Effect of indium incorporation on the optical properties of spray pyrolyzed $Cd_{0.22}Zn_{0.78}S$ thin films

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In this study, effect of indium incorporation on the optical properties is investigated for the spray pyrolyzed onto glass substrates at 275°C substrate temperature undoped and indium doped $Cd_{0.22}Zn_{0.78}S$ thin films. The average optical transmittance of all the films was over 77% in the wavelength range between 450 and 800 nm. The optical band gap energies of the thin films have been investigated by the measurement of the optical absorbance as a function of wavelength. The optical absorption studies reveal that the transitions are direct band gaps of 3.02 and 3.05 eV for undoped and doped indium $Cd_{0.22}Zn_{0.78}S$ thin films, respectively. The Urbach tail parameter and optical constants such as refractive index, extinction coefficient, and dielectric constants were calculated for these films. The dispersion parameters such as single-oscillator energy and dispersive energy were discussed in terms of the single-oscillator Wemple–DiDomenico model.

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Key words: spray pyrolysis, optical constants, single-oscillator model

1 Introduction

Polycrystalline thin film semiconductors play an important role in solar cells due to their favourable optical properties. The II–VI compounds, CdS ($E_g = 2.42$ eV) and ZnS ($E_g = 3.65$ eV) have proved to be useful for the fabrication of a wide range of optoelectronic devices. $Cd_xZn_{1-x}S$ films have been prepared by a variety of methods, including spray pyrolysis [1–3], co-evaporation [4, 5], chemically deposited [6], molecular beam epitaxy (MBE) [7–9], chemical method synthesize [10], contact-free technique [11]. Among these, the spray pyrolysis method is cheaper, simpler and more versatile than the others and gives the possibility of obtaining films with suitable properties for optoelectronic applications and also when large areas are needed.

The study of optical absorption has proved to be very useful for elucidation of the electronic structure of these materials. It is possible to determine indirect and direct transition occurring in band gap of the materials by optical absorption spectra. The data transmittance can be analyzed to determine optical constants such as refractive index, extinction coefficient and dielectric constant. The evaluation of refractive indices of optical materials is of considerable importance for applications in integrated optic devices such as switches, filters and modulators, etc., where the refractive index of a material is the key parameter for device design. The knowledge

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of real and imaginary parts of complex refractive index, as a function of wavelength, is necessary to make effective use of these materials for optoelectronic devices [12–14], particularly as an antireflective coating [15]. The variation of refractive index with doping also provides the means to tailor the refractive index to any desired value required for use in filters [16].

The optical parameters for $Zn_xCd_{1-x}S$ thin films were reported by Torres et al. [17]. But in the available literature we did not found data for optical parameters of spray pyrolyzed indium doped $Cd_{0.22}Zn_{0.78}S$ thin films. Thus, the aim of this study is to investigate optical properties of indium doped $Cd_{0.22}Zn_{0.78}S$ thin films to calculate optical constants such as refractive index, extinction coefficient and dielectric constant, the Urbach energy E_{U} and the dispersion parameters such as E_0 (single-oscillator energy) and E_{d} (dispersive energy). In the present work, we are to investigate optical properties of indium doped $Cd_{0.22}Zn_{0.78}S$ semiconductor thin film so that this information would help the researchers toward applying these materials in optical devices and heterojunction solar cells [5, 17].

2 Experimental details

Spray pyrolysis is basically a chemical process, which consist of a solution that is sprayed into a substrate held at high temperature, where the solution reacts forming the desired thin film. In this method, the film precursor is sprayed onto a heated substrate ($T = 275°\mathrm{C}$) using nitrogen as carrier gas. Undoped and 1 at.% indium doped $Cd_{0.22}Zn_{0.78}S$ thin films have been deposited onto glass substrates. Cadmium chloride dihydrate, zinc chloride, and thiourea were used as starting materials and indium chloride was used as a dopant source. The flow-rate of the solution during spraying was adjusted to be about $3.5\,\mathrm{ml\,min^{-1}}$ and kept constant throughout the experiment. The spray pyrolysis deposition system and preparation of these films was reported in detail elsewhere [18–19]. The adhesion of the films onto the substrates was quite good. The indium doped $Cd_{0.22}Zn_{0.78}S$ thin film exhibited yellow colour with a slight greyish tinge. The thickness of all the deposited thin films was measured by weight difference method using a sensitive semi-microbalance.

The optical absorption spectra of all the thin films at room temperature were analyzed on a SHIMADZU UV-2450 PC UV-VIS Scanning Spectrophotometer in the wavelength range (190–900) nm.

The absorption coefficient (α) at frequency (ν) of radiation was calculated using the formula

$$\alpha(\nu) = 2.303\,\frac{A}{d}\,, \tag{1}$$

where d is the film thickness and A is the optical absorbance. Also, $\alpha(\nu)$ is related to the optical transmission (T) and reflection (R) as follows [20]:

$$\alpha(\nu) = \frac{1}{d}\log\left\{\frac{(1-R)^2}{2T} + \frac{(1-R)^2}{[(2T)^2 + R^2]^{1/2}}\right\} \tag{2}$$

and the refractive index was obtained from

$$n = \frac{1+R}{1-R} + \left[\frac{4R}{(1-R)^2} - k^2\right]^{1/2}, \tag{3}$$

where k is the extinction coefficient which is related to the absorption coefficient and the wavelength as

$$k = \alpha \frac{\lambda}{4\pi}. \tag{4}$$

On the other hand, if the refractive index and extinction coefficient are known, the real and imaginary parts of dielectric constant of the films can be also estimated. The real and imaginary parts of complex dielectric constant are expressed as [21]

$$\varepsilon_1 = n^2 - k^2, \qquad \varepsilon_2 = 2nk, \tag{5}$$

where ε_1 is the real part and ε_2 is the imaginary part of the dielectric constant.

3 Results and discussion

The transmission spectra of undoped and indium doped $Cd_{0.22}Zn_{0.78}S$ thin films of thickness ≈ 600 nm are shown in Fig. 1. The average transmission values are 81% and 77% in the wavelength range (450–800) nm for undoped and 1 at.% indium doped $Cd_{0.22}Zn_{0.78}S$ thin films, respectively.

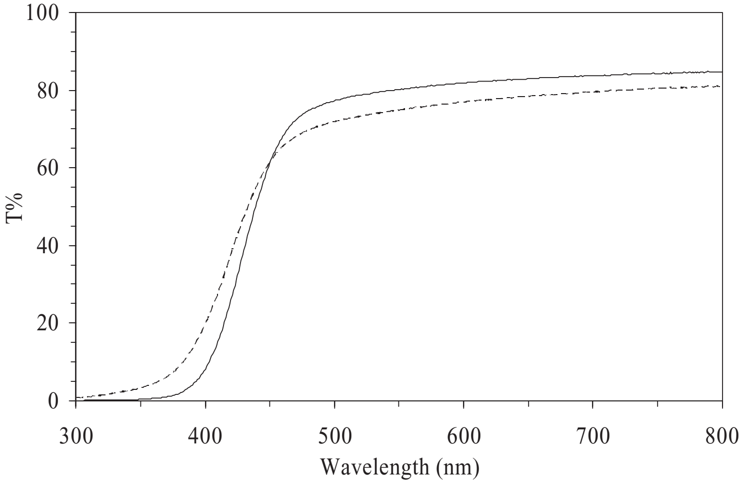

Fig. 1. Optical transmission spectra of the undoped (—) and 1 at.% indium doped (- - -) $Cd_{0.22}Zn_{0.78}S$ thin films.

For the optical band gap where the minimum of the conduction band and the maximum of the valence band occur, the absorption begins at $h\nu = E_g$. The optical band gap, E_g, can be determined from the experimental spectra of the absorption

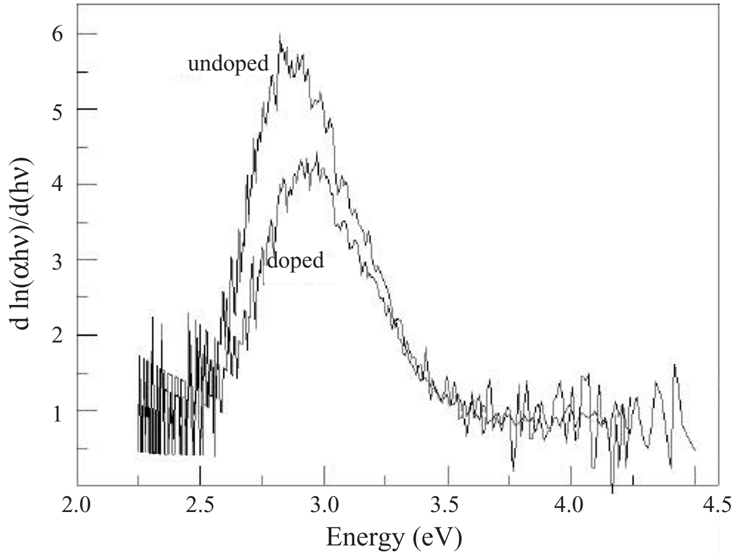

Fig. 2. The plots of d[ln($\alpha h\nu$)]/d($h\nu$) versus hν of the films.

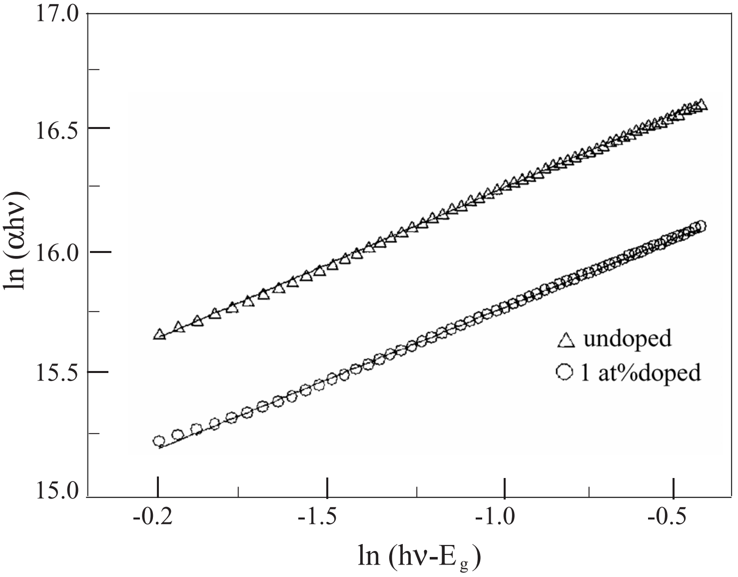

Fig. 3. The plots of ln($\alpha h\nu$) vs. ln($h\nu - E_{\rm g}$) of the films.

coefficient, α, as a function of the photon energy, $h\nu$, using the following equation [22]:

$$\alpha h\nu = A(h\nu - E_{\mathrm{g}})^m \,, \tag{6}$$

where m is equal to 1/2 and 2 for direct and indirect transitions, respectively, and A is a constant. Equation (6) can be written as

$$\frac{\mathrm{d}[\ln(\alpha h\nu)]}{\mathrm{d}[h\nu]} = \frac{m}{h\nu - E_{\mathrm{g}}} \,. \tag{7}$$

The type of transition can be obtained finding the value of m. A discontinuity in the $\mathrm{d}[\ln(\alpha h\nu)]/\mathrm{d}(h\nu)$ versus $h\nu$ plot at the band gap energy (E_{g}), i.e. at $h\nu = E_{\mathrm{g}}$, can be observed. The $\mathrm{d}[\ln(\alpha h\nu)]/\mathrm{d}(h\nu)$ versus $h\nu$ was plotted (Fig. 2). The discontinuity at a particular energy value gives the band gap, E_{g}. The curves of $\ln(\alpha h\nu)$ vs. $\ln(h\nu - E_{\mathrm{g}})$ were plotted using the E_{g} value to determine the m value from the slope of these curves. A value of about 1/2 has been found (Fig. 3). The graph plots of $(\alpha h\nu)^2$ against the photon energy $h\nu$ for undoped and indium doped $\mathrm{Cd_{0.22}Zn_{0.78}S}$ thin films are shown in Fig. 4. The values of the direct optical band gap $E_{\mathrm{g}}^{\mathrm{d}}$ determined by extrapolating the linear portion of the curves to $(\alpha h\nu)^2 = 0$ are in agreement with those reported in the literature [23, 24]. The optical band gap of thin films increases with the incorporation of indium.

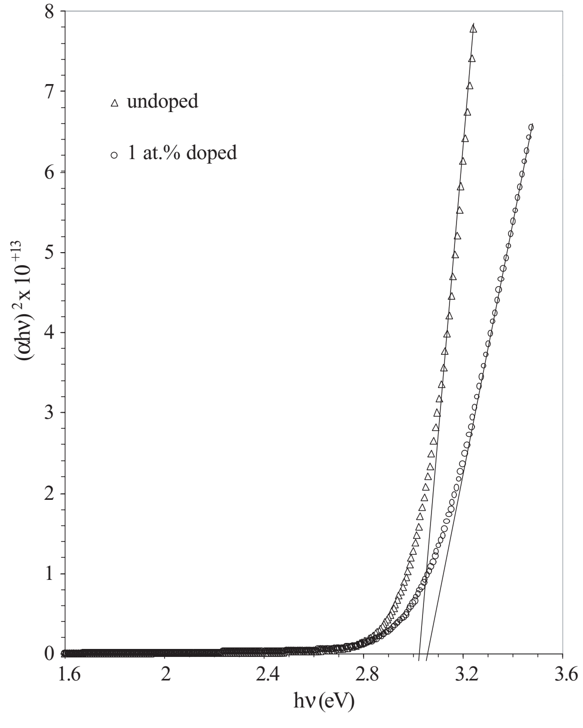

Fig. 4. The plots of $(\alpha h\nu)^2$ vs. photon energy of the undoped and indium doped $\mathrm{Cd_{0.22}Zn_{0.78}S}$ thin films.

The width of the band tail of the films can be estimated by the relation [21]

$$\alpha = \alpha_0 \exp\left(\frac{h\nu}{E_\mathrm{U}}\right), \tag{8}$$

where α_0 is a constant and E_U is the Urbach energy, which is interpreted as the width of the tails of localized states. The Urbach plots of all the films are shown in Fig. 5. In Table 1 the empirical parameter E_U has also been listed. It is seen

Table 1. The direct energy band gaps, Urbach energies and the dispersion parameters for the $\mathrm{Cd_{0.22}Zn_{0.78}S}$ thin films.

Material	E_g^d (eV)	E_U (meV)	E_0 (eV)	E_d (eV)	M_{-1}	M_{-3} (eV)$^{-2}$
Undoped	3.02	195	3.937	4.576	1.162	0.075
1 at.% In-doped	3.05	266	3.783	5.265	1.392	0.097

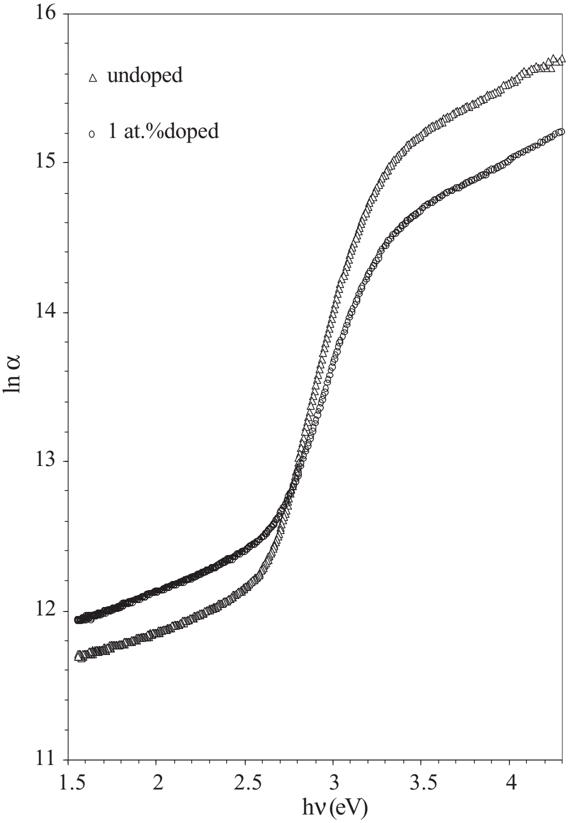

Fig. 5. Urbach plots of all the thin films.

that the values obtained for the undoped thin film are smaller than that of the indium doped thin film. It can be noticed that the band tail width influences with the incorporation of indium.

The calculated values of refractive index (n) and extinction coefficient (k) were plotted as a function of the wavelength as shown in Fig. 6. We also calculated the imaginary and real parts of the dielectric constant as these are directly related to the density of states within the energy gap of the films. The real (ε_1) and imaginary (ε_2) parts of the dielectric constant of the films are respectively shown in Figs. 7a and b. It is seen that both ε_1 and ε_2 decreases with increasing wavelength. The real and imaginary parts follow the same pattern and it is seen that the values of the real part are higher than the imaginary parts. Increasing indium content causes important changes in these optical constants.

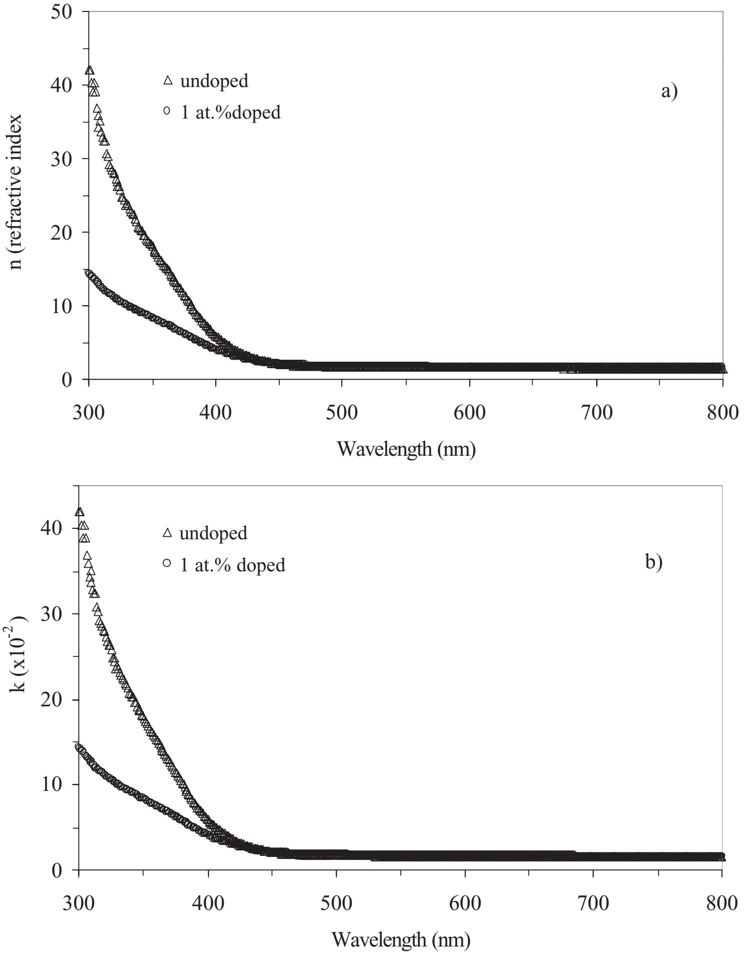

Fig. 6. The variation of refractive index and extinction coefficient with wavelength: a) refractive index, b) extinction coefficient.

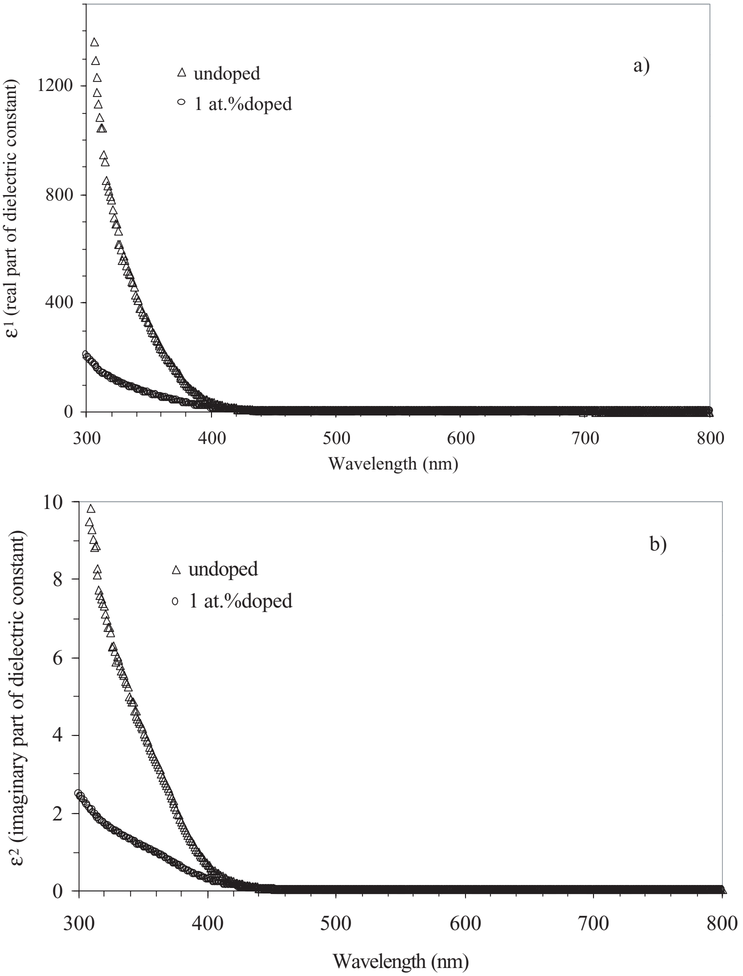

Fig. 7. The variation of real and imaginary part of the dielectric constant with wavelength. a) Real part and b) imaginary part.

The single-oscillator parameters were calculated and discussed in terms of the Wemple–DiDomenico model. The dispersion parameters of various materials were investigated by using this model in the literature [25–27]. This model describes the dielectric response for transitions below the optical gap. It plays an important role in determining the behaviour of the refractive index. The dispersion data of the refractive index can be described by a single-oscillator model [28]:

$$n^2 - 1 = \frac{E_\mathrm{d} E_0}{E_0^2 - (h\nu)^2}\,, \tag{9}$$

where E_0 and E_d are single-oscillator constants. E_0 is the single oscillator energy

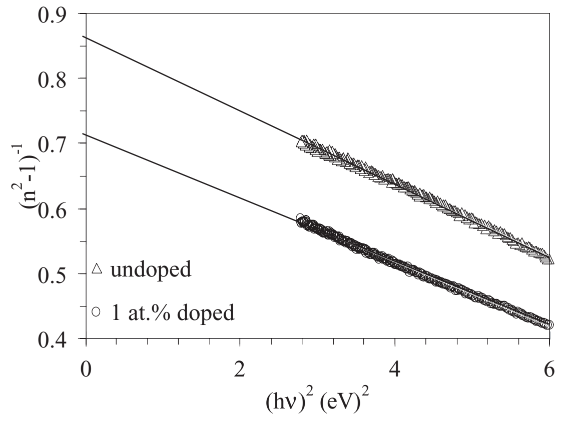

Fig. 8. Plots of $(n^2-1)^{-1}$ vs. $(h\nu)^2$ for undoped and 1 at.% In-doped $Cd_{0.22}Zn_{0.78}S$ thin films.

and E_d is the dispersion energy which is a measure of the strength of interband optical transitions. By plotting $(n^2-1)^{-1}$ versus $(h\nu)^2$ and fitting a straight line shown in Fig. 8, E_0 and E_d are determined directly from the gradient, $(E_0\,E_d)^{-1}$ and the intercept (E_0/E_d), on the vertical axis. The values of the single-oscillator parameters for the indium doped $Cd_{0.22}Zn_{0.78}S$ thin films are given in Table 1. The oscillator energy, E_0 is an average energy gap as pointed out in many references [29–32]. We found that E_0 value of the films is related empirically to the lowest direct band gap by $E_0 \approx 1.3\,E_g$. This relation is in agreement with the obtained relation $(E_0 \approx 1.4\,E_g)$ obtained from the single oscillator model [29]. Also, the long wavelength refractive index (n_∞) for all the thin films was determined from the interception of the vertical axis in Fig. 8. n_∞ values was found to be 1.47 and 1.55 for the undoped and indium doped thin films, respectively. The M_{-1} and M_{-3} moments of the optical spectra can be obtained from the relationships

$$E_0^2 = \frac{M_{-1}}{M_{-3}}\,, \qquad E_d^2 = \frac{M_{-1}^3}{M_{-3}}\,. \tag{10}$$

The obtained values are given in Table 1. It is seen that M_{-1} and M_{-3} moments increase with the incorporation of indium.

4 Conclusion

Undoped and 1 at.% indium doped $Cd_{0.22}Zn_{0.78}S$ thin films have been deposited by the spray pyrolysis method at 275°C substrate temperatures. These spray pyrolyzed thin films show average transmission values are 81% and 77% in the wavelength range (450–800) nm for undoped and 1 at.% indium doped $Cd_{0.22}Zn_{0.78}S$ thin films, respectively. The optical constants such as refractive index (n), extinction coefficient (k), the real (ε_1) and imaginary (ε_2) parts of the dielectric constant of the films were calculated for the films. All of these constants decrease with wavelength. The optical absorption spectra of the films studied show that the absorption spectra mechanism is due to direct transition. The Urbach energies (E_U) were calculated. The optical dispersion (E_0 and E_d) using Wemple–DiDomenico model were also analyzed. In conclusion, the influence of the indium incorporation on optical properties of $Cd_{0.22}Zn_{0.78}S$ thin films is noticeable.

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