Growth, thermal and surface microtopographical studies of ZnSe single crystals

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Single crystals of ZnSe were grown by chemical vapor transport (CVT) technique using iodine as transporting agent. The stoichiometric composition and the crystallographic lattice parameters of the as-grown crystals were determined by EDAX and XRD techniques respectively. The optical band gap of the as-grown single crystals was determined from optical absorption spectra obtained by optical spectroscopy. The thermal analysis of the crystals has been studied by the well known TGA and DTA techniques. The results obtained during the analysis showed the stability of ZnSe phase at higher temperatures. The surface microtopographic studies of the as-grown single crystals by the optical microscopy provided insight into the single crystal growth mechanism. The microtopography study showed that the crystals grow by layer mechanism via lateral spreading of layers. Also, kinks growth and striations were equally common features, suggesting higher under-cooling or minor fluctuations in temperature during single crystal growth.

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1. Introduction

The wide band gap semiconductors of the IIB-VIA group family forms a promising material for the optoelectronic devices like light emitting diodes (LEDs) and laser diodes (LDs). The search for blue-green diode lasers centered on this group material, ultimately culminated to the selection of ZnSe [1]. The ZnSe has received extensive attention due to its technological importance with successful application in blue-green semiconductor lasers, mid infrared lasers and other optoelectronic devices [2, 3]. In recent past, lots of work has been reported on the doping of ZnSe crystals during the growth of bulk single crystals [3, 4] and via diffusion [5, 6], depending on its use. Single crystals of ZnSe were doped with Cobalt and used in fabrication of passive optical Q-switches for erbium glass lasers [7]. Laser demonstrations were conducted using Bridgman grownCr^{2+}ZnSe crystals and demonstrated room-temperature tuning from 2,150-2800 nm [8]. It could be used in the fabrication of modulated heterostructures and optical waveguides [9, 10].

Due to the technological importance of ZnSe, the authors decided to carry out its single crystal growth by chemical vapor transport (CVT) technique and make systematic study of thermal analysis and surface microtopography. The thermal analysis has been carried out by TGA and DTA and the results are presented in this paper. The surface microtopography of the as-grown ZnSe single crystals was studied to determine the growth mechanism.

2. Experimental

2.1. Crystal growth

Single crystals of ZnSe were grown by chemical vapor transport (CVT) technique. For this, pure elements of zinc (99.999%) and selenium (99.999%) (Alfa Aesar, USA) were taken in stoichiometric proportion and sealed in an evacuated (~ 10^{-3} Pa) quartz ampoule for compound preparation. The ampoule was placed in a two-zone horizontal furnace having a linear temperature of 1073 K along the length of the ampoule. After 24 hours, the ampoule was allowed to cool. The synthesized compound was then homogenized by grinding with agate mortar and was identified to be single phase ZnSe by X-ray diffraction (XRD).

The powder synthesized compound thus prepared was then transferred into another evacuated (~ 10^{-3} Pa) quartz growth ampoule containing 4 mg/c.c. iodine transporter. A vapor transport growth in a two zone furnace with the reaction zone at higher temperature and growth zone at lower temperature was carried out. The details of the growth run are tabulated in Table1.

Table 1. Growth parameters of ZnSe single crystals.

Compound preparation		Single crystal growth			
		Temperature distribution		Growth time hours	Ampoule dimensions mm x mm(I.D.)
Temperature K	Time hours	Hot zone K	Cold zone K		
1073	24	1173	1123	168	250 x 20

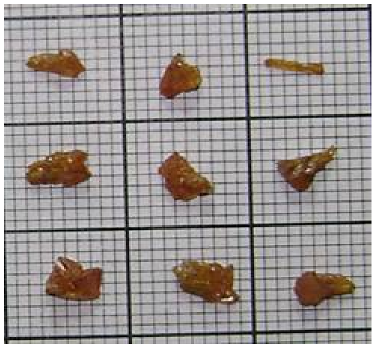

Fig. 1. Maximum size of the CVT as-grown ZnSe single crystals.

The resulting single crystals were yellowish brown in color. The average dimensions of the large size single crystals thus grown were about 5 x 4 x 2 mm^3, Fig. 1.

3. Characterization

3.1. Composition

The stoichiometric composition of the as-grown CVT single crystals was determined through energy dispersive analysis of X-ray (EDAX) attached to a Philips XL30 ESEM TMP Scanning Electron Microscope. The EDAX data of atomic % of CVT as-grown ZnSe single crystals (Fig. 2) are Zn: 43.02 % and Se: 56.98 %.

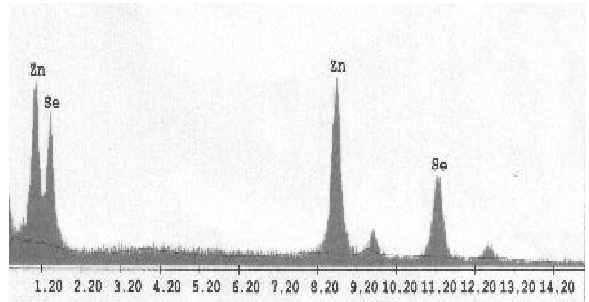

Fig. 2. EDAX spectrum of stoichiometric ZnSe single crystal.

3.2. Crystal structure

The crystallographic lattice parameters of the as-grown CVT single crystals were determined using X-ray diffraction using Phillips X-ray diffractometer (X-pert_MPD) employing CuK_α radiations. From the XRD peaks shown in Fig. 3, lattice parameters were deduced and compared with the reported values in Table 2.

Table 2. Lattice parameters of ZnSe single crystals obtained using X-ray diffraction analysis.

Parameters	Observed	Reported	Reference JCPDS card No.
a = b = c	5.662 Å	5.668 Å	37-1463
Unit cell volume	181.513 $(Å)^3$	182.17 $(Å)^3$	
X-ray density	5.281 $gm.cm^{-3}$	5.263 $gm.cm^{-3}$	

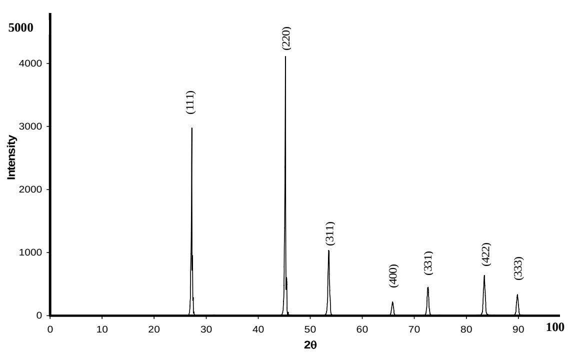

Fig. 3. X-ray powder diffraction pattern of ZnSe.

3.3. Optical properties

The optical absorption spectra on ZnSe single crystal samples was obtained in an UV-VIS-NIR Shimadzu Spectrophotometer in the wavelength range 400 nm to 900 nm. For these measurements, thin crystals of thickness about 0.3 mm were used. The samples were pasted on a thick black paper with a cut exposing the crystal to the incident radiation. The reference used was a replica of the black paper having the cut in exactly the same position. The absorption data was analyzed in terms of the theory of Bardeen et al. [11], which gives

$$\alpha = \frac{\beta\left(h\nu - E_g\right)^\gamma}{h\nu}$$

where β is a constant, E_g is the optical bandgap and hν is the energy of the incident photon, γ assumes values ½ and 2 for allowed direct and indirect transitions respectively.

It is observed that for ZnSe single crystals, the absorption can be satisfactorily explained with γ = ½ in the energy range 400 nm to 900 nm. A plot of $(\alpha h\nu)^2$ versus hν is shown in Fig. 4. Ideally the graph should be linear, the deviation from linearity at low and high incident photon energies can be attributed to the presence of structural irregularities and imperfections in these layered crystals.

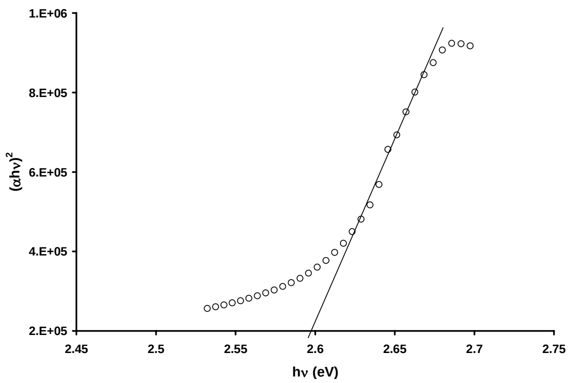

Fig. 4. $(\alpha h\nu)^2$ Vs photon energy $h\nu$ of CVT as-grown ZnSe single crystal.

The intercept obtained by extrapolation of the linear portion of the plot on the energy axis gives a bandgap value of 2.59 eV. From the functional dependence obtained for the absorption coefficient on photon energy, it may be seen that the transition is a direct allowed one.

3.4. Thermal analysis

The thermogravimetric analysis (TGA) (Perkin-Elmer, Pyris-1) and differential thermal analysis (DTA) (Perkin-Elmer, Pyries-7) of ZnSe samples were carried out in an inert nitrogen atmosphere in the temperature range 300 to 1273 K. The heating rate employed was 5 °C/min. The obtained TGA and DTA curves are shown in Figs. 5 and 6 respectively.

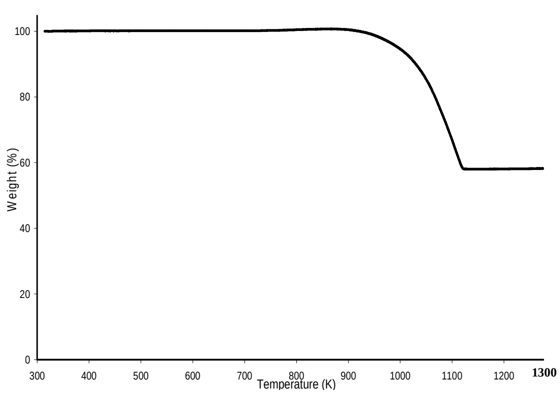

Fig. 5 TGA curve for ZnSe taken in inert nitrogen atmosphere.

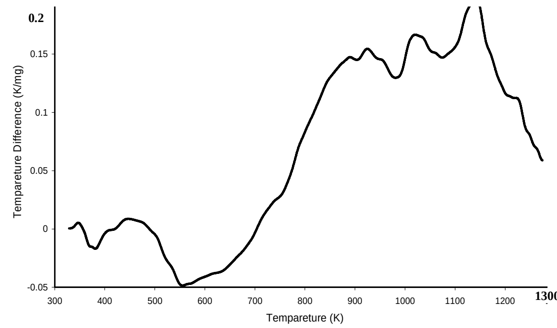

Fig. 6. DTA curve for ZnSe taken in inert nitrogen atmosphere.

3.4. Microstructure

The fresh as-grown faces of ZnSe single crystals grown by CVT were examined under 'Axiotech 100 HD' optical microscope (Carl Ziess India Private Limited, Bangalore, India) for their microstructures. Figs. 7 - 9 shows photographs of such microstructure visible on the CVT as-grown faces of ZnSe single crystals.

4. Discussion

Single crystals of ZnSe of fairly large size have been grown by a chemical vapor transport (CVT) technique. The chemical composition of the as-grown single crystals using EDAX showed that the crystals possessed near stoichiometry. The crystallographic lattice parameters of the as-grown single crystals were determined using X-ray diffraction, Fig. 3. All the peaks could be indexed as that of ZnSe on a cubic crystal structure (JCPDS Card No.37-1463) with space group of $F\bar{4}3m$. The deduced lattice parameters were compared with the reported values (Table 2) and were in good agreement.

A direct optical band gap energy value of 2.59 eV has been obtained for ZnSe single crystal from optical absorption spectra (Fig. 4), which is in good agreement with the reported value [12].

The TGA curve (Fig. 5) shows a very small weight increase in the range from room temperature to 883 K. This is due to the nitrogen adsorption on the surface during the thermal analysis as was seen for SnSe [13]. This nitrogen adsorption on the ZnSe sample between room temperature to 883 K is supported by an endothermic region having two humps in the DTA curve (Fig. 6). A continuous weight loss in TGA between 883 to 1113 K indicates selenium volatilization. This suggests that the volatilization in ZnSe starts at a temperature much lower than its melting point of 1373 K. The DTA curve between 883 K to 1113 K show exothermic region having two humps. This exothermic region in the DTA can be attributed to a thermally induced phase transition of ZnSe.

Above 1113 K to 1273 K there is no weight change seen in the TGA curve. However, in the DTA curve, there is an exothermic peak in this temperature range. The exothermic peak may be due to the decomposition of the ZnSe.

The as-grown surfaces of the ZnSe single crystals consisted of a variety of structure, whose study leads us to derive the mechanism and condition of crystal growth. Since the as-grown faces of ZnSe crystals did not show any spiral growth patterns, one can infer that growth was not promoted by screw dislocation mechanism. Typical surface features of the kind shown in Fig. 7 were frequently observed. Advancement of layers on an otherwise homogeneously flat surface of ZnSe single crystal confirmed that the layer mechanism is operative during crystal growth. One can clearly identify that the face appears to be flat and smooth having growth layers, suggesting that the crystal face is growing by lateral spreading of the layers.

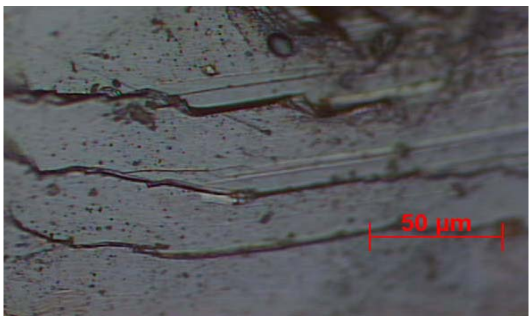

Fig. 7. Flat and smooth faces with growth layers.

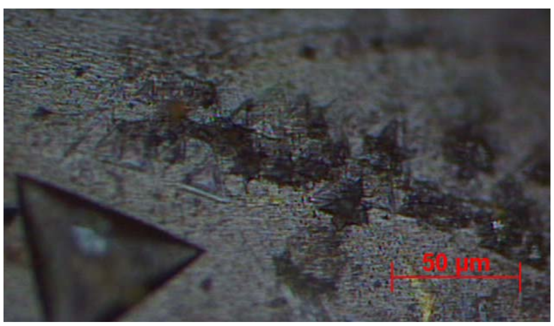

Fig. 8. Kinks formed due to higher under-cooling or minor fluctuations in temperature.

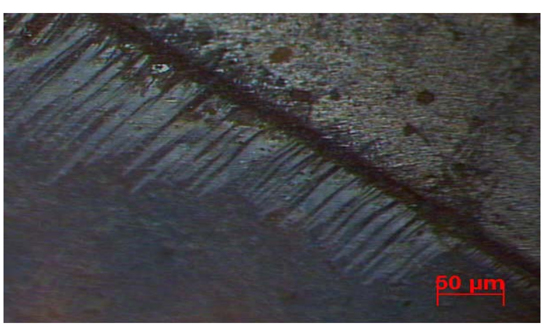

Fig. 9. Striations due to thermal stresses induced by the under-cooling or minor fluctuations in temperature in the final stage of growth.

In addition to the patterns representing evidences for layer growth mechanism, kinks growth is equally common on the as-grown faces of ZnSe single crystals (Fig. 8). The growth of kinks confirms higher under-cooling or minor fluctuations in temperature during growth. Owing to the thermal stresses induced by the under-cooling or minor fluctuations in temperature in the final stage of growth, striation are generated in the crystal bulk and appears on the growing surface as shown in Fig. 9. Thus the formation of kinks and striations supports the conjecture of under-cooling or minor fluctuations in temperature during crystal growth.

5. Conclusions

Average size good quality single crystals of ZnSe have been successfully grown by CVT technique using iodine as transporting agent. The as-grown crystals have been characterized by EDAX and XRD techniques. The thermal analysis of the samples has shown that ZnSe is thermally stable between room temperature (300 K) and 883 K. The surface microtopography studies of the as-grown single crystal showed no spiral traces, confirming that the growth is not driven by screw dislocation mechanism. Advancement of layer on a flat surface confirmed the layer mechanism by lateral spreading of layers. Kinks growth and striations are equally common suggesting higher under-cooling or minor fluctuations in temperature during single crystal growth.

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