 with thicknesses of 0.028 and 0.088 cm. respectively. The log of the absorption coefficient α varies linearly with the log of the incident photon energy $h\nu$ according to Eq. 6. The slopes of the plots of Figs. 2a, 2b, 3a and 3b yield $n = 1/2$,

a result indicating that the transition process in this compound is a direct allowed transition. E_g could also be estimated from this equation by plotting $(\alpha h\nu)^{1/n}$ against $h\nu$, the intercept of the straight line with the $h\nu$ axis gives the value of E_g for S1 and S2 as shown in Figs. 2a, 2b, and 3b in the temperature range 290-394 K for the two samples (Goodchild *et al.* 1982).

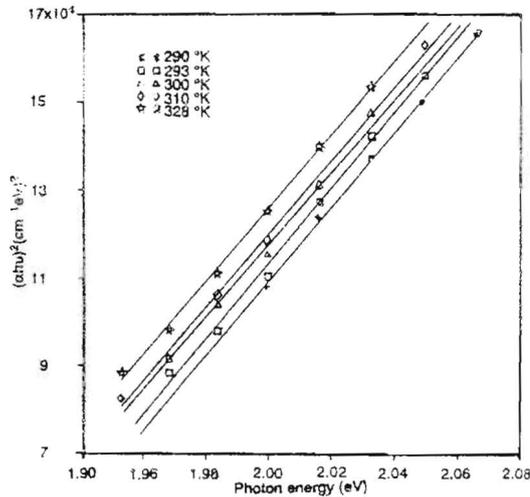


Fig. 2a. $(\alpha h\nu)^2$ plotted vs $h\nu$ for S1.

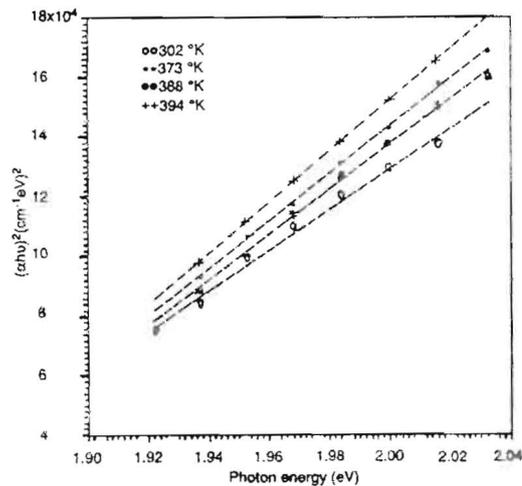


Fig. 2b. $(\alpha h\nu)^2$ plotted vs $h\nu$ for S2 at a higher temperature range.

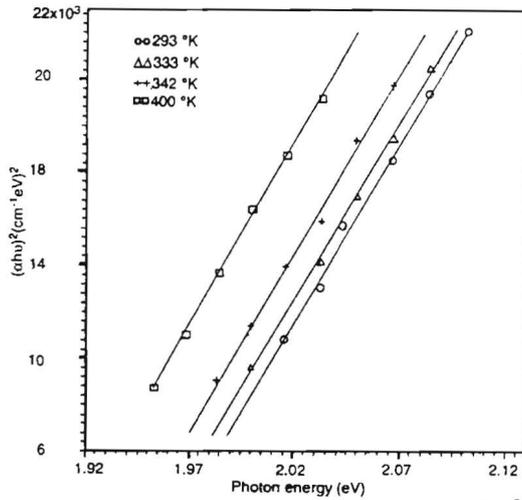


Fig. 3a. $(\alpha h\nu)^2$ plotted vs $h\nu$ for S2.

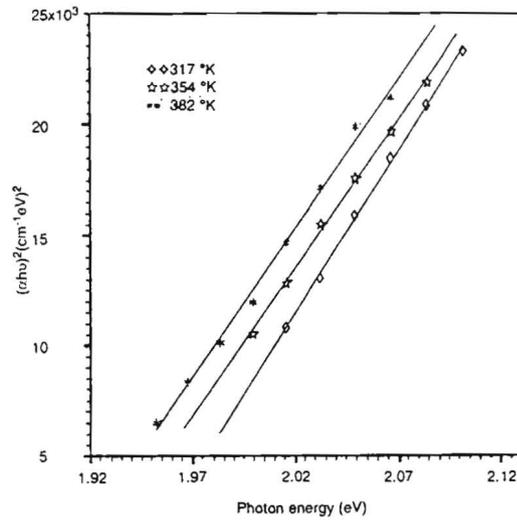


Fig. 3b. $(\alpha h\nu)^2$ plotted vs $h\nu$ for S2.

The experimental result for S1 at room temperature can, for allowed indirect transitions, be compared with the theoretical value obtained from the relation. (Smith 1979):

$$\alpha = \alpha_0 (h\nu - E_g)^{1/2} \dots\dots\dots (7)$$

$$\alpha_0 = \frac{e^2(2m_r)^2 f}{n^* ch^2 m \epsilon_0} \dots\dots\dots (8)$$

where f is the oscillator strength of the transition and is considered unity. The slope α^2 of this plot is about $1.7 \times 10^5 \text{ cm}^{-2} \text{ eV}^{-1}$, while the calculated value of α^2 is $9 \times 10^8 \text{ cm}^{-2} \text{ eV}^{-1}$, refractive index $n = 3.085$ (Babonas *et al.* 1986), m_0 , m_r are free and reduced electron masses, c is the speed of light, $\epsilon_0 = 8.854 \times 10^{-12} \text{ C}^2 \text{ N}^{-1} \text{ m}^{-2}$ (Shionoya and Ebina 1964). The plot of the square of the absorption coefficient versus photon energy is shown in Fig. 4.

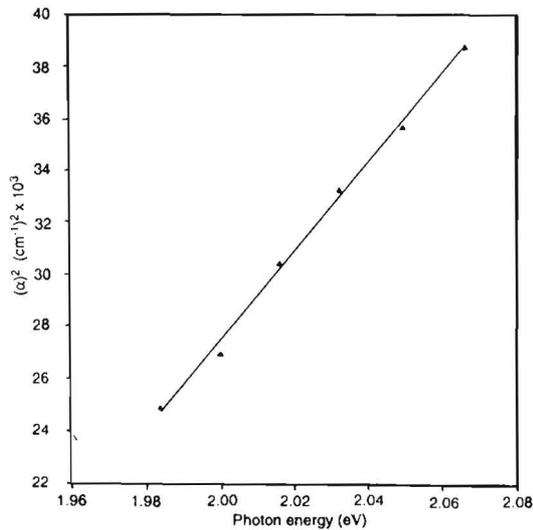


Fig. 4. α^2 plotted vs Photon energy for S1.

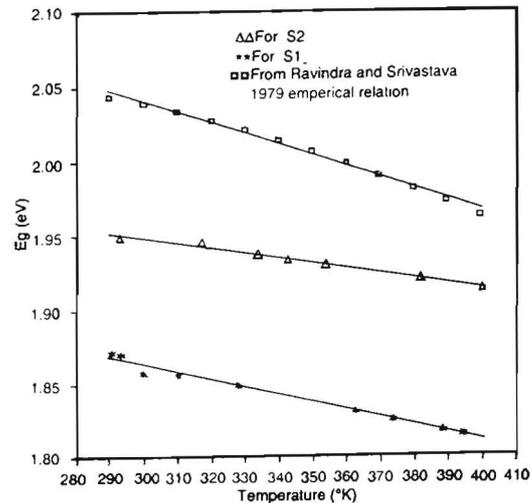


Fig. 5. Temperature dependence of E_g for S1 and S2.

The optical data gives the value of energy gap E_g to be 1.87 eV and 1.94 eV at room temperature for S1 and S2, respectively. The temperature dependence of E_g for the two samples is shown in Fig. 5, this dependence can be expressed through the linear relation:

$$E_g = E_{g_0} - bT \quad \dots\dots\dots (9)$$

where E_{g_0} is an energy gap extrapolated to 0K, T is the absolute temperature, b is an empirical constant evaluated near 300 K and was found equal to -5.18×10^{-4} and -4.99×10^{-4} eV/K for S1 and S2, respectively, as shown in Fig. 5. However, these results are similar to those of other semiconductors (Bhar and Samanta 1980, Horig *et al.* 1979). The empirical relation proposed by (Ravindra and Srivastava 1979) was also used for $ZnGeP_2$, yielding results in good agreement with the experimental data obtained from Fig. 5. The relation could be rewritten as:

$$E_g(T) = E_g(0) - \frac{[(2.25 \times 10^{-5} \theta_D) - (4.275 \times 10^{-3})] T^2}{5(T + 5 \theta_D - 1135)} \quad \dots\dots\dots (10)$$

where $E_g(T)$ is the energy gap of the semiconductor at T K, $E_g(0)$ is the energy gap at 0K and θ_D is the Debye temperature which is 420K for $ZnGeP_2$ (Ravindra and Srivastava 1979, Wasim 1979).

Discussion

The linearized absorption curves in Figs. 2 and 3 for the two samples of the compound $ZnGeP_2$ obtained through Eq. 6 suggest direct interband transition (Kou and Seehra 1978). Direct transitions in the chalcopyrite structure semiconductors correspond to the indirect transitions in the zincblend structures. This transition, however, appears to be pseudodirect since its strength is lower than those of direct transitions. Moreover, its transition energy is still lower than the lowest energies of direct transitions. Evidence for a pseudodirect gap in $ZnGeP_2$ stems from the strength of interaction estimated from the slope of the absorption edge. This slope is characterized by the parameter S [$S = \Delta \ln \alpha / \Delta h\nu$] whose value usually lies within 6 to 9 eV⁻¹. As it is obvious from Fig. 6, the value of S for the semiconductor $ZnGeP_2$ was found equal to 6.01 eV⁻¹ (Zakharov and Chaldysher 1986).

It is generally observed in semiconductors that the absorption rises rapidly as the photon energy is increased through the gap energy which is only true for pure semiconductors. For impure semiconductors, the mobile charge carriers in a band absorb energy from a light wave and thus prevent the band-to-band absorption at energies below the absorption edge. The latter increases the value of α due to possible scattering by free carriers or impurities. The contributions to α can take the form of $\alpha = \alpha_0 (h\nu)^{-n}$. However, the scattering effect increases as the photon energy is decreased, and this can be observed at energies below the absorption edge (Goodchild *et al.* 1982 and Keyes 1977)

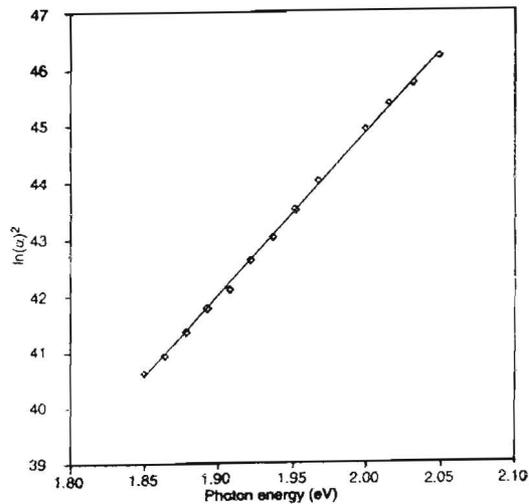


Fig. 6. $\ln(\alpha)^2$ plotted against $h\nu$ for S1.

The position and the shape of the absorption edge are sensitive to impurity content of the semiconductor sample. The absorption slope increases with the extent of doping where heavy doping leads to an effective shrinkage of the energy (Bankove 1971, Shaw and Watson 1978, Dixon and Ellis 1961). The higher value of E_g for S2 indicates a lower impurity or carrier concentration than those of S1. Accordingly the change in E_g can be given by the following relation (Moss 1954).

$$\Delta E_g = \frac{h^2}{8m} (3n/\pi)^{2/3} \dots\dots\dots (11)$$

where n is the carrier concentration. However, Shaw and Watson in 1978 obtained the same result for other semiconductors such as CdTe. Also the effect of rising temperature is manifested by a parallel displacement of the absorption edge to lower energy (Bankove 1971, Shaw and Watson 1978, Dixon and Ellis 1961). Generally, it is observed in semiconductors that the forbidden band width decreases linearly as the temperature increases. This is manifested by two mechanisms; the lattice thermal expansion decreases the separation between the valence and the conduction band and this constitutes a minor effect. The major effect is related to some changes in the interaction between the electron and the lattice vibration which causes some broadening of the electron energy levels (Bardeen and Shockly 1950, Radkowsky 1948, Fan 1950).

Conclusions

1. The energy gap for ZrGeP_2 is found to be quite sensitive to temperature in the range 300-400K. This is similar to that of the ZnSiP_2 .
2. Different samples exhibit varying changes in their estimated energy gaps due to differences in impurity levels.

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تأثير درجة الحرارة على الخواص البصرية للمركب شبه الموصل الثلاثي $ZnGeP_2$

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تم بحث تأثير درجة الحرارة على الخواص البصرية للمركب شبه الموصل الثلاثي $ZnGeP_2$ وتبين أن فجوة الطاقة للنموذجين من هذا المركب 1.87 و 1.94 إلكترون فولت وتعود إلى إنتقال إلكتروني مباح شبه مباشر . كما وجد أن المعامل الحراري لفجوة الطاقة للنموذجين في المدى الحراري من 300K إلى 400K يساوي 4.99×10^{-4} و 5.18×10^{-4} إلكترون فولت . وهذا يتفق مع النتائج المنشورة لأشباه الموصلات الأخرى كما اتفق أيضاً مع الصيغة التجريبية المقترحة ، إن شكل وموقع حافة الامتصاص حساس للتطعيم ، إذ أن التطعيم الشديد يؤدي إلى إنخفاض فاعل في طاقة الفجوة . إن الاختلاف في قيم E_g للعينتين S1, S2 يعود إلى أن تركيز النواقل أو التطعيم فيها أقل من S1 . كما يؤدي ارتفاع درجة الحرارة إلى إزاحة حافة الامتصاص نحو طاقة أقل ويقل عرض الشريط المحظور خطياً مع ارتفاع درجة الحرارة .

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