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# Characterization of ZnSe single crystal grown by VBT using two zone tubular furnace: An excellent material for optoelectronic devices

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ABSTRACT

ZnSe single crystal of size ~25 mm lengths and ~10 mm diameter was grown by vertical Bridgman technique using two zone tubular furnace from the synthesized polycrystal of the compound. The powder X-ray diffraction analysis confirmed the crystal system of the grown crystal. The optical band gap of the grown crystal was calculated and found to be ~2.704 eV by UV–vis–NIR analysis. The crystalline perfection was assessed by using high-resolution X-ray diffractometer (HRXRD) and chemical etching studies which reveals that the grown crystal has good crystalline perfection. The etch pit dislocation density was calculated and found to be $2 \times 10^6$ cm$^{-2}$. Good crystalline perfection and less dislocation density of the grown crystals makes, it important for optoelectronic device fabrications. The dielectric studies were also done over a wide range of frequency 100 Hz to 10 MHz at room temperature.



## 1. Introduction

ZnSe is a direct wide band gap II–VI semiconductor with a band gap of 2.7 eV at room temperature which has been recognized as an important candidate for the fabrication of blue light-emitting diode (LED) [1], laser diode (LD) [2], ZnSe based mixed-color LEDs [3] and nonlinear optoelectronic devices [4] etc. ZnSe is also a promising material for windows, lenses, output couplers, beam expanders, and optically controlled switching due to its low absorptivity at infrared wavelength, visible transmission and giant photoresistivity [5]. The preparation of high-quality ZnSe substrates is essential to promote the practical application of the materials. Due to the twins and the high density of dislocations in ZnSe crystals grown from the melt many others methods, such as physical vapor transport (PVT) [6–9], chemical vapor transport (CVT) [10–14] and solid state recrystallization (SSR) [15,16], are applied to obtain perfect ZnSe single crystals. In the CVT method with low temperature the single crystal of ZnSe have been grown with different transporting agents [10–14,17]. Single crystals of ZnSe were grown by many researchers using vertical Bridgman technique (VBT) [18,19]. But it is very difficult to grow good quality single crystal of ZnSe by VBT as reported because of the change in its stoichiometry and high melting point. To grown the good quality single of ZnSe lots of modifications are going on or done. The VBT is one of the major technique to grow the bulk size single crystals of the title compound with high quality which is mandatory for device fabrications. Many properties of the single crystals are affected by the dislocations, twins and low angle grain boundaries which are very unsatisfactory properties for substrates. In order to better control the quality of the melt grown ZnSe crystals, fundamental thermodynamic material data should be understand more precisely. Many of the physical and optical properties of single crystals are direction dependent and get deteriorate or completely diminish when these are not in the single domain or having the defects like structural grain boundaries [20,21]. So, in addition it is very important to study the various properties like crystalline perfection, etching, optical and

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dielectric to know the suitability of the grown crystal for device fabrications.

In the present investigation, first we have synthesized the titled compound using rocking furnace. The synthesized material with some flux ($B_2O_3$) was used to grow the single crystal by Bridgman–Stockbarger technique using the double zone tubular furnace [22]. The grown single crystal was characterized by single crystal as well as powder X-ray diffraction to know the crystal system and lattice parameters. The optical study was carried out to check the optical transparency and to calculate the optical band gap. The crystalline perfection was assessed by using high resolution X-ray diffraction (HRXRD) and etching studies. The dielectric studies were carried over a wide range of frequency 100 Hz to 10 MHz at room temperature.

## 2. Experimental details

### 2.1. Synthesis

It should be kept in mind that it is very important to synthesize the compound in its appropriate phase for which the choice of furnace is very important. In the present work we have chosen rocking furnace which was indigenously fabricated at our laboratory with high stability and can go up to 1200 °C. For the synthesis of Zinc Selenide, we have used 7Ns purity Zn and Se in equimolar ratio (1:1) in a quartz ampoule of dimensions 20 cm long, 19 mm inner diameter and 3 mm wall thickness was used before using the ampoule first we have cleaned it in acetone for two to three times, dipped in chromic acid for 12 h and then washed thoroughly several times in double distilled water to get the perfectly clean ampoule. After washing the quartz ampoule we kept it in the furnace at 800 °C for 6 h. The quartz ampoule containing the materials in powder form was evacuated to a pressure of $\sim 10^{-6}$ Torr and vacuum process was done very slowly so that the material should not be sucked during vacuum. By taking its phase diagram of ZnSe into account, the sealed ampoule was placed in the rocking furnace at 950 °C for synthesis by solid state reaction. The ampoule was rocked slowly by the rate of 10 r/h for proper mixing and complete homogenization of the material. Then the temperature was slowly cool down to RT and then the material was taken and crushed completely. The crushed material was finally confirmed with powder X-ray diffraction measurements. After confirming the synthesized material, the growth process was started. The temperature reached within 5 h without explosion or breaking the ampoule and kept constant for more than 8 h after that the cooling was started by 25 °C/h up to 400 °C and then the furnace was switched off for natural cooling. After cooling we have taken out the ampoule and broken by light weight hammer and get the polycrystal of the titled material. To confirm the synthesis of title material again the powder XRD was performed.

### 2.2. Growth of ZnSe single crystal

The growth was performed with different ampoule configurations and the growth experiment was successful when the wall thickness of the ampoule was around 3 mm. The synthesized material was taken in the quartz ampoule of length 12 cm with inner diameter of 15 mm. The melting point was reduced by using some flux ($B_2O_3$). After achieving an atmosphere of $10^{-6}$ Torr inside the ampoule then it was vacuum sealed. The sealed ampoule was placed inside another high quality alumina crucible and the kept inside the furnace connected with eurotherm temperature controllers of accuracy ±0.01 °C. A reverse temperature profile was developed across the ampoule for about 24 h to remove the sticking powder if any at the growth zone by keeping the source zone at lower temperature and growth zone at higher temperature. The temperature was raised at a rate of ~25 °C/h up to 1400 °C of the grown material. After holding the ampoule at this temperature for 3 h, during this period, the melt was homogenized with the help of Bridgman system BCG365 (UK) by giving rotation for some time. After that the crystal puller was started and the ampoule was allow to move downwards at the rate of 0.4 mm/day to grow the good quality ZnSe single crystals. After 10 days of growth the temperature of the furnace was lowered at the rate of 10 °C/h up to 300 °C and then power was switched off to allow natural cooling to room temperature.

### 2.3. Characterization

To confirm the crystal system and the lattice parameters of the grown ZnSe single crystal the powder X-ray diffraction pattern was recorded using a Bruker D8 Advance Powder X-ray diffractometer with nickel filtered Cu $K_\alpha$ radiation (35 kV, 30 mA) at the scan rate 0.01°/s for the 2-theta angular range of 20–70° at room temperature.

The peak width at half maximum was used to determine the crystallite size ($D$) by using Deby–Scherrer formula [23].

$$D = \frac{K\lambda}{\beta \cos\theta} \tag{1}$$

where $K = 0.9$ is the Scherer constant, $\lambda = 1.54056$ Å is the wavelength of the X-ray radiation, $\beta$ is the peak full width at half maximum in radians and $\theta$ is the Bragg diffraction angle. Also, the strain ($\varepsilon$) value was evaluated using the relation [24].

$$\varepsilon = \frac{\beta \cos\theta}{4} \tag{2}$$

The dislocation density ($\delta$) was calculated by using the formula [24,25].

$$\delta = \frac{15\varepsilon}{a * D} \tag{3}$$

Optical studies have been carried out by using a Perkin Elmer lambda 35, UV–vis spectrophotometer in the range of 190–900 nm.

The crystalline perfection of the grown single crystals was assessed by HRXRD by employing a multicrystal X-ray diffractometer developed at NPL [26]. The well-collimated and monochromated Mo $K\alpha_1$ beam obtained from the three monochromator Si crystals set in dispersive (+, −, −) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+, −, −, +) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant [27]. The specimen can be rotated along the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arcsec. The rocking or diffraction curves were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position $\theta_B$ (taken as zero for the sake of convenience) starting from a suitable arbitrary glancing angle and ending at a glancing angle after the peak so that all the meaningful scattered intensities on both sides of the peak include in the diffraction curve. The DC was recorded by the so-called $\omega$ scan wherein the detector was kept at the same angular position $2\theta_B$ with wide opening for its slit. Before recording the diffraction curve to remove the non-crystallized solute atoms remained on the surface of the crystal and also to ensure the surface planarity, the specimen was first lapped and chemically etched in a non preferential etchent.

The chemical etching is an important tool for the identification of the defects present in the crystals, which enables to develop some