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# STRUCTURAL AND OPTICAL CHARACTERIZATION OF ZnSe CRYSTALS GROWN BY PHYSICAL VAPOR TRANSPORT TECHNIQUE

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*Crystalline Zinc Selenide having a direct wide band gap has attracted many researchers due to its important luminescence properties. In this paper authors present their study on the growth of ZnSe crystals by Physical Vapor Transport Technique. The energy dispersive analysis has been carried out by X-Ray (EDAX) to determine the stoichiomatric proportion of Zn and Se. From X-Ray diffraction (XRD) studies the structure of the grown crystals were found to be cubic. The optical characterization has been done by means of UV-VIS-NIR spectrophotometer and optical band gap has been calculated.*

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## 1. Introduction

Zinc Chalcogenides (ZnS, ZnSe ,ZnTe) are the wide band gap II-VI compounds. II-VI compounds possess high iconicity (0.77, 0.63, 0.49 respectively for ZnS, ZnSe ZnTe) [1] of chemical bond, therefore they have smaller energy of formation of vacancies and these accounts for the large II-VI nonstoichiometry, and also they are very sensitive to any strain. Thus high ionic character of these compounds makes it difficult to control the growing interface both from melt and vapor phase. Because of the wide band gap, II-VI compounds are the promising material for their use in many optoelectronic applications. ZnSe, one of the candidate of II-VI compounds group, possess the wide direct band gap of 2.7eV at room temperature [2] also has many potential applications in optical devices and components. Bulk ZnSe is very important material to be used as a substrate for operating in blue range. Optical devices based on ZnSe having a ZnSe substrate (homojunctions) have many advantages over the optical devices having GaAs substrate (hetrojunction) [3- 6].

There was a tremendous research development of III-V compounds in comparison to that of II-VI compounds [7]. In early 90's GaAs was used in optical devices (particularly in laser industries), as substrate to make ZnSe based optical devices. But the lattice mismatch and the mismatch in thermal expansion coefficient between GaAs and ZnSe had shortened the lifetime of such devices [8].

Thus to increase the lifetime of the devices based on ZnSe and to enhance their performance by reducing the defects in them, it was necessary to improve the basic characteristics of ZnSe. But due to the lack of high purity commercially available ZnSe bulk crystals, limited work has been done in this field. Hence there was a need of large and high purity substrates for homoepitaxial growth.

Most of the bulk crystal growth techniques used for the growth of ZnSe crystals yields heavily twinned and impure materials whose luminescence spectra are dominated by impurity bound excitations and/or donor-acceptor pair (DAP) bands. The Physical Vapor Transport technique for the growth of crystals is experimentally simple in comparison to the melt-growth technique and also has minimal needs of process control. In recent years, significant progress has been achieved in terms of material purity and structural quality [9- 15].

## 2. Experimental procedure

### 2.1 Preparation of ZnSe charge

A 7.5 gm of mixture of Zn (purity 99.99 %), Make: Fluka Chemic GmbH) and Se (Purity 99.99 %) Make: Chiti Chem corp. Baroda was filled in a dried ampoule of 25 mm of diameter and 250 mm of length in stoichiometric proportion. Before filling of the materials the ampoule was properly washed and rinsed with a distilled water to avoid a contamination of the sample by the ampoule in stoichiometric proportion. The ampoule was than sealed at pressure $10^{-5}$ Torr. This sealed ampoule was placed in a dual zone furnace to obtain a charge of ZnSe at constant reaction temperature. Ampoule was maintained at constant temperature of 1123 K for 36 hours and than cooled down to room temperature. The charge thus prepared was rigorously shaken to ensure the proper mixing of the constituents. The energy dispersive analysis by X-Ray (EDAX) has been carried out of the orange yellow colored charge for determination of the stoichiometric proportion of Zn and Se.

### 2.2 Crystal Growth Process

The synthesized compound was transferred into another quartz ampoule and was sealed at pressure of $10^{-5}$ Torr. This sealed ampoule was now loaded in to double zone furnace for crystal growth. The source zone was kept at higher temperature compared to that of the growth zone for a finite period of time. In order to avoid any influence of mechanical vibration to the crystal quality, ampoule was kept motionless during the growth process. After definite time period, it was slowly cooled down at the rate of 20 K /hour to the room temperature. To optimize the gradient between the source and growth zones of furnace, several runs were taken. The process was initially started with the temperature gradient of 100 K. This gradient was then reduced to 10 K after investigating the results. Thus finally after six runs, the gradient was set to 50 K that resulted in formation of small crystals. The selection of upper temperature and the gradient of temperature between source and growth zones were made on the basis of an extensive literature survey. Complete details of the growth parameters for growth cycles of about 168 hours are shown in Table 1. The grown crystals are also shown in the Fig. 1.

*Table 1. Growth conditions for various cycles for ZnSe crystals.*

| **Run No.** | **Temperature Distribution** | | | **Result** |
|---|---|---|---|---|
| | **Hot Zone (K)** | **Cold Zone (K)** | **Diff. (K)** | |
| 1 | 1200 | 1100 | 100 | Ingots |
| 2 | 1200 | 1110 | 90 | Ingots |
| 3 | 1200 | 1120 | 80 | Ingots |
| 4 | 1200 | 1130 | 70 | Ingots |
| 5 | 1200 | 1140 | 60 | Ingots |
| 6 | 1200 | 1150 | 50 | Crystals of 7mm× 6mm× 3mm size (App.) |

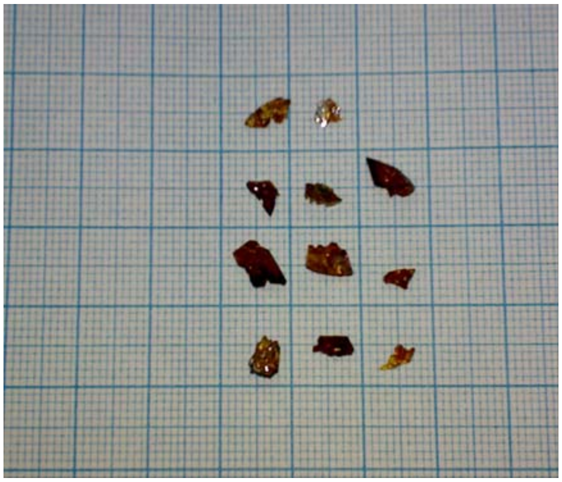

*Fig. 1. As grown crystals of ZnSe.*

For X-Ray diffraction study, several small crystals were finely ground with the help of an agate mortar and filtered through 100-micron sieve to obtain grains of nearly equal size. X-Ray diffractograms were taken with Philips X-Ray diffractometer PW 1820 employing CuK$_\alpha$ radiation. The patterns obtained are shown in Fig. 2. The absorption spectra were obtained by means of UV-VIS-NIR Dk-2A spectrometer in the range of 200 – 3000 nm.

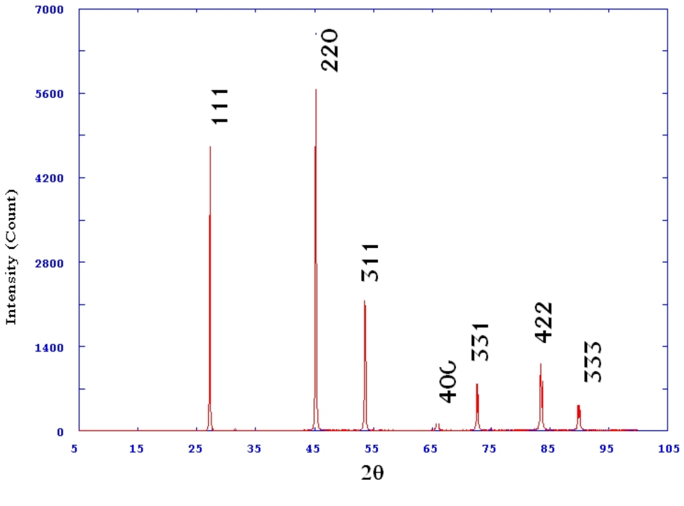

*Fig. 2. X-Ray powder diffractigram of ZnSe*

## 3. Results and discussions

The result of the EDAX analysis confirms the stoichiometric proportion of Zn and Se for the grown crystals. The X-Ray diffractogram of ZnSe shows a well defined sharp diffraction peaks as shown in Fig. 2, which indicates a good crystallinity of the specimens. The (hkl) values corresponding to prominent reflections, d values, peak width and peak intensities are shown in Table 3 along with the particle size for a number of reflections. The values of lattice parameters a,b,c, the volume (V) and X-ray density (ρ) obtained from the analysis of the diffractogram of the crystal are presented in Table 2. The values of lattice parameters obtained for ZnSe crystals were found to be in agreement with the same reported earlier. The obtained values of lattice parameters indicate a cubic structure of the sample. The particle size has been evaluated using Scherrer's formula

$$t = \frac{K\lambda}{\beta \cos\theta}$$

*Table 2. Crystallographic data of ZnSe crystals grown using PVT.*

| **Parameters** | **JCPDS data** | **Present Work** |
|---|---|---|
| a =b=c (Å) | 5.66 | 5.65 |
| Unit cell Volume V $(Å)^3$ | 182.17 | 180.69 |
| X-ray density ρ (gm . $cm^{-3}$) | 5.26 | 5.30 |

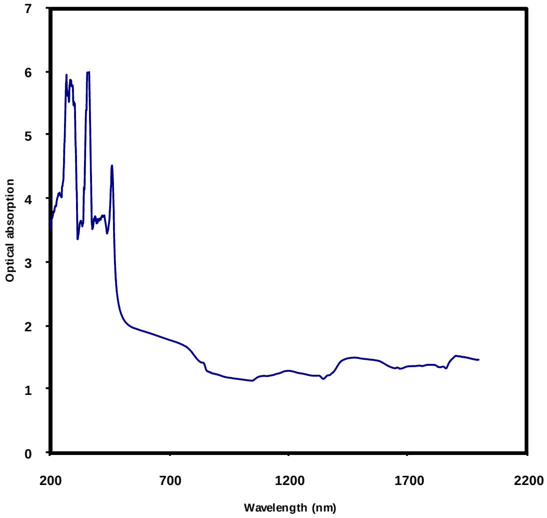

*Fig. 3. Optical spectra of ZnSe crystal.*

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 particles are of spherical shape, λ is the wavelength of X-ray radiation, β the half width intensity which is measured in radians and θ is the Bragg angle. The (h k l) planes corresponding to the prominent reflections, d-values, half width, peak intensities and particle size for ZnSe crystals are shown in Table 3.

*Table 3. X-ray diffraction data for ZnSe crystals grown by PVT*

| **(h k l)** | **d-spacing (Å)** | **Peak Width ($^o2\theta$)** | **Peak Intensity (Counts/second)** | **Particle size (Å)** |
|---|---|---|---|---|
| (1 1 1) | 3.2526 | 0.21 | 1307.40 | 389.52 |
| (2 2 0) | 1.9955 | 0.21 | 5526.33 | 410.21 |
| (3 1 1) | 1.7035 | 0.28 | 1361.00 | 318.18 |
| (4 0 0) | 1.4146 | 0.28 | 185.04 | 338.34 |
| (3 3 1) | 1.2982 | 0.35 | 478.03 | 282.01 |
| (4 2 2) | 1.1561 | 0.21 | 1075.28 | 507.31 |
| (3 3 3) | 1.0903 | 0.21 | 227.81 | 534.51 |

The optical absorption spectrum was taken over the spectral range of 200 nm -2000 nm. The optical absorption spectra of as grown crystals are shown in Fig. 3. For the determination of band gap the best fit of all the experimental points were observed in $(\alpha h\nu)^2$ vs $h\nu$ plot as shown in Fig. 4 for ZnSe. The obtained value for direct band gap is 2.60 eV for ZnSe crystals.

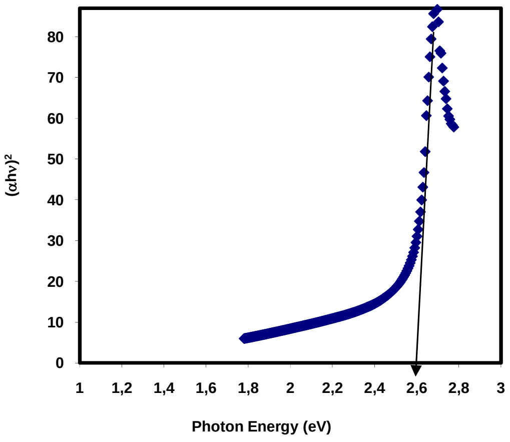

*Fig. 4.* $(\alpha h\nu)^2$ *vs* $h\nu$ *plot of ZnSe crystals*

## 4. Conclusions

Physical Vapor Transport Technique is suitable for the growth of ZnSe crystals. It is found that the temperature gradient of 50 K is appropriate for the growth of small yellowish shining crystals. The EDAX study confirms a stoichiometry of the grown crystals. The X-Ray diffraction analysis confirms a cubic structure of as grown crystals. The optical band gap of the as grown crystals is found to be 2.6 eV.

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