

PRESSURE DEPENDENCE OF OPTICAL BAND GAP ZnSe SINGLE CRYSTALS GROWN BY CHEMICAL VAPOUR TRANSPORT TECHNIQUE

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We report here the growth and measurement of pressure dependent optical absorption in ZnSe single crystals in the range of 200 nm to 800 nm. Single crystals of ZnSe were grown by chemical vapour transport technique using iodine as a transporting agent. Stoichiometric proportion of constituent elements was confirmed by EDAX. Zinc blende crystal structure of grown crystals is identified by powder XRD. Optical absorption measurements were performed on ZnSe crystal at different pressures up to 10.25 GPa using diamond anvil cell and obtained results are discussed.

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1. Introduction

ZnSe is a wide band gap (2.6 eV) II-VI compound having zincblende structure at ambient condition. This material forever remained of considerable interest due to its optical and optoelectronic properties [1-6] and several researchers reported various techniques for the growth of high quality single crystals of ZnSe [7-12]. It has also remained as a material of intense interest due to its pressure dependent optical and electrical properties as well as due to a phase transition occurring from wurtzite (WZ) or zincblende (ZB) to rocksalt (RS) at high pressure [13-20]. A high pressure transition was first reported by Samara and Drickamer at 16.5 GPa [13]. They predict the transition by high pressure resistance measurements. After that resistivity and Raman measurements using the modern ruby pressure scale have located the same transition at 13 GPa [14, 15] and 13.5 GPa [16]. An EDXRD study proposed the existence of unstable cinnabar phase between zincblende and rocksalt at 10.4 GPa [17]. ZnSe is widely studied by both experimental techniques and theoretical modelling for its pressure dependent optical, electrical and mechanical properties however the effect of pressure on the optical properties of zincblende ZnSe is not reported [18-24]. We report here the work carried out for the growth of zincblende structured ZnSe single crystals by chemical vapour transport method and dependence of its optical band gap on high pressure up to 10.25 GPa.

2. Experimental

ZnSe crystals were grown by chemical vapor transport technique using iodine as a transporting agent in a manner similar to that proposed by H. Hartmann [12]. Stoichiometric mixture of constituent elements (Zn, purity: 99.99%, make: Fluka and Se, purity: 99.99%, make: Aldrich) were sealed in an evacuated (10^{-5} Torr) quartz ampoule and heated at 1000 °C for 72 hours for compound formation. The process results in the formation of yellowish orange coloured polycrystalline powder of ZnSe. Single crystals of ZnSe were grown from this polycrystalline powder by chemical vapour transport

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technique using iodine as a transporting agent. Growth parameters of this process are described in Table 1. Figure 1 shows grown crystals. Stoichiometric proportion of constituent elements in the grown crystals was confirmed using EDAX.

Table 1. Growth parameters for ZnSe single crystals

Growth condition	Temperature of Source Zone 1000 °C
	Temperature of Growth Zone 900 °C
Growth time	168 hours
Average dimensions of grown crystals	7 mm × 6 mm × 3 mm

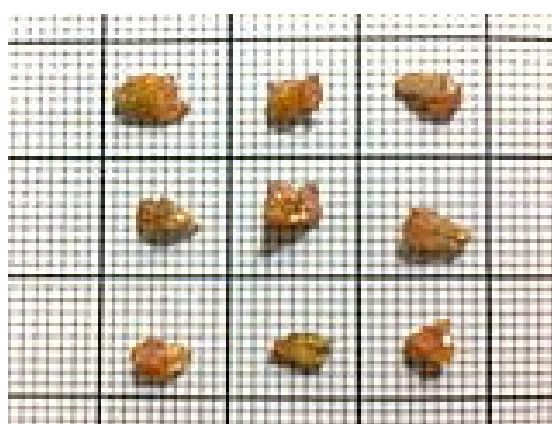


Figure 1. ZnSe single crystals grown by chemical vapour transport technique

Confirmation of crystal structure and determination of lattice parameters were done using powder XRD. The X-ray powder diffractogram was recorded with the help of Philips X-Ray diffractometer (Model: PW 1820) employing CuK α radiation. Average apparent crystallite size perpendicular to the reflecting plane has been calculated using Scherrer's formula

$$t = \frac{K\lambda}{\beta \cos \theta} \quad (1)$$

Where t is the crystallite size as measured perpendicular to the reflecting plane, K is the Scherrer constant whose value is taken to be unity assuming that the grains are of spherical shape, λ is the wavelength of X-ray radiation, β is the integral breadth of peak measured in radians and θ is the Bragg angle. Parameters calculated from X-ray diffraction data are tabulated in Table 2. Figure 3 shows indexed X-ray diffraction pattern on ZnSe crystals.

Optical absorption measurements in the range 200 nm to 800 nm on grown crystals were carried out at different pressure up to 10.25 GPa using a diamond anvil cell (DAC). Measurements were performed using a light from a quartz tungsten halogen lamp dispersed by a 0.32 m monochromator. A photomultiplier tube was used for measurement of light transmitted through sample. Figure 2 schematically shows the absorption apparatus adopted for measurement in 200 nm to 800 nm region. A Merrill-Bassett type

DAC with a culet and table diameter of $400\mu\text{m}$ and 4 mm respectively was used for pressure generation. Sample was cut in to a small chip of $\sim 100 \times 100 \times 5\ \mu\text{m}^3$ and mounted on a gasketed DAC.

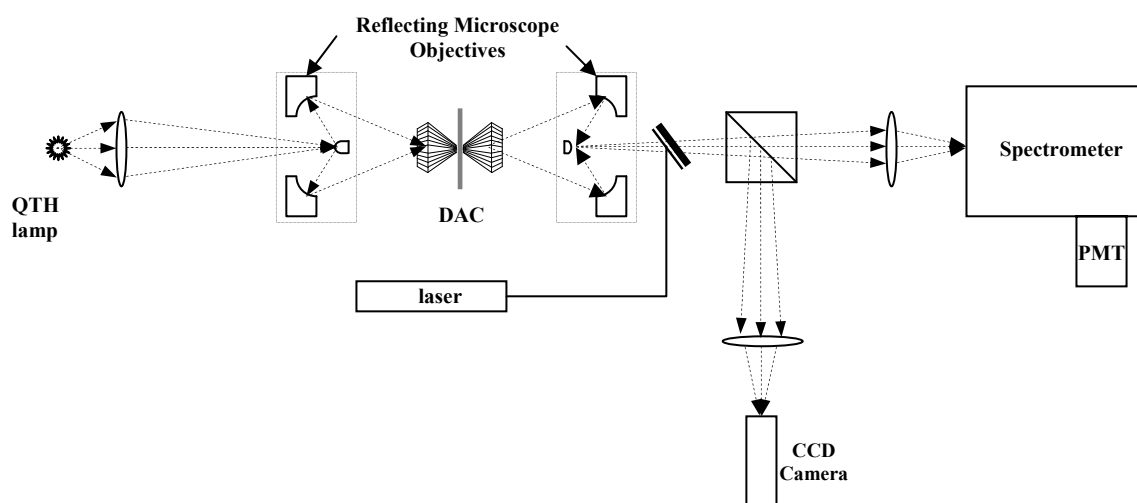


Figure 2. Schematic of experimental arrangement for optical absorption measurement under high pressure

T-301 stainless steel pre-indented to $100\ \mu\text{m}$ and drilled in the centre having $250\ \mu\text{m}$ diameter was used as a gasket. Fine NaCl powder was used as a pressure transmitting material. Applied pressure was determined by the standard method of monitoring the redshift of Ruby R_1 line.

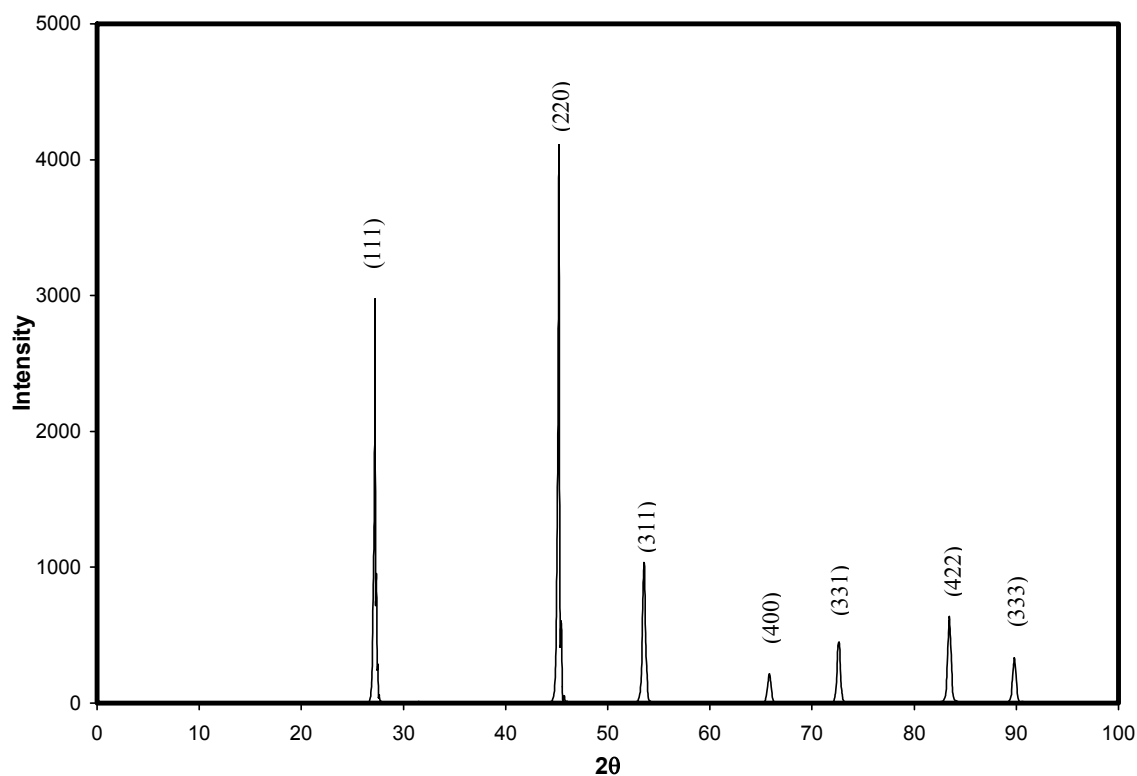


Figure 3. X-ray powder diffraction pattern of ZnSe

3. Results and Discussion

High quality single crystals of ZnSe could be grown by chemical vapour transport technique using iodine as a transporting agent. Peak behaviour of the X-ray diffractogram shown in figure 3 corroborates crystalline nature of ZnSe. Results obtained are in good agreement with JCPDS card no. 37-1463 [25] and all the peaks obtained in the diffractogram could be indexed to a zincblende crystal structure having lattice parameters shown in Table 2.

Table 2. Crystal parameters of ZnSe crystals obtained by powder XRD analysis

Parameters	JCPDS data Card no. 37-1463	Present Work
Crystal Structure	Zinc blende	Zinc blende
Space Group	$F\bar{4}3m$	$F\bar{4}3m$
$a = b = c$ (Å)	5.66	5.65
Unit cell Volume (Å) ³	182.17	180.69
X-ray density (gm . cm ⁻³)	5.26	5.30
Average apparent crystallite size (nm)	-----	197

Typical Absorption spectrums obtained for ZnSe crystal at different pressures up to 10.25 GPa are shown in figure 4.

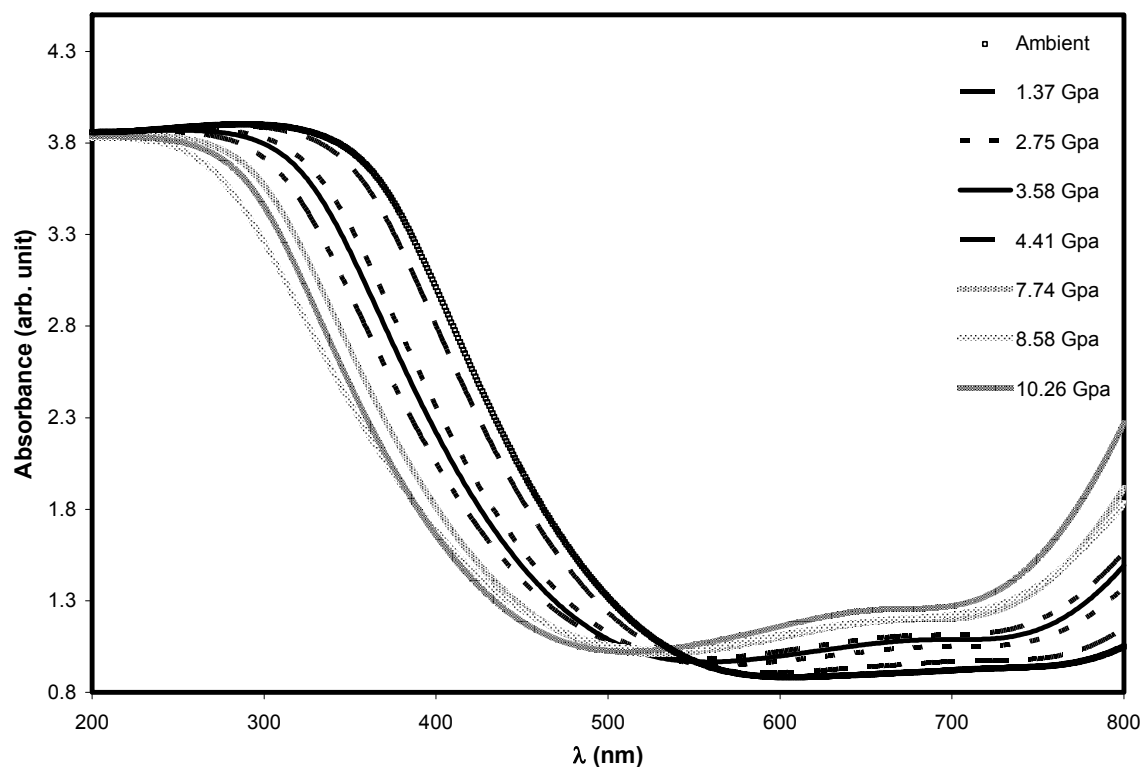


Figure 4. Pressure dependent Absorbance of ZnSe.

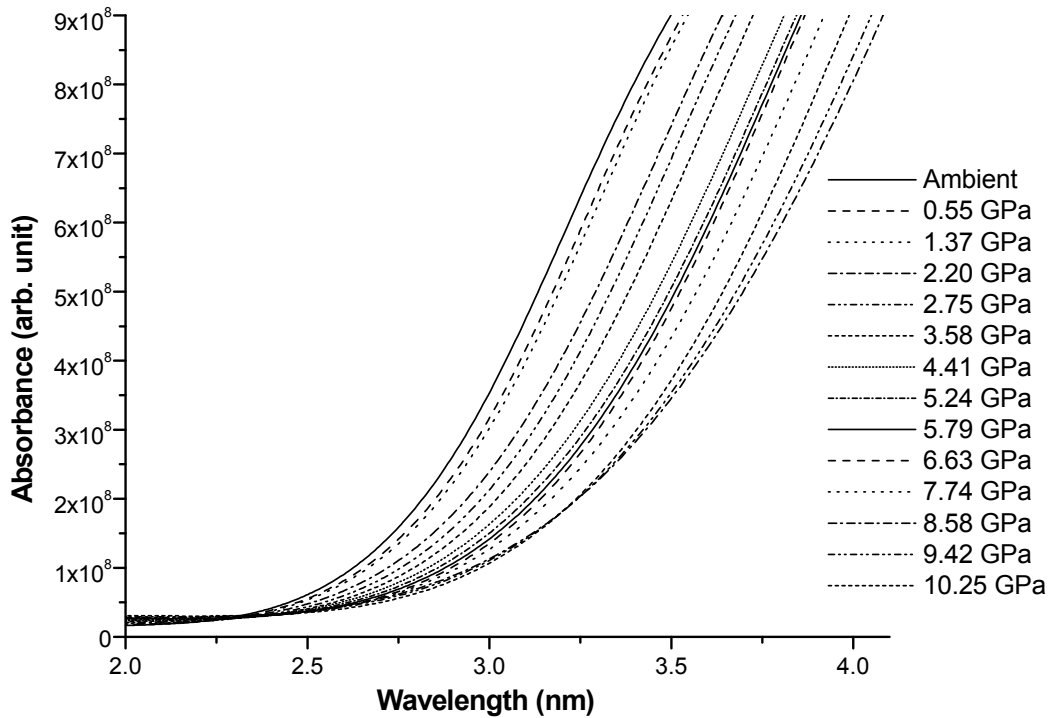


Figure 5. $(\alpha hv)^2$ versus hv for ZnSe crystals at different pressure

The absorption coefficient is known to be related to photon energy hv by the expression,

$$\alpha hv = (hv - E_g)^{1/n} \quad (2)$$

where the exponent n can take values 2, 1/2, 2/3 and 1/3 for be allowed direct, indirect, and the forbidden direct, indirect transitions respectively. In our case the best fit is obtained with $n = 2$, implying that ZnSe is a direct band gap material. From the graph of $(\alpha hv)^2 \rightarrow hv$ shown in figure 5, the pressure dependent fundamental edge is quite obvious. Variation of band gap of ZnSe single crystal with pressure is shown in figure 6. The extinction coefficient (K) shown in Figure 7. is calculated using the equation

$$K = \frac{\alpha \lambda}{4\pi} \quad (3)$$

It is apparent from the graph of pressure dependent $(\alpha hv)^2 \rightarrow hv$ shown in figure 5 that the absorption edge suffers a blue shift under pressure. The obtained value of direct band gap of ZnSe is 2.6 eV at ambient pressure is found to increase with pressure and reaches up to 3.03 eV at 10.25 GPa. The pressure coefficient is calculated to be 39.3 meV/ GPa.

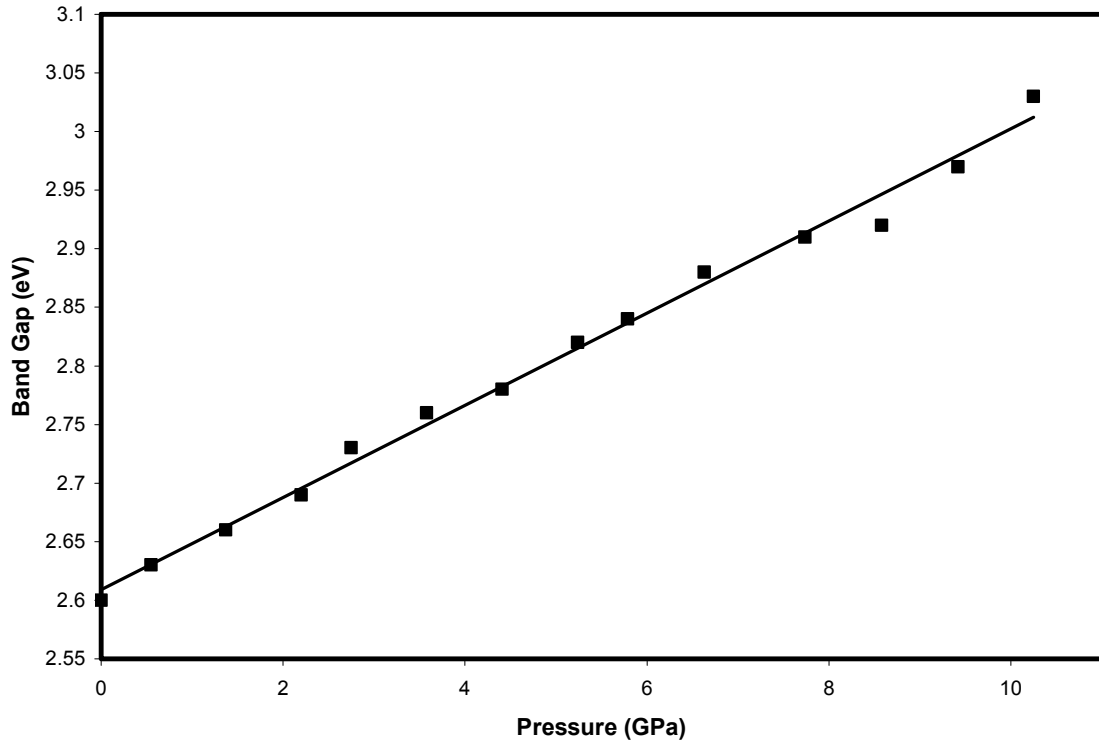


Figure 6. Pressure dependent band gap of ZnSe single crystals.

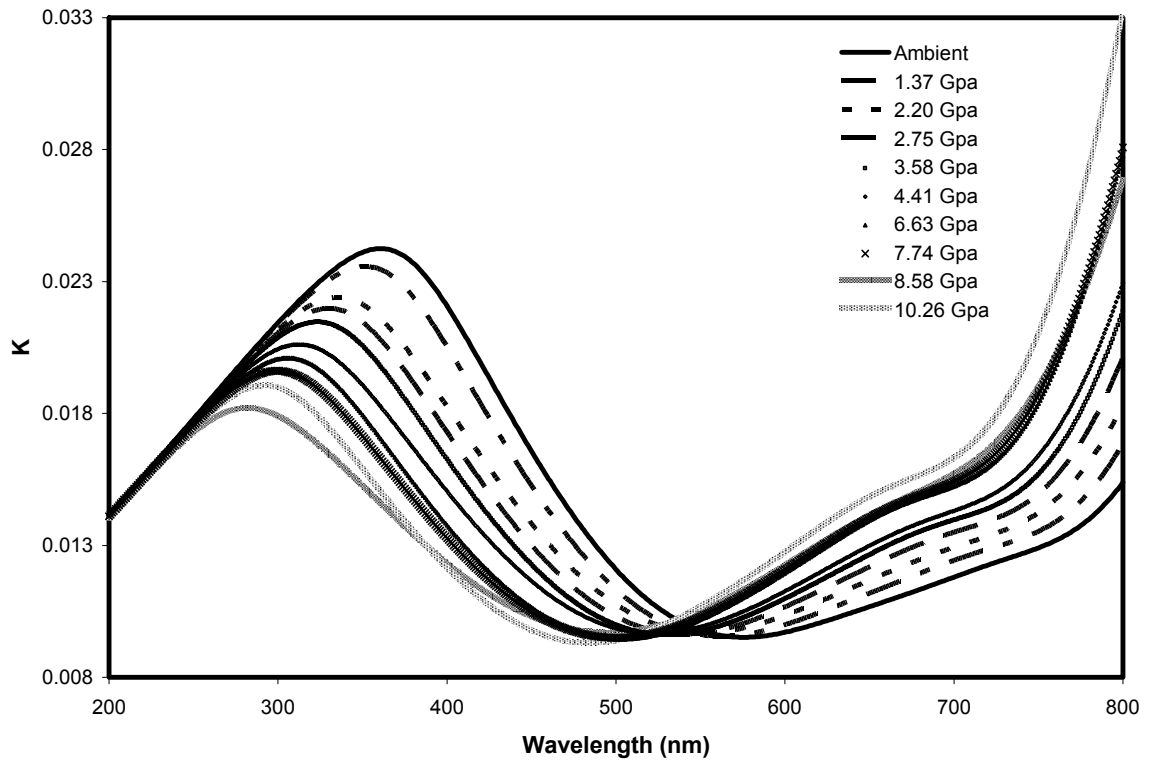


Figure 7. Extinction coefficient K versus wavelength of ZnSe crystal at different pressure

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