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# Temperature dependence of band gaps in sputtered SnSe thin films

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ABSTRACT

Temperature-dependent transmission experiments were performed for tin selenide (SnSe) thin films deposited by rf magnetron sputtering method in between 10 and 300 K and in the wavelength region of 400–1000 nm. Transmission spectra exhibited sharp decrease near the absorption edge around 900 nm. The transmittance spectra were analyzed using Tauc relation and first derivative spectroscopy techniques to get band gap energy of the SnSe thin films. Both of the applied methods resulted in existence of two band gaps with energies around 1.34 and 1.56 eV. The origin of these band gaps was investigated and it was assigned to the splitting of valence band into two bands due to spin-orbit interaction. Alteration of these band gap values due to varying sample temperature of the thin films were also explored in the study. It was seen that the gap energy values increased almost linearly with decreasing temperature as expected according to theoretical knowledge.

## 1. Introduction

Transition metals based chalcogenides are alluring materials in terms of their optical and electrical properties since they provide wide range of electronic transitions between localized and delocalized band states. This property offers convenience to be used in different field of device applications. Binary compounds consisting in transition metals have become important for the optoelectronic and solar cell systems. Thanks to their electronic and optical properties, binary compounds of metal chalcogenides have been greatly investigated by many researchers [1–5]. Tin monoselenide (SnSe) belongs to family of IV–VI group semiconducting materials. It has orthorhombic crystal lattice with parameters of $a = 11.496$ Å, $b = 4.151$ Å and $c = 4.444$ Å and this crystal structure transformed into tetragonal as the higher temperatures are applied below its melting point [6]. The compound exhibits promising physical properties which are useful in various fields such as photovoltaic devices, radiation detectors, Na-ion and Li-ion batteries, supercapacitors, phase-change memory devices, optoelectronics, holographic recording systems and memory switching devices [7–12]. In literature, there are studies on preparation and characterization of SnSe thin films. Some of the preparation methods are flash evaporation [12], thermal evaporation [13], chemical bath deposition [14], chemical vapor deposition [15], hot wall epitaxy [16] and vacuum deposition [17]. Analyses of experiments performed to determine band gaps of SnSe thin films resulted in values between 1.24 and 1.74 eV whereas band gap energy for single crystal structure of the compound was found as 0.95 and 0.90 eV for two different orientations of incident light [17–19]. The wide range of reported gap energies for thin film structures is due to different grown techniques and film thicknesses. Recently, Yao et al. investigated the optical properties of the SnSe by depositing on a sapphire substrate to minimize the effect of substrate on the optical properties [20]. As a result of the absorption analyses, indirect and direct transitions with energies of 0.9 and 1.56 eV, respectively, were found. Due to obtained absorption curve which is relatively associated with the standard AM 1.5 G solar irradiation, authors suggested the SnSe as a significant applicant for harvesting of solar energy [20]. Photoconductivity characteristics of SnSe thin films was also investigated and the existence of continuous distribution of localized states in the band gap was reported by analyzing the photocurrent data [13,17]. The mechanical properties of SnSe single crystals were investigated by means of nanoindentation measurements [21]. Young's modulus and hardness of the crystals were determined as 25.3 GPa and

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0.82 GPa, respectively. Shi et al. published a detailed review paper on SnSe reporting structural, optical, electrical properties, preparation methods and application areas of the compound [11]. The paper also presents various characteristic parameters of bulk, thin film and nanostructure forms of the material.

One of the most significant semiconducting parameters is the band gap energy which takes a very important role in determination of usage fields of materials. Therefore, detailed investigation on characteristics of band gap gets a remarkable importance for possible application areas. Temperature is one of the factors affecting the gap energy since temperature creates change in structures of the compounds. Temperature dependency of band gap energy is tremendously significant for especially two reasons; (i) to understand the fundamental points about getting knowledge on the origin of band gap shrinkage and influence of electron-phonon interaction and phonon dispersion on band gap shrinkage, (ii) to develop semiconducting devices working within a wide temperature range. SnSe semiconducting thin films were explored in terms of their optical properties in many studies. However, to the best of our knowledge, there is no detailed study on temperature dependency of absorption coefficient and so on that of band gap energy of SnSe thin films. In the present study, the effect of temperature applied between 10 and 300 K on the transmittance of the thin film was investigated in the range of 400–1000 nm using UV-VIS spectrophotometer to present a significant knowledge to possible usage areas (especially photovoltaic and optoelectronics) of SnSe. The transmission curves recorded at all studied temperatures were analyzed using both Tauc relation and derivative spectral method. The determined energy values from both techniques were discussed regarding their temperature dependencies. Crystal field and spin-orbit interactions were also discussed to elucidate the nature of band gaps occurring due to valence band splitting.

## 2. Experimental details

SnSe thin films were deposited by RF sputtering technique from high purity 3 inch-diameter compound SnSe sputtering target using Vaksis three magnetron DC/RF sputtering system. Soda-lime glass substrates cleaned ultrasonically before deposition were used through the thin film growth. Deposition process was conducted under conditions of substrate temperature at room temperature and system base pressure of $10^{-6}$ Torr. Sputtering process was performed with deposition rate of around 1.0 Å/sec with a power density of 1.75 W/cm$^2$ and it was conducted by Inficon XTM/2 deposition monitor connected to the quartz thickness crystal inside the vacuum chamber. The deposited thin film thickness was measured electromechanically as 300 nm using Dektak 6M thickness profilometer. X-ray diffraction (XRD) and energy dispersive spectroscopy (EDS) techniques were used to structurally characterize the SnSe thin films. Rigaku Miniflex diffractometer with CuKα radiation (λ = 0.154049 nm) was used to perform XRD experiments in the 20–80° range. The scanning speed of diffractometer was 0.02°/s. EDS experiments were carried out using a ZEISS EVO 15 scanning electron microscope.

Transmission measurements of deposited SnSe thin films were carried out for different sample temperatures in between 10 and 300 K by embedding the sample in the closed cycle helium gas cryostat (Advanced Research Systems, Model CSW 202) which keeps pressure at $10^{-3}$ Torr. Sample temperature was kept constant at the intended value using a temperature controller (Lakeshore Model 331) until the scanning was completed. Shimadzu UV 1201 model spectrophotometer operating with 5 nm resolution was employed for transmittance scanning between 400 and 1000 nm. The normal incidence of light with a polarization direction along the (001) plane was established for transmission measurements. The transmittance was calculated and recorded using a software written in Labview.

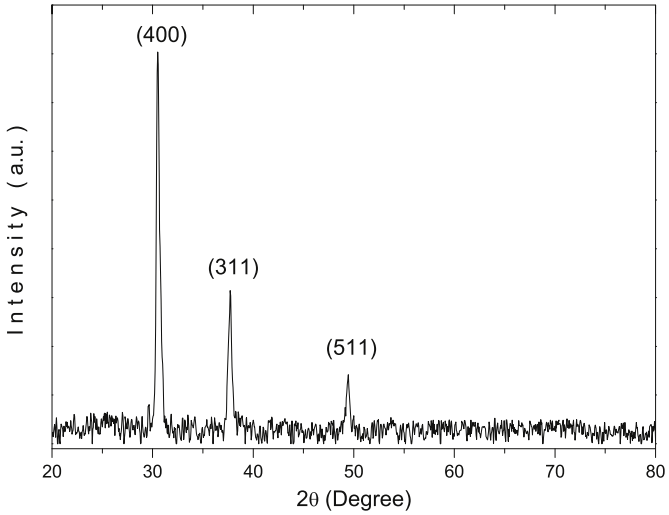


**Fig. 1.** X-ray diffraction pattern of SnSe thin films.

## 3. Results and discussions

### 3.1. Structural properties

The typical XRD diffraction pattern of SnSe thin film is presented in Fig. 1 for the diffraction angle (2θ) range of 20–80°. Three sharp diffraction peaks which sign good crystallinity of the deposited thin films are exhibited in the diffractogram. The peaks appear around at 30.50°, 37.60° and 49.50°. Since there exist insufficient number (three) of peaks in XRD pattern to accomplish reliable indexing and get information about the crystalline structure, it would be worthwhile to utilize the results of previously reported papers. The crystalline structure of the SnSe compound was previously reported as orthorhombic with lattice parameters of $a = 11.501$ Å, $b = 4.153$ Å and $c = 4.445$ Å [22]. The atomic planes corresponding to observed diffraction peaks in the XRD was given in Fig. 1 under the light of reported XRD patterns [23,24] and Joint Committee of Powder Diffraction Standards JCPDS Card No: 89-0236. The atomic compositions of the elements constituting SnSe thin films were determined by EDS analyses. Fig. 2 indicates the EDS spectrum in which peaks related to characteristic x-rays emitted from the constituent elements were observed. The atomic compositions of the elements (Sn: Se) were determined as (49.6 : 50.4) which is consistent with the chemical formula of SnSe.

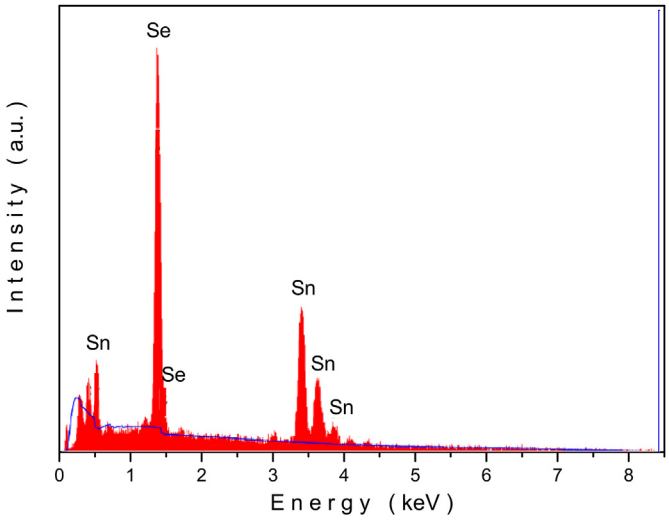


**Fig. 2.** Energy dispersive spectrum of SnSe thin films.

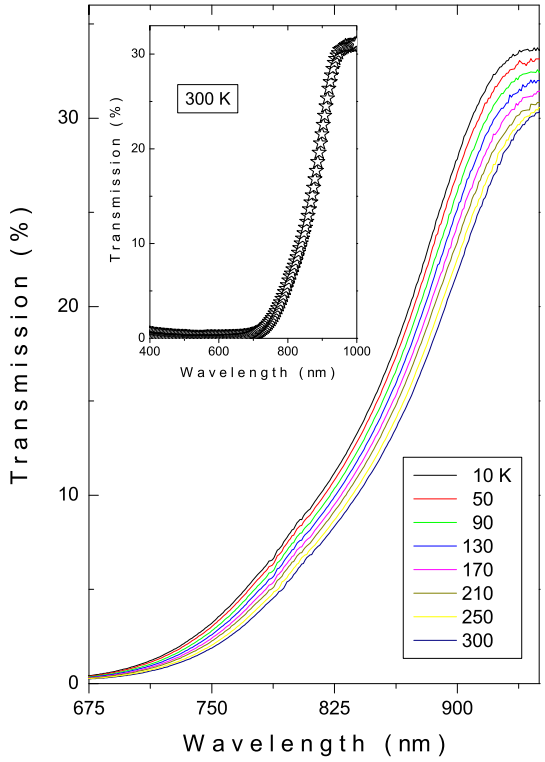


**Fig. 3.** Transmission spectra of SnSe thin films at different temperatures between 10 and 300 K. Inset shows the full spectrum detected between 400 and 1000 nm at 300 K.

### 3.2. Optical properties

Transmittance is an essential phenomenon for a semiconducting material since its behavior reveals absorption rate which provides information about band gap energy. The transmittance value suddenly drops off near the absorption edge due to band-to-band transitions. Therefore, optical band gap energy of a semiconducting materials which is important characteristics for device applications can be found out from the analyses of transmittance spectrum. Temperature dependence of band gap $E_g(T)$ is also significant to fabricate devices operating in a large temperature interval. Fig. 3 indicates the transmission curves of SnSe thin films detected at various temperatures between 10 and 300 K in the active wavelength region of 675–950 nm. Inset of Fig. 3 shows the transmittance of the thin film at room temperature in the wavelength range of 400–1000 nm. It is observed that increasing temperature led to shift of transmission curves at the absorption edge towards higher wavelengths (smaller energies). This behavior indicates that band gap of the thin films decreases with increase of temperature as consistent with theoretical expectations. The corresponding energy band gap values for each transmission curve were found from the variation of absorption coefficient ($\alpha$) depending on the photon energy ($h\nu$). The fundamental equation for $\alpha$ vs. $h\nu$ dependency is given as [25]

$$(\alpha h\nu) = A(h\nu - E_g)^p \quad (1)$$

where $A$ is related to transition probability and $p$ is exponent taking values of either 1/2 for direct transition or 2 for indirect transition. Fig. 4 presents the absorption coefficient variation $(\alpha h\nu)^2$ as a function of incident photon energy ($h\nu$) at various temperatures. As seen, two strong absorption regions (labelled as A and B) within the energy ranges of 1.4–1.5 eV and 1.7–1.8 eV were observed in the Tauc plot. Associated band gap energies were obtained by fitting the linear part of the absorption edges. The interceptions of linear fits on the energy axis yielded energy values of $E_{gA}$ = 1.34 eV and $E_{gB}$ = 1.56 eV at 300 K (Insets of Fig. 4a and b). As the same analysis were achieved for the data obtained at 10 K, the band gap energy values were found to be 1.38 and 1.60 eV for $E_{gA}$ and $E_{gB}$, respectively. Explicit change of energy values between room temperature and 10 K revealed the extension of the band gap with decreasing temperature.

For the reliability of the absorption coefficient method, derivative spectral analyses were also accomplished for the transmission curves recorded for all temperatures. According to this method, first derivative of the transmittance spectrum ($dT/d\lambda$) as a function of wavelength generates peaks with maxima at wavelengths corresponding to band gap energies [26,27]. Fig. 5 illustrates the gradient of the transmission spectra with variation of wavelength in the range of 650–950 nm. It can be deduced from the figure, the curve maximum positions shift to higher wavelengths as the temperature increased from 10 to 300 K. From the analysis of the derivative spectral method, the band gap energies were calculated as $E_{gA}$ = 1.38 eV and $E_{gB}$ = 1.57 eV at 300 K. The analysis for the derivative curves at 10 K resulted in energy values of $E_{gA}$ = 1.40 eV and $E_{gB}$ = 1.61 eV. The similar extensions of the band gap values were indicated from the derivative analyses. The extracted energy values from applied two methods were consistent with each other with negligible variations. Moreover, when the relation of band gap energy-solar cell efficiency was taken into consideration, it is seen that the revealed band gap energies of SnSe thin films are suitable for photovoltaic applications. According to Shockley–Queisser limit, maximum efficiency occurs for gap energy value of ~1.4 eV [28]. When the thickness dependency of gap energy of SnSe thin films was kept in mind, optimum thickness value of the films may be considered around 300 nm [18].

Alterations of band gap values obtained from both Tauc relation and first derivative techniques with applied temperatures between 10 and 300 K are shown in Fig. 6a and b for $E_{gA}$ and $E_{gB}$, respectively. As seen from the figures, the band gap energies decreased almost linearly as the thin film temperature was increased to room temperature. The variation of gap energy with temperature was explained by two mechanisms; (i) shift in relative position of conduction and valence bands due to expansion of lattice by temperature, (ii) shift in relative position of these bands due to electron-lattice interaction which is affected by temperature [29]. Similar behavior of the band gap was observed also in single crystal form of SnSe [30]. The band gap energy and temperature coefficient of SnSe single crystals were found as 0.95 eV and $-5.4 \times 10^{-4}$ eV/K, respectively. Our revealed energy values for thin films are larger than that of single crystal. This behavior is consistent with theoretical fact that gap energy increases with decrease in size due to quantum confinement effect [8]. The temperature-dependent gap energy behavior was previously investigated for various IV–VI semiconducting compounds [31–33]. Although the gap energy may significantly change according to elements consisting in IV–VI semiconductor, temperature coefficient values get closer values. As an example, temperature coefficient of SnS and SnTe compounds were reported as $-1.3 \times 10^{-4}$ eV/K [33] and $-2.6 \times 10^{-4}$ eV/K [32], respectively. The experimental variations of band gap values obtained from both methods were well-fitted and corresponding straight lines were depicted in the figures. The variation rates of the band gaps with temperature procured from the slopes of the straight lines were given in Table 1.

Here, the band gap energies $E_{gA}$ and $E_{gB}$ found from mentioned techniques need to be elucidated in terms of their origin of existences. To that end, the analyses results of our study were compared with the reported values by different studies on tin selenide thin films with different thickness [18,20]. Kumar et al. [18] investigated the optical properties of SnSe thin films and they found that the direct band gap of the material increased from 1.24 to 1.74 eV as the film thickness was decreased from 500 to 150 nm, respectively. Also, the direct band gap of 1.56 eV was reported for SnSe thin films deposited on sapphire substrate by Yao et al. [20]. As compared with the results of these studies, the $E_{gB}$ value found around 1.56 eV in our study shows well consistency. However, the band gap energy value around 1.34 eV

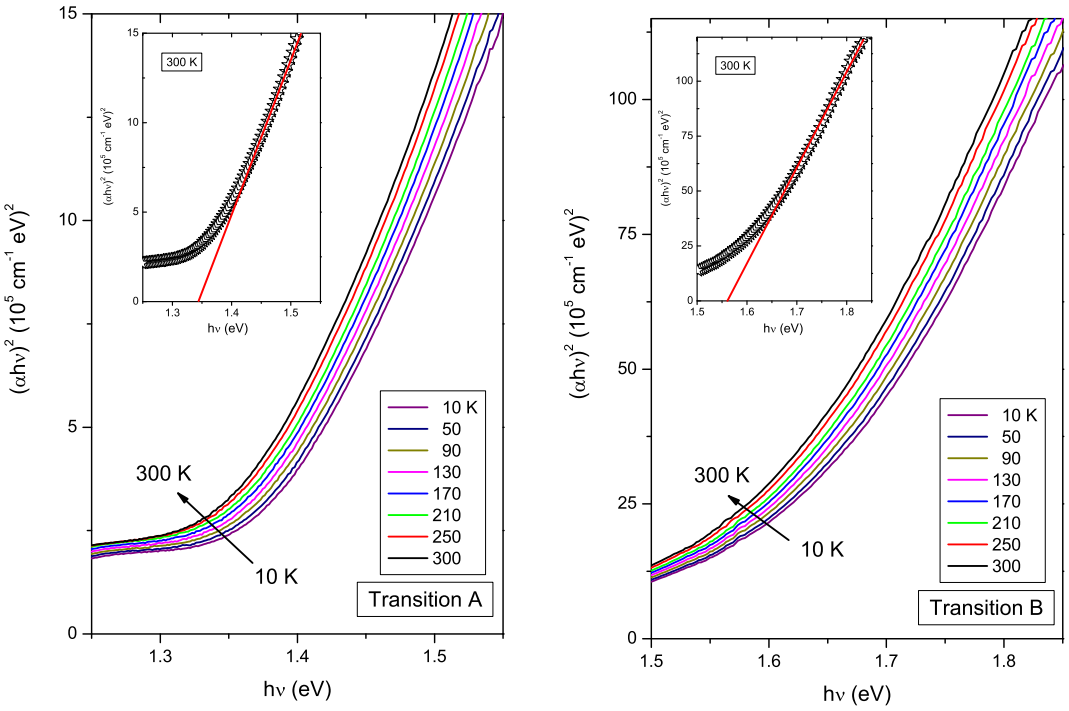


**Fig. 4.** $(ahv)^2$ vs. $hv$ plots in the absorption regions of (a) 1.25–1.55 eV and (b) 1.50–1.85 eV at various temperatures. Insets indicate the analyses according to Eq. (1) for room temperature data. Stars are experimental data and solid lines are fitted straight lines.

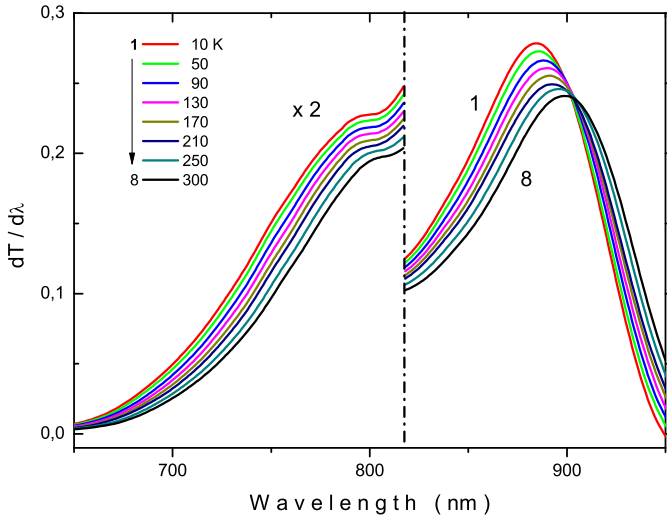


**Fig. 5.** Temperature dependent plots of $dT/d\lambda$ vs. λ of SnSe thin films.

(labelled as $E_{gA}$) was not observed in the above compared experimental studies. At this point, we referred to theoretical studies on modelling the band structure of SnSe which were achieved by the density-functional theory [34,35]. Makinistian and Albanesi [34] used full potential linearized augmented plane waves method in order to determine the optimal position of the band gap in SnSe. They revealed the band structure by including the spin-orbit interactions in their calculations and they asserted that s-p hybridization of valence band must be taken into account for the band structure of SnSe. Zhu et al. [35] reported a study concerning s-p orbital interactions and spin-orbit coupling causing band degeneracy. They proposed that s-p interaction and spin-orbit coupling are strongly responsible for convergence of carrier pockets for IV–VI semiconducting chalcogenides. In literature, there are many studies revealing the interband transitions take place via splitted energy levels in chalcopyrite, zincblende, wurtzite and rock-salt structures [36–39]. Therefore, spin-orbit and crystal field interactions may dominate the formation of band structure of SnSe thin films due to s-p hybridization of localized bands. In order to elucidate the effect of spin-orbit and crystal-field interactions, we employed the following relation

$$E_{1,2} = -\frac{1}{2(\Delta_{CF} + \Delta_{SO})} \pm \frac{1}{2}\left((\Delta_{CF} + \Delta_{SO})^2 - \frac{8}{3(\Delta_{CF}\Delta_{SO})}\right)^{1/2}. \quad (2)$$

Here, $E_1$ and $E_2$ are energy differences determined as $E_1 = E_B - E_A$ and $E_2 = E_C - E_B$ where $E_A$, $E_B$ and $E_C$ are band gap energies. $\Delta_{SO}$ and $\Delta_{CF}$ are spin-orbit and crystal-field parameters. When revealed band gap energies of SnSe thin film and spin-orbit parameter −0.24 eV reported in Ref. [35] were used in Eq. (2), third band gap energy value was found as 0.96 eV. $\Delta_{CF}$ was also calculated from the equation as 0.47 eV. Unfortunately, the calculated band gap energy 0.96 eV, which corresponds to wavelength of ~1290 nm, was not observed in the transmittance curves due to the limited spectral range of measurement device (400–1000 nm). As a result of comparative studies, the band structure of tin selenide thin films is thought to be dominated by existences of the spin-orbit and crystal field interactions most probably due to s-p hybridization which is mostly shown in IV–VI semiconducting chalcogenides.

## 4. Conclusion

As one of the significant optical characteristics of semiconducting SnSe thin films, the band gap phenomenon was studied by means of transmittance measurements carried out in the wavelength range of 400–1000 nm for various applied temperature between 10 K and room temperature. Moreover, structural properties were determined by means of x-ray diffraction and energy dispersive spectroscopy techniques. EDS analyses pointed out that chemical formula of the deposited thin films corresponds to SnSe. The XRD analysis revealed that deposited SnSe films are in polycrystalline nature with the main intense reflection along the (400) direction corresponding to the orthorhombic structure. The transmittance spectra was analyzed in the strong absorption regions utilizing Tauc and first derivative spectroscopy methods to reveal the band gap energy of the material. Analyses results

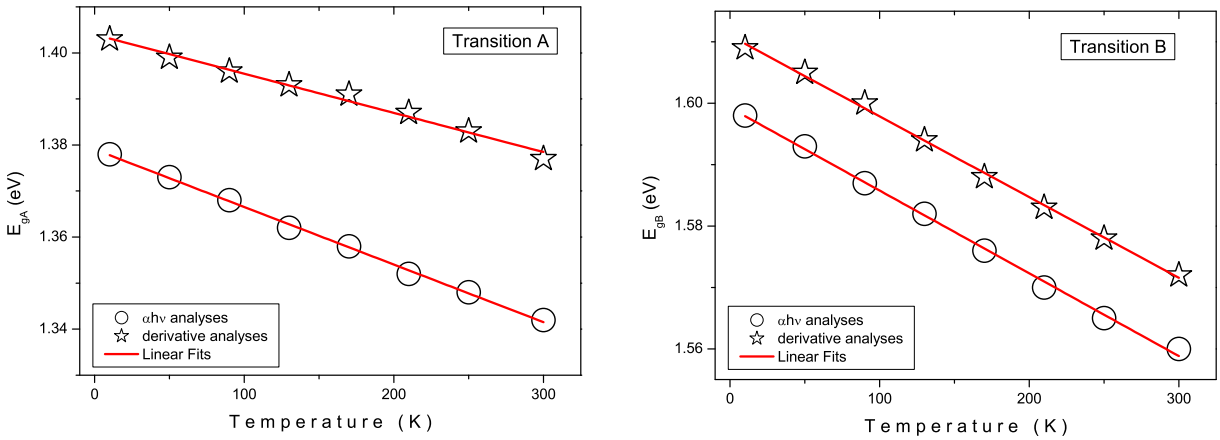


**Fig. 6.** The variations of (a) $E_{gA}$ and (b) $E_{gB}$ as a function of applied temperature for obtained data from both methods. Solid lines indicate the linear fitted lines.

**Table 1**
Optical parameters of SnSe thin films obtained under the light of two different analysis methods.

| Transition | Analysis method | $E_g$ (eV) | | $dE_g/dT$ (eV. K$^{-1}$) |
|---|---|---|---|---|
| | | 300 K | 10 K | |
| A | Absorption | 1.34 | 1.38 | $-1.25 \times 10^{-4}$ |
| | Derivative Spectroscopy | 1.38 | 1.40 | $-0.85 \times 10^{-4}$ |
| B | Absorption | 1.56 | 1.60 | $-1.35 \times 10^{-4}$ |
| | Derivative Spectroscopy | 1.57 | 1.61 | $-1.31 \times 10^{-4}$ |

of both methods were in good agreement with the presence of two band gap energy values around $E_{gA} = 1.34$ eV and $E_{gB} = 1.56$ eV. These revealed gap energies and high absorption coefficient make SnSe semiconducting compound a possible material for optoelectronic device and solar cell applications. Nature of existence of two band gaps was thought to arise from spin-orbit splitting due to s-p hybridization of valance band. Temperature dependencies of the revealed band gaps were also investigated and it was indicated that the band gap values increased almost linearly to 1.38 eV for transition A and 1.60 eV for transition B at 10 K.

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