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The effect of Sn doping Urbach Tail and optical absorbtion measurements of InSe crystal

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Absract. InSe and n-InSe:Sn crystals grown by Bridgman-Stockbarger method. Absorption measurements have been carried out in InSe and InSe:Sn samples in the temperature range 10–320 K with a step of 10 K. Sn doping to InSe have increased the absorption intensity and caused both increasing in the Urbach energy, decreasing in the steepness parameters and shifting of the absorption edge towards the shorter wavelengths. The steepness parameters and Urbach energy values for InSe and InSe:Sn samples have also increased with increasing sample temperature in the range 10-320 K.

1. Introduction

In recent years, owing to very interesting physical properties, the binary semniconductor crystals such as InSe, GaSe have raised considerable deal of research interest followed by technological application in the fields solar cells [1-3], batteries [4], optoelectronics [5] and photoconductive [6, 7] as well as in commercial and industrial applications in micro-devices where the compounds are used as solid-state ionic conductors [8].

Measurements of absorbance and transmittance in In_XSe_{1-x} thin films in the spectral range of 1.1 to 3.9 eV carried out at room temperature [9]. Gürbulak et al. have grown InSe:Ho single crystals by a method which is similar to the direct freezing. The first exciton energies for n=1 were calculated as 1.315 eV in n-InSe:Ho, 1.331 eV in InSe and 1.326 eV in InSe:Dy at 10 K [10, 11].

Ateş et al. reported that the absorption edge shifted towards longer wavelengths and a decrease of intensity in absorption spectra occurred under an electric field of 5 kV/cm. At 10 and 320 K, in InSe the first exciton energies were calculated as 1.350 and 1.311 eV for zero voltage and 1.334 eV 1.301 eV for electric field, respectively [12].

The cleaved surfaces do not need any additional treatment at p–n-junction formation and are chemically inert at ambient conditions [3, 13]. Bonding within the layers is ionic-covalent while the layers are bonded together by Van der Waals-like interactions. Owing to these relatively weak interlayer forces, there are different stacking arrangements of the layers leading to the four polytypes $\gamma, \varepsilon, \beta$ and δ [14] and also cleaving InSe and InSe:Sn ingots into the perpendicular planes can easily be done. Each layer is formed in packets of two In and two Se sublayers in the sequences of Se-In-In-Se. [15]. InSe single crystals can be grown as both p and n type depending on dopant elements added during the growth process. Detailed information on impurity levels in InSe is important in view of its possible application in high-quality devices. There are few studies available on the impurity levels of n-InSe doped with group IV atoms of Sn, Si and Ge [16, 17]. The behaviour of semiconductor optical properties in the presence of electric field is an important issue, both from the standpoint of understanding the basic physics involved and in terms of potential applications in opto-electronic devices. The modification of the band edge absorption under the application of an external electric field

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was studied independently by Franz [18] and Keldysh [19] known as Franz–Keldysh effect (FKE). The FKE occurs in bulk semiconductors when a strong dc electric field is applied, resulting in a red-shift of the fundamental absorption edge and oscillations in the optical absorption above the band gap.

In the present paper, the effects of both Sn doping and electrical field were investigated on the absorption edge, the steepness parameter and Urbach energy for InSe and InSe:Sn crystals in the temperature range 10-320 K. To our knowledge, this is the first results for the effect of an electric field on the absorption edge of Sn-doped InSe single crystals.

2. Experimental procedures

InSe and InSe:Sn (0.03 wt% Sn) monocrystals were grown in our growth laboratory by the modified Bridgman-Stockbarger at the same time. For the constituent of monocrystal $A^{III}B^{VI}$, the basic elements having high purity (5N) elements were weighed in a stoichiometric ratio accurate to 0.1 mg. The total mass of the elements was about 20 g. The growth programme for InSe and InSe:Sn single crystals are given in Fig. 1. The melting point of InSe which is 660±5 °C [20], was determined from the phase diagram. The detailed knowledge about the quartz ampoules used this study has been given Ref. [21].

The grown InSe and InSe:Sn single crystal ingots were cleaved into perpendicular planes of naturally cleaved planes using a razor blade and cut into 48±5 μm thicknesses had no cracks or voids on the surface. Since the cleaved faces of the grown ingots had the natural mirror-like cleavage faces, no polishing or cleaning treatments were carried out on the cleaved faces of these crystals. It was found that our samples exhibited n-type conductivity by the means of hot probe technique.

The optical absorption measurements as a function of temperature were made in closed-cycle He cryostat. A Perkin Elmer UV/Vis Lambda 2S Spectrometer with spectral range of 190-1100 nm and better than ±0.3 nm wavelength accuracy was used. Therefore E_g can be calculated with an accuracy of approximately better than 0.6 meV considering the wavelength accuracy of our spectrometer. The sample temperature was varied from 10 K to 320 K with a step of 10 K.

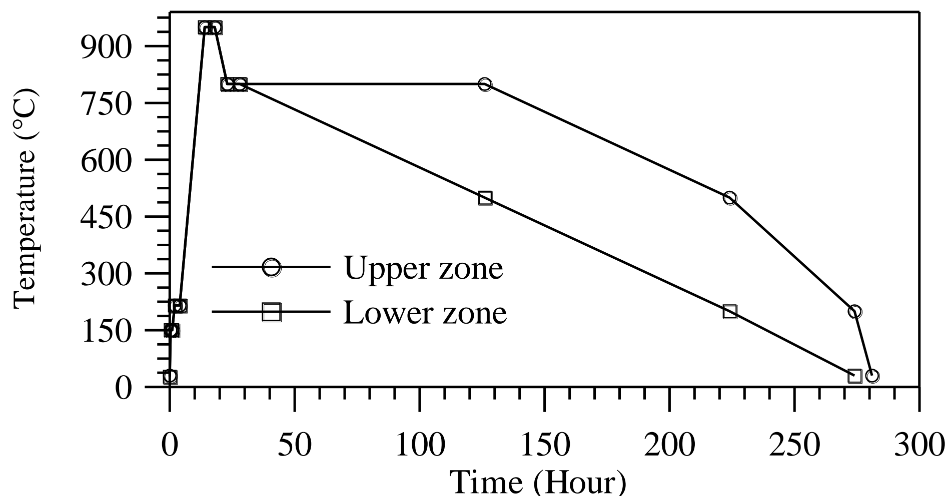

Figure 1. Growth programme for InSe and InSe:Sn single crystals

3. Basic equations

The optical absorption coefficients (α) of the samples were determined from the following transmission data relationship [22]

$$T = (1-R)^2 \exp(-A) = (1-R)^2 \exp(-\alpha d)$$

(1)

where R is the reflectivity of the sample, A is absorbance and d is thickness.
The change of the band gap with temperature is given as following:

$$\frac{dE_g}{dT} = \left(\frac{dE_g}{dT}\right)_{l-ex} + \left(\frac{dE_g}{dT}\right)_{e-p} \tag{2}$$

where the first and second terms depend on crystal lattice thermal expansion and electron-phonon interaction, respectively.

In most semiconductors, the following empirical expression suggested by Varshni is used to describe the temperature dependence of the excitonic transition energy [23]:

$$E_{ex}(T) = E_{ex}(0) - \delta \frac{T^2}{T+\beta} \tag{3}$$

where $E_{ex}(T)$ is the excitonic energy at sample temperature T, $E_{ex}(0)$ is the excitonic transition energy at 0 K, and δ and β are parameters being characteristics of the material. The parameter β is usually used to estimate of Debye temperature (θ_D). The temperature variation of excitonic peak or band gap energy of semiconductors have been fitted by Cody as below [24]:

$$E_{ex}(T) = E_{ex}(0) - B\left[\left((\theta_E / T) - 1\right)^{-1}\right] \tag{4}$$

where B is a constant and θ_E is the Einstein characteristic temperature and corresponds to the average phonon temperature. It is known that θ_E is closely related to the θ_D by the relation $\theta_D \approx \frac{4}{3}\theta_E$ [25].

That absorption edge increases exponentially in a number of insulators, including ionic crystals, semiconductors, and organic crystals follows the below empirical expression [25]:

$$\alpha(E,T) = \alpha_0 \exp\left[\frac{\sigma(T)}{k_B T}(E - E_0)\right] \tag{5}$$

where $E = \hbar w$ is the photon energy, α_0 and E_0 are characteristic parameters of the material, $\sigma(T)$ is the steepness parameter, and k_B is the Boltzmann constant . Eq. (5) implies that logarithm of α plotted as a function of E can be approximated by a straight line in energies just below the fundamental absorption edge (AE). The extrapolations of those lines for various temperatures usually converge at the same point (E_0, α_0), which is called the 'converging point'. This empirical rule was found by Urbach [26] for silver halides and established by Martienssen [27] for alkali halides.

The steepness parameter $(\sigma(T))$, which is characterizing the steepness of the straight line near the absorption edge, is expressed empirically as a function of temperature by [26-28] as

$$\sigma(T) = \sigma_o \left(\frac{2k_B T}{\hbar w_p} \right) \tanh\left(\frac{\hbar w_p}{2kT} \right) \tag{6}$$

where σ_0 is a parameter, non depending on the temperature and depending on the material, being inversely proportional to the strength of the coupling between excitons and phonons [29]. Some researchers have stated that $\hbar w_p$ corresponds to the energy of phonons associated with the Urbach tail [29, 30]. kT/σ which can be derived from above equation is called Urbach's energy (E_u). E_u represents the thermal disorder or the occupancy level of phonon states in crystals [28]. E_u can be modelled as an Einstein oscillator taking into account contributions of structural and thermal disorder in the sample by considering Skettrup's theory [31]. According to this model, Urbach's energy can be expressed by:

$$E_u(X,T) = [E_u(X) + E_u(T)] = A + B\left(\frac{1}{e^{\theta_E/T} - 1} \right) \tag{7}$$

where A and B are the parameters related to structural and thermal disorders.

4. Result and discussion

Figs. 2 shows the absorption spectra of InSe and InSe:Sn at 10, 80, 160, 240 and 320 K under zero electric field (ΔU= 0 V). Sn doping to InSe caused an increasing in absorption peak intensities. As can be seen in Fig. 2 the absorption edge shifts towards to shorter wavelengths and band gap energy increases by Sn doping.

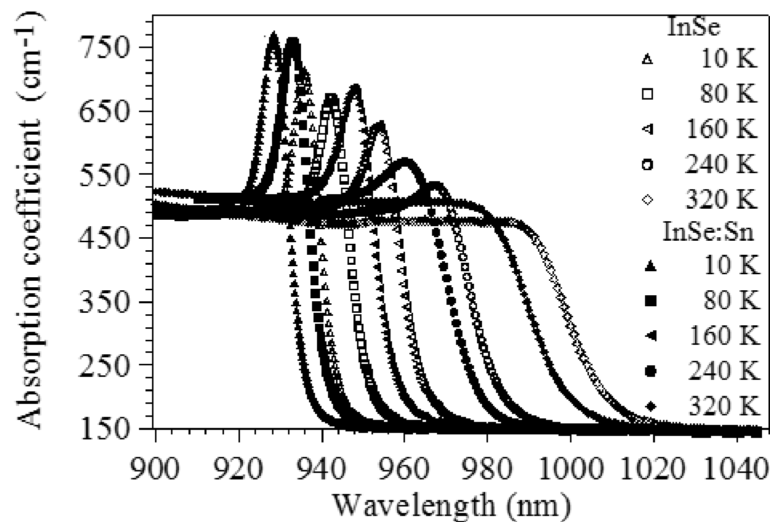

Figure 2. Absorption spectra of InSe and InSe:Sn crystals obtained at 10, 80, 160, 240 and 320 K.

The Urbach tail was observed for both samples between 10-320 K. The absorption spectra for both samples obey the Urbach rule and typical Urbach tails for various temperatures are shown in Fig. 3. Sn doping into InSe has changed both E_0 and logarithm of absorption coefficient values.

Figs. 4 and 5 show the E_u which corresponds to the inverse of a slope of the Urbach tails of the InSe and InSe:Sn samples and steepness parameters (σ) of these samples as a function of temperature, respectively. Fig. 4 represents the experimental data together with the solid curves representing the curves fitted to Eq. (7) for Urbach's energy. A, B and θ_E parameters of InSe and InSe:Sn crystals were obtained from a fit to Eq. (7). These obtained parameters are given in the Table 1. By taking into the account these parameters, it has been seen that the structural disorder contribution has increased with Sn doping and thermal disorder contribution decreases.

Table 1. Values of the parameters A, B and θ_E obtained from a fit to Eq. (7).

Fit to Eq. (17)	A (meV)	B (meV)	θ_E (K)
n-InSe	7.980	19.280	260±10
n-InSe:Sn	9.370	18.250	260±10

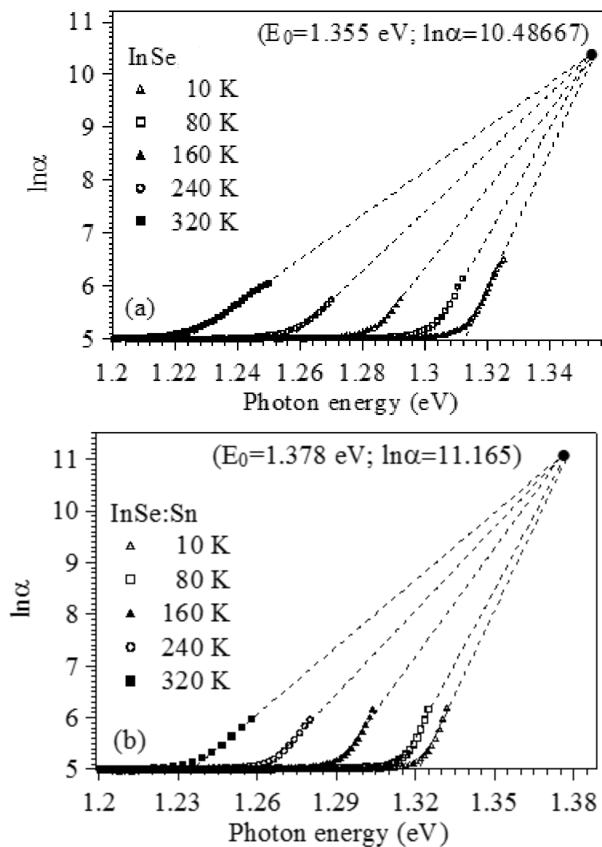

Figure 3. $\ln\alpha$ vs. photon energy ($\hbar w$) plots for (a) InSe, (b) InSe:Sn

The Sn doping to InSe decreased steepness parameter and increased Urbach energy. To compare the experimental σ(T) data with theoretical values, the theoretical steepness parameter σ(T) was estimated using Eq. (6). σ_0 and $\hbar w_p$ parameters of InSe and InSe:Sn crystals were obtained from a fit to Eq. (6). The obtained parameters are given in the Table 2.

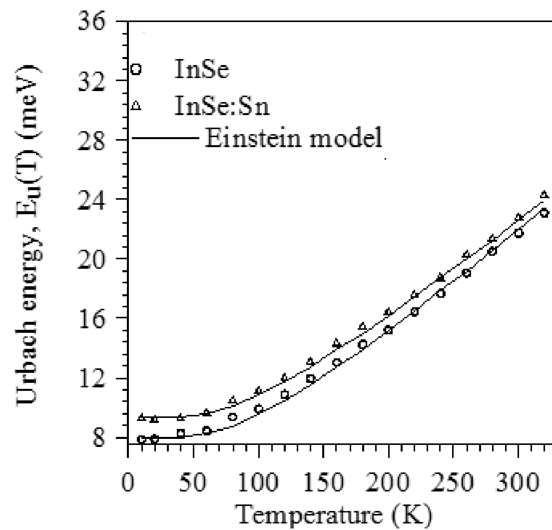

Figure 4. The Urbach energy of InSe and InSe:Sn as a function of temperature.

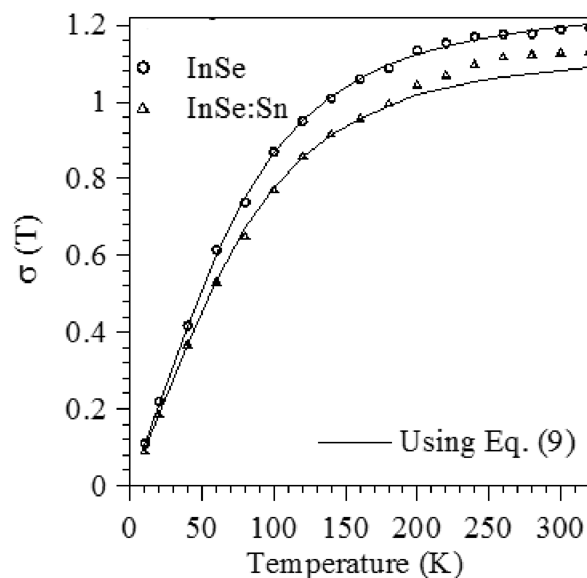

Figure 5. The stepness parameter of InSe and InSe:Sn as a function of temperature.

Table 2. Values of the parameters σ_0 and $\hbar w_p$ obtained from a fit to Eq. (6).

Fit to Eq. (6)	σ_0	$\hbar w_p$ (meV)
InSe	1.260	21.0
InSe:Sn	1.145	21.5

As can be seen in Figs. 4 and 5 the experimental data and theoretical fittings are correlated with each others. The steepness parameters and Urbach energy of InSe and InSe:Sn increased with increasing sample temperature in the range 10-320 K. The steepness parameter of InSe is greater than that of InSe:Sn sample at the same temperature. It is the first time that the effect of Sn on the

absorption measurements, Urbach rule and Steepness parameter of InSe sample has been investigated. As a result, Sn doping (0.03%) have caused a shift to shorter wavelength and an increase in intensity of absorption spectra. The Urbach energy has increased with Sn doping and temperature.

4. Conclusion

InSe and InSe:Sn single crystals used in this research were grown by using the modified Bridgman/Stockbarger method. The optical absorption measurements of semiconductor crystals n-InSe and n-InSe:Sn were performed as a function of temperature with 10 K increments in the range 10-320 K. The effect of Sn doping on the optical absorption measurements, Urbach energy and stepness parameters for InSe:Sn has been investigated. Sn doping to InSe crystal increased the absorption intensity and caused the shifting of the absorption edge towards the shorter wavelength of the spectrum.

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