

## Temperature dependent photoluminescence studies of ZnSe:I single crystals grown by chemical vapor transport

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**Abstract.** The single crystal ZnSe:I sample was grown by the chemical vapor transport (CVT) method using iodine as the transporting agent. The iodine incorporates itself effectively as a donor in the lattice. The sample shows a  $\langle 111 \rangle$  optical quality surface and has an absorption edge at 2.55 eV due to a deep impurity band nearly 0.15 eV below the conduction band. The photoluminescence emission spectra of this crystal have been measured for its temperature dependence as well as for excitation energy dependence. The photoluminescence is in accordance with a donor-acceptor complex formation involving iodine activated donors and self-activated acceptors. The configuration coordinate model has been used to explain the temperature dependent changes in the peak position and the bandwidth of the emission band. The decrease in luminescence efficiency with increasing temperature is explained by using a simple model for thermal quenching. The activation energy at low temperature range ( $T < 200$  K) is different from that at high temperature range ( $200 \text{ K} < T < 300 \text{ K}$ ).

**Keywords.** ZnSe; chemical vapor transport; photoluminescence.

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### 1. Introduction

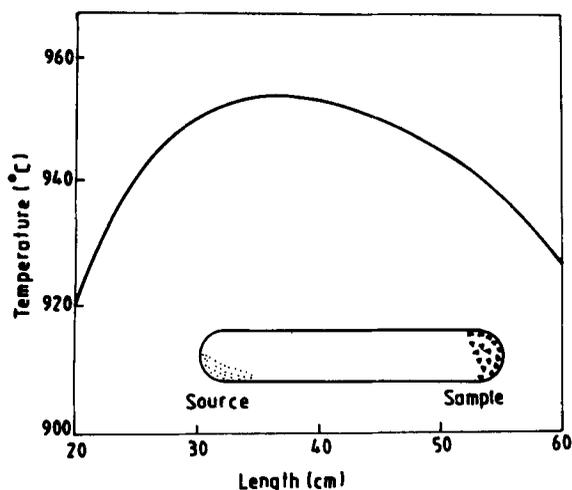
ZnSe has received great attention [1–4] recently due to its potential and technological importance, as it has a wide band gap of 2.7 eV at room temperature. It shows great promises for the fabrication of blue semiconductors lasers, high efficiency electroluminescent blue/green light emitting diodes (LEDs) and windows for high power lasers. ZnSe is also widely used in the fabrication of modulated heterostructures and optical waveguides both in its binary and alloy forms. ZnSe needs incorporation of *n*- and *p*-type dopants for its use as electroluminescent devices and LEDs. Although *n*-type doping is easily achieved in ZnSe, successful *p*-type doping have been achieved [2, 3] only recently in materials prepared by molecular beam epitaxy (MBE) process. Since MBE is an expensive method, other growth and doping methods should be explored, and the present work reports studies on the ZnSe:I samples grown by the chemical vapor transport (CVT) method using iodine as a transporting agent. These samples are characterized by optical transmission, X-ray diffraction and Raman spectroscopy. The photoluminescence for the well characterized crystal is studied in detail.

In the present study, ZnSe:I single crystals have been grown by the CVT technique, which permits growing the sample at lower temperatures than those in other methods (e.g. melt and sublimation methods) using iodine as the transporting agent. The iodine, which incorporates effectively as a dopant in the lattice, produces donor-activated centers and changes the optical properties of the sample. Raman scattering and optical transmission studies have been carried out to characterize the optical properties. The optical phonon positions and widths in the Raman spectra are used to ascertain the crystallinity of the material. The optical transmission spectrum indicates the onset of absorption at 2.55 eV due to iodine impurity, which is 0.15 eV below the band gap of pure ZnSe crystal. This agrees with the previous observation of Lebacabue *et al* [5] in 1993.

The CVT grown samples exhibited strong photoluminescence band in the red region, centered around 2.015 eV at room temperature. This photoluminescence is ascribed to the donor-acceptor complex formation involving iodine activated donors and self-activated (SA) acceptors. This complex is formed during the photoexcitation and is short-lived ( $\approx 10^{-16}$  s). The room temperature photoluminescence studies at various excitation energies show a maximum photoluminescence efficiency for the excitation energy close to 2.5 eV with a peak at 2.015 eV, which is in good agreement with the band gap of 2.55 eV observed in the optical transmission studies. The temperature dependent photoluminescence studies for a fixed excitation laser energy (2.4 eV) show changes in the peak position, bandwidth and intensity of the emission band. As the temperature is changed from 10 to 300 K, the peak position shifts from 2.005 to 2.015 eV, the bandwidth increases from 190 to 280 meV and the intensity decreases by more than an order of magnitude. The temperature variation in the peak position and bandwidth are explained using the configuration coordinate (CC) model [6–8] whereas the temperature variation in the intensity is explained by a simple model for thermal quenching [6, 9]. The activation energies are found to be 11 meV at temperatures below 200 K and 107 meV at higher temperatures.

## 2. Growth procedure

The process of CVT with iodine as the transporting agent has been widely applied [10–13] to the growth of ZnSe single crystals because of the advantages of its greatly reduced growth temperatures compared to the melt and sublimation methods. In addition to the need of expensive and complex furnaces for the crystal growth by melt and sublimation methods, there are many disadvantages of these methods, like defects produced by thermal strains including dislocations, fracture or twins and uncontrolled impurities incorporation from the crucible. The CVT on the other hand is a simple process with lower growth temperature. For the CVT growth process, the source in the powder form is kept at one end of a quartz ampoule of inner diameter 10 mm and length 250 mm and the crystal is obtained at the other end, when the two ends are maintained at two different temperatures with the source at higher temperature. Figure 1 shows the geometry and the temperature variation in the ampoule during the growth process. Before starting the growth process, the ampoule was subjected to reverse temperature gradient (i.e. the sample end at a higher temperature compared to the source end) for 24 h to remove sticking powders from deposition zone and diminish the active sites.



**Figure 1.** The sketch and the temperature variation in the ampoule for the CVT process.

The source temperature ( $T_s$ ) and deposition temperature ( $T_d$ ) values have been optimized for an iodine concentration in order to obtain good quality crystals. The best sample was grown for  $T_s = 953^\circ\text{C}$ ,  $T_d = 940^\circ\text{C}$ . The ampoule was loaded with 3 g of presynthesized source powder along with iodine at a concentration of  $2\text{ mg/cm}^3$  of the empty volume. The ampoule was placed stationarily in a horizontal double zone furnace controlled by Eurotherm controllers with the accuracy of  $\pm 0.1^\circ\text{C}$ . The source and deposition temperatures were kept at 953 and  $940^\circ\text{C}$  respectively. The process was carried out for about 100 h. At the end of the growth process, the furnace was slowly cooled to room temperature at a cooling rate of  $50^\circ\text{C/hr}$  to prevent thermal strains. After cooling, the sample chunk was taken out by breaking the tube. The sample chunk was further broken and a crystallite with well-developed smooth shiny surface was chosen. This surface was identified as the  $\langle 111 \rangle$  surface by Raman spectroscopy as well as by X-ray Laue diffraction studies.

### 3. Characterization

The ZnSe:I sample grown by the CVT method was characterized by the optical transmission measurements, X-ray diffraction and Raman scattering studies. The optical transmission measurements were performed by employing the Hitachi-U4300 spectrophotometer in visible-UV ranges. The optical transmission spectra for this sample is shown in figure 2. This figure shows an absorption edge at 489.7 nm (2.55 eV) which is about 0.15 eV below the conduction band. The complex shape of the absorption band also indicates existence of levels deeper into the band gap. The CVT grown sample was also studied by obtaining the X-ray Laue pattern. This study indicates that the sample surface is oriented perpendicular to the  $\langle 111 \rangle$  direction.

The quality of the crystal grown by the CVT technique was examined by employing laser Raman spectroscopy. The Raman spectroscopy experiments were performed in

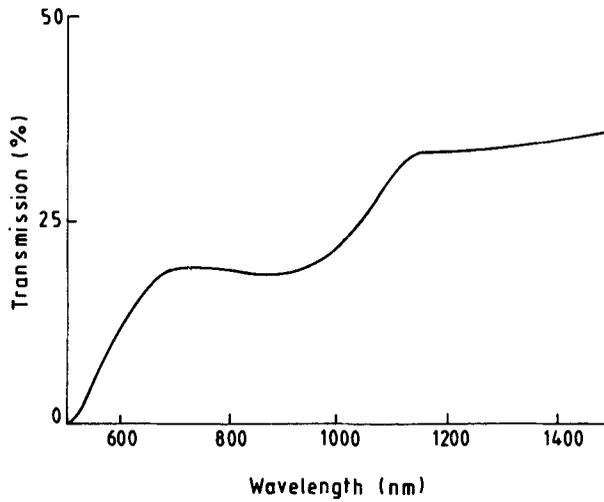


Figure 2. Optical transmission spectrum of CVT grown ZnSe:I.

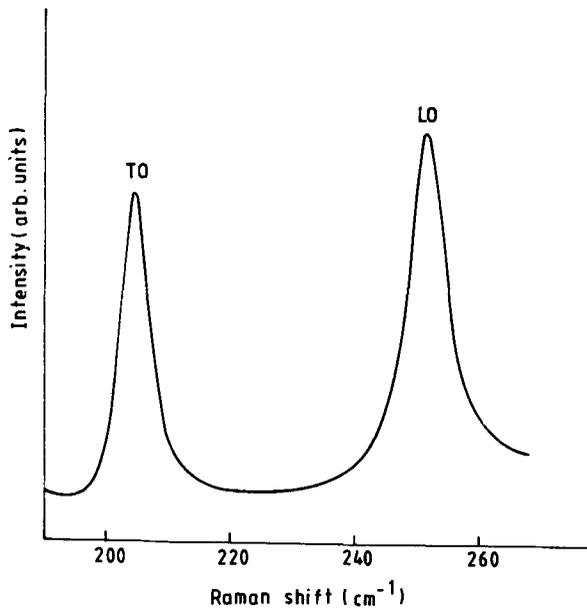


Figure 3. Raman spectrum of CVT grown ZnSe:I showing the TO and LO phonons.

the backscattering geometry with  $Z(XX + XY)\bar{Z}$  polarization at room temperature by employing the 514.5 nm line of an argon-ion laser, Ramanor double monochromator and the usual photon counting electronics. The monochromator was calibrated using strong plasma lines of the argon-ion laser and for better accuracy the slit-

**Table 1.** LO and TO phonon positions for ZnSe crystal measured by various authors.

References	TO phonon position ( $\text{cm}^{-1}$ )	LO phonon position ( $\text{cm}^{-1}$ )
Mel'nik <i>et al</i>	205	252
Islam <i>et al</i>	204	251
Anand <i>et al</i>	205	251.5
Present work	204	251.5

width of the monochromator was reduced to  $100\ \mu\text{m}$ . Figure 3 shows a room temperature Raman spectrum of the sample between  $200$  and  $300\ \text{cm}^{-1}$ . The spectrum shows two prominent phonon modes at  $251.5$  and  $204\ \text{cm}^{-1}$ , which are identified as the longitudinal optic (LO) and transverse optic (TO) phonons respectively at the center of the Brillouin zone. The LO and TO phonons are observed with comparable intensity in figure 3. According to the momentum selection rules, this is allowed only for the  $\langle 111 \rangle$  face in a back scattering geometry Raman spectrum [14]. Thus we conclude that the sample is oriented in the  $\langle 111 \rangle$  direction. The peak positions and the symmetry of the Raman lines for the CVT grown ZnSe crystal are in agreement with those obtained for ZnSe single crystals [15–17]. Table 1 gives a comparison between earlier results and our observations. This indicates that the CVT process yields good quality single crystals of ZnSe.

#### 4. Experimental results and discussion

The photoluminescence was excited in the CVT grown ZnSe:I sample using the argon-ion laser, and was dispersed using a double monochromator. The sample was fixed on the cold finger of a cryostat using silver paste and the temperature was regulated down to  $10\ \text{K}$  from the room temperature using a Helitron closed cycle liquid He cryostat. The temperature of the sample was measured accurately by mounting a Au-Cr thermocouple on the cold finger. The accuracy in the temperature measurement was  $\pm 0.2\ \text{K}$ . The cryostat was evacuated to  $1 \times 10^{-6}$  torr to avoid condensation of moisture on the sample at low temperatures. The monochromator was calibrated using the strong plasma-lines of the argon-ion laser.

It is generally found that small amounts of copper incorporated intentionally or as an impurity [9], gives an emission band from the grown ZnSe:I crystals. The self-activated emission associated with iodine and the low energy copper emission overlap in the red region of the spectrum at room temperature. As the temperature is decreased the self activated band shifts towards the higher wavelength side whereas the copper emission band shifts towards the lower wavelength side. Therefore the two bands are separated at low temperatures. The copper band is reasonably strong even if the copper concentration is a few part per million. Since copper band is not seen even at low temperatures, we conclude that the CVT grown ZnSe:I sample does not contain any trace of copper.

The photoluminescence was excited in the crystal using various lines of argon-ion laser in the range  $2.4$  to  $2.7\ \text{eV}$  with the incident power adjusted to  $10\ \text{mW}$  for each

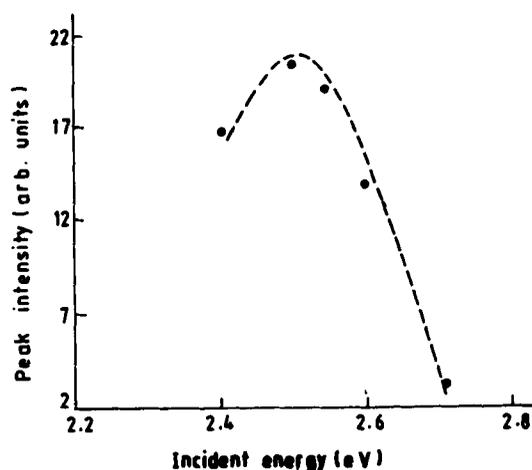
line at room temperature. The photoluminescence spectra were obtained in the range 1.750 to 2.250 eV, which show a broad band with the maximum at about 2.015 eV. It is seen that the intensity of the luminescence band first increases and then decreases when the laser energy is varied from 2.4 to 2.7 eV with a maximum at about 2.5 eV. Figure 4 shows the plot of band intensity versus incident energy at room temperature.

The temperature dependent photoluminescence studies were performed for various temperatures between 10 and 300 K using the 2.4 eV laser line. Figure 5 shows the photoluminescence spectra at various temperatures. The spectrum at room temperature shows a broad band with a maximum at about 2.015 eV and the bandwidth is about 280 meV. It can be seen in figure 5 that the peak position shifts towards higher energy side and the bandwidth increases as the temperature is increased from 10 to 300 K. Apart from the changes in the peak position and the bandwidth, the band intensity is also found to decrease with increase in temperature.

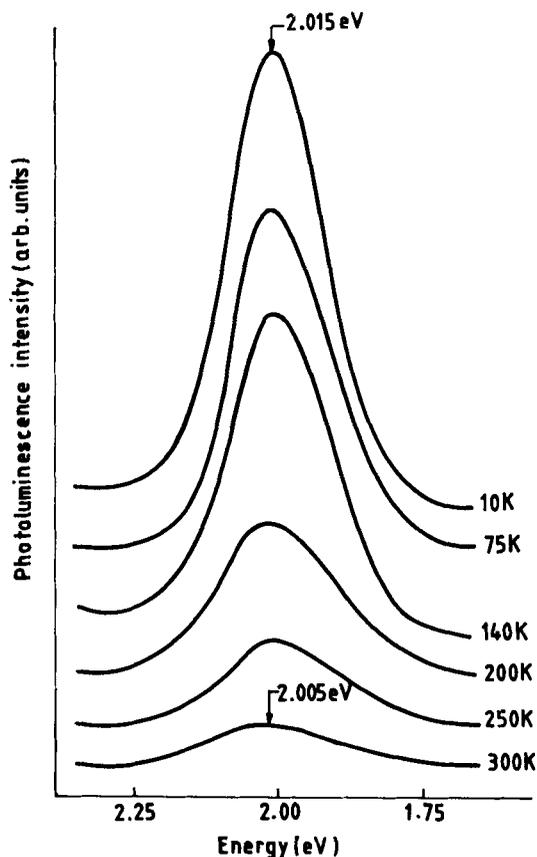
The broad peak observed at 2.015 eV which is ascribed to the self activated (SA) luminescence band [5, 11, 13], is typical of the ZnSe:I single crystals. This peak is mainly due to the incorporation of iodine [18] which leads to well-known self-compensation of the iodine-related donors by the SA acceptor, which is a  $(V_{Zn}I_{Se})$  complex with Zn vacancy  $V_{Zn}$  and iodine on the nearest-neighbor Se site  $I_{Se}$ . The complex is formed during the photoexcitation and its decay gives rise to the SA luminescence. The SA luminescence band could be fitted to a Lorentzian line shape confirming the model for photoluminescence involving the formation of a short-lived complex. From the width of the Lorentzian band, the life-time of the complex is estimated as  $\approx 10^{-16}$  s.

#### 4.1 Thermal broadening and shift

The bandwidth and the peak position for the SA band shows a temperature dependent behavior. It is found that the SA band in the luminescence spectra of the CVT grown



**Figure 4.** The peak intensity of photoluminescence band at various incident laser energies for the CVT grown ZnSe:I.



**Figure 5.** Self-activated photoluminescence spectra for the CVT grown ZnSe:I sample at various temperatures.

sample shifts towards higher energy and its bandwidth increases as the temperature is raised from 10 to 300 K. The temperature dependence of the bandwidth of the SA band can be explained in terms of a simplified form of the configuration coordinate model used for localized centers. According to this model, the temperature dependence of the halfwidth of the emission spectrum is given [6–8] by

$$\Gamma(T) = \Gamma_0 \{ \coth(\hbar\omega_e/2k_B T) \}^{1/2}, \quad (1)$$

where  $\omega_e$  is the frequency of the local vibrational mode associated with excited state of the luminescent centre for the emission process and  $\Gamma_0$  is a temperature independent term and gives the bandwidth at low temperatures.

Equation (1) has been used to obtain the values of  $\Gamma_0$  and  $\omega_e$  for the best fit to the experimental data. The values of  $\Gamma_0$  and  $\omega_e$  are estimated to be 190 meV ( $1520 \text{ cm}^{-1}$ ) and 26 meV ( $208.3 \text{ cm}^{-1}$ ) respectively. The resultant curve is shown in figure 6. The experimental data points fall on this curve reasonably closely. The value of  $\omega_e$  is close to the TO phonon frequency, which indicates that the TO phonon interacts strongly with the excited state of the luminescent center.

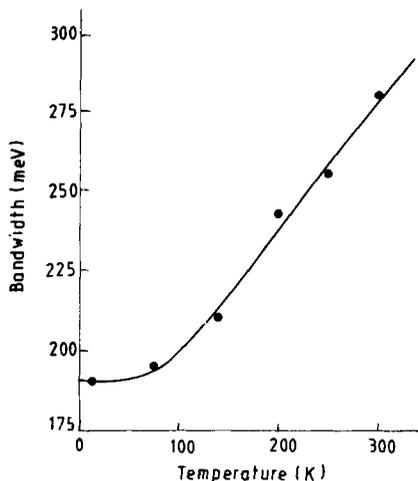
The occupation number in the vibrational level can be assumed to follow the Boltzmann distribution. This introduces a Gaussian factor in the shape function of the emission spectrum, assuming that the displacement between the minima in the coordinate of the excited and ground states is sufficiently large. In the process of emission, the Einstein coefficient for spontaneous emission, which is proportional to the third power of photon energy, has to be taken into consideration. Thus if the emission spectrum is divided by the third power of the photon energy, it should yield a Gaussian curve. This fact was confirmed [19] long time back. Making simple assumptions that the shapes of the CC curve do not change with temperature and the temperature shift in the SA band peak position ( $E_e$ ) is predominantly due to the temperature change of the occupation number in vibrational levels, Shionoya *et al* [20] derived the expression for the temperature dependent shift of the peak of the emission band using the configuration coordinate model on the basis of the above discussion. This temperature dependence is given by

$$E_e(T) = Ak_B T, \tag{2}$$

where  $A$  is a temperature independent coefficient, which includes the frequencies of the local vibrational modes associated with the excited and ground states, and the emission and absorption peak energies at zero temperature. Equation (2) gives a linear temperature dependence of the emission band peak position. Figure 7 shows the best linear fit to our experimental values. The constant  $A$  is estimated to be 0.41 from the linear portion of the plot.

#### 4.2 Thermal quenching

It is well-known [9] that the photoluminescence from many materials quenches with an increase in temperature. We have also observed a rapid thermal quenching of the SA emission band as the temperature was raised from 10 to 300 K. The curve in figure 8 shows how the intensity (peak height) of self-activated band decreases with increase in



**Figure 6.** The temperature dependence of photoluminescence bandwidth. The figure shows experimental data points as well as the theoretical curve using eq. (1).

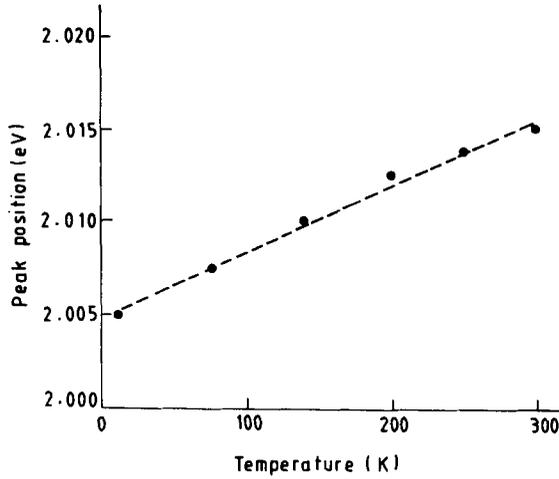


Figure 7. Temperature dependence of the luminescence band peak position showing a linear behavior.

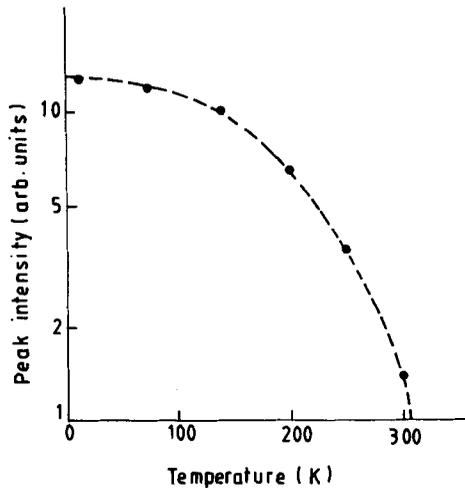


Figure 8. The peak intensity of the photoluminescence band at various temperatures for the CVT grown ZnSe:I sample.

temperature. The intensity of this band decreases slowly in the low temperature range ( $T < 200$  K) and falls rapidly at the higher temperatures.

The luminescence efficiency [9, 20],  $\eta$ , which is the normalized value of luminescence intensity, can be described by a simple equation

$$\eta = \{1 + C \exp(-W/k_B T)\}^{-1}, \quad (3)$$

where  $C$  is a constant and  $W$  is the activation energy for quenching.

Equation (3) was used to fit the experimentally observed values of the luminescence intensity to calculate the best estimations of the constants involved. This equation can

be rewritten as

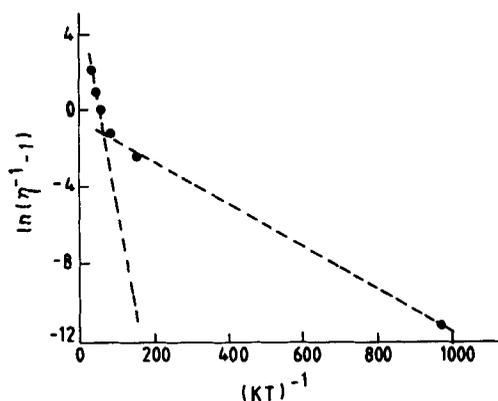
$$\ln(1/\eta - 1) = -W/k_B T + C', \quad (4)$$

where  $C'$  is another constant. According to (4),  $\ln(1/\eta - 1)$  is linearly dependent on  $1/k_B T$ . However, the experimental results do not show this linear behavior for the temperature range between 10 and 300 K. A similar result was observed earlier by Jones *et al* [9]. The plot of the experimental values of  $\ln(1/\eta - 1)$  versus  $1/k_B T$  is shown in figure 9. Figure 9 shows an average linear dependence at low temperatures ( $T < 200$  K) with a slope of 11 meV and an average linear dependence at high temperatures ( $T > 200$  K) with a slope of 107 meV. These values of the slopes give the activation energies in the two temperature ranges. We ascribe the energy of 11 meV and 107 meV to the activation energies for the loss of donor and acceptor concentrations of the conduction and valence bands respectively.

## 5. Conclusions

ZnSe:I single crystal was grown by the chemical vapor transport (CVT) method using iodine as the transporting agent. The characterization processes such as optical transmission measurements, X-ray diffraction and Raman scattering studies indicate that it is a well-grown single crystal with a good quality optically plane  $\langle 111 \rangle$  surface. The sample has an absorption edge at 2.55 eV, which is about 0.15 eV below the bandgap energy. This indicates the presence of a deep impurity band nearly 0.15 eV below the conduction band.

The CVT grown sample was studied for the photoluminescence using various excitation energies between 2.4 and 2.7 eV at room temperature and also for various temperatures between 10 and 300 K when the excitation energy was fixed at 2.4 eV. The room temperature spectra shows a maximum luminescence emission for incident laser energy of about 2.5 eV, with peak position at 2.015 eV. The temperature dependent photoluminescence spectra show that the peak position shifts towards higher side, the bandwidth increases and the intensity decreases as the temperature is increased from 10



**Figure 9.** Plot of  $\ln(1/\eta - 1)$  versus  $1/k_B T$  showing two different slopes at low and at high temperatures.

to 300 K. The shift in the peak position and the bandwidth are explained on the basis of the CC model. It is found that the TO phonon mode interacts strongly with the excited state of the luminescence center. The intensity change is explained by employing a simple model for the thermal quenching of the luminescence band. The activation energies calculated from the thermal quenching process are 11 meV at low temperatures and 107 meV at elevated temperatures.

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