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# Annealing-induced phase transformation in $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$ thin films and its structural, optical and morphological changes for optoelectronic applications†

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$\text{In}_2\text{Se}_3$  and  $\text{In}_2\text{Te}_3$  have great importance in various device fabrications. The present report is based on the annealing-induced phase formation of both  $\text{In}_2\text{Se}_3$  and  $\text{In}_2\text{Te}_3$  from  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films at different annealing temperatures as found from the XRD analysis and well supported by the Raman study. The average crystallite size increased with a decrease in the dislocation density. The surface morphology changed with annealing and increased in particle size as noticed from the FESEM images. The uniform distribution and presence of constituent elements in the film were verified using EDX data. The increase in transmittance is accompanied by a decrease in extinction coefficient, optical density and increase in skin depth with annealing. The increase in optical bandgap from 0.418 eV to 0.645 eV upon annealing at 250 °C is associated with a decrease in disorder. The steepness parameter increased and the  $S_{\text{e-p}}$  value decreased with annealing. The refractive index decreased with an increase in oscillator energy and decrease in dispersion energy. The quality factor, dielectric loss, optical conductivity and electrical susceptibility decreased. The optical electronegativity and plasma frequency increased with annealing. There is a significant change in the non-linear susceptibility and non-linear refractive index with annealing. The observed changes in the film structure and optical behaviour are due to the annealing-induced phase formation from the  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  host matrix upon annealing. Such materials are suitable for optoelectronic and phase change devices.

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## 1. Introduction

The large transparency window in IR regions by Te- and Se-doped chalcogenide films is important owing to their applications in phase change memory devices, photodetectors, photovoltaics, solar cells, infrared detectors, *etc.*<sup>1–5</sup> Se-based materials are used for imaging and biomedical applications, whereas Te-based materials are used for infrared detectors and phase-change memory devices.<sup>6</sup> Se-based chalcogenide compounds possess high transmission ability in the mid and far IR range and possess strong non-linearity.<sup>7</sup> Se-based materials have advantages such as low melting point, low thermal conductivity, and stability, and they possess the property of easy formation of compounds with doping elements.<sup>8,9</sup> Similarly, Te has unique properties for cutting-edge technologies with chalcogenides.<sup>10</sup> The high transmittance in the far infra-red regime is used for IR optics and optical fibers.<sup>11,12</sup> The ultrafast

crystallization of Te-based materials is used in phase change optical data storage devices.<sup>13–16</sup> Binary compounds based on Te–Se alloys have been studied widely because they have fast access to information, great storage capacity, and electro photographic applications, such as laser printing and photo-receptors in photocopying.<sup>17,18</sup> Se–Te binary compounds have more advantages than pure Se because of their greater hardness, high photosensitivity, higher crystallization temperature, and low aging effects. The thin film forms of Se–Te compounds are promising owing to their wide applications.<sup>19</sup> Se–Te alloys are prime candidates for thermoelectric power, and many semiconducting chalcogenide compounds have been reported for the direct energy conversion of thermal to electrical energy.<sup>20,21</sup> Thermally evaporated  $\text{Se}_x\text{Te}_{1-x}$  thin films with tuneable energy gaps are used for high-performance SWIR photodetector fabrication.<sup>2</sup> The additive of metallic components to the Se–Te matrix has led to high thermal stability.<sup>17</sup> The introduction of In into either Te or Se is very attractive for various applications.

$\text{In}_2\text{Te}_3$  is a layer III–IV type material that is sensitive to strain and pressure and is used for superconductor applications.<sup>22</sup> The  $\alpha\text{-In}_2\text{Te}_3$  films have stable photo switching ability ranging from 370–1064 nm with a short response time of 15 ms. The good

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figure-of-merit, stability and broad spectral range of  $\alpha$ - $\text{In}_2\text{Te}_3$  are used for next-generation photo detectors.<sup>23</sup>  $\text{In}_2\text{Te}_3$  is having a direct band gap of  $\sim 1.1$  eV with a high absorption coefficient value of over 500–2500 nm, which makes it a suitable absorber layer in photovoltaic cells.<sup>24,25</sup>

Similarly,  $\text{In}_2\text{Se}_3$  has shown attractive properties and great potential in the applications of ferroelectric devices.<sup>26</sup> The leveraging of the semiconducting and ferroelectricity nature of  $\alpha$ - $\text{In}_2\text{Se}_3$  and ferroelectric semiconductor field-effect transistors (FeSFETs) are made for neuromorphic instruments for brain-inspired intelligent systems.<sup>27</sup> The  $\beta$ - $\text{In}_2\text{Se}_3$  nanosheets are a type of indirect band gap semiconductors with  $E_g$  of  $\sim 1.55$  eV. Single nanosheet photodetectors possess fast response times and high photoresponsivity.<sup>28</sup> The facile integration, patterning, and packaging of high-quality 2D chalcogenide  $\text{In}_2\text{Se}_3$  are used for wearable electronics, next-generation photodetector arrays, and integrated optoelectronic circuits.<sup>29</sup> However, ternary compounds with In–Se–Te are of great importance in research.

In–Se–Te-based ternary alloys have various structural changes, such as  $\beta$  and  $\alpha$  phases, and vacant of In sub-lattices for one-third or two-third for other dopant impurities. Therefore, the appearance of the In–Se and In–Te phases from the phase diagram infers the formation of  $\text{In}_2\text{Se}_3$  and  $\text{In}_2\text{Te}_3$  phases. Among them, indium-doped Se–Te alloys have found great importance in various devices because of their enhanced optical properties.<sup>30</sup> Elkatlawy *et al.* prepared  $\text{Se}_{80}\text{Te}_{20-x}\text{In}_x$  thin films with different compositions and revealed that In doping  $\text{Se}_{80}\text{Te}_{20-x}\text{In}_x$  improved the transmittance range and refractive index in visible and near IR regions.<sup>31</sup> Saxena *et al.* reported an increase in thermal conductivity and thermal diffusivity in  $\text{Se}_{80}\text{Te}_{20-x}\text{In}_x$  bulk with indium addition.<sup>32</sup> Se–Te–In ternary compounds have wide applications in photoreceptors, optical recording media, xerography, infrared spectroscopy, and laser fiber techniques.<sup>33,34</sup> Such ternary compounds under different energy treatments, such as laser irradiation, ion irradiation, thermal annealing, proton and irradiation, show profound property modifications, which are useful for many applications.<sup>35–38</sup>

The  $\text{In}_2\text{Se}_3$  band gap is found to be reduced by annealing for the increase in the width of localized states near the band edges. The change in film density reduced the transmittance and increased the absorption, making it suitable for solar cell applications.<sup>39</sup> The reduction in the band gap in  $\text{Se}_{75-x}\text{Te}_{25}\text{In}_x$  with annealing is a good one because of the material to be used in optical storage.<sup>40</sup> Thermal annealing on  $\text{Se}_{80}\text{Te}_{20-x}\text{In}_x$  thin films changed the structure from amorphous to crystalline with annealing temperature and an increase in refractive index with a reduction in bandgap with annealing time duration.<sup>41</sup> By considering the importance of thermal annealing, this study is based on the thermal annealing of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films at various temperatures.

The prime objective of the study is to observe (i) the thermal annealing-induced structural changes in  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films at various annealing temperatures, (ii) the change in linear-nonlinear optical properties and (iii) morphological changes due to phase transformation in the films. The prepared film samples were thermally annealed at the following temperatures:

100, 150, 200, and 250 °C. X-ray diffraction (XRD) confirms the structural properties, which are strongly corroborated by performing Raman analysis. Field emission scanning electron microscopy (FESEM) was used for the surface morphology imaging. The composition of the films was confirmed by energy dispersive X-ray analysis (EDX). The optical parameters of the annealed  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films were analysed using UV-Visible spectroscopy.

## 2. Experimental

### 2.1. Thin film preparation

The bulk  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  samples were prepared using high pure In, Se, Te (Sigma Aldrich, 99.999%) elements by applying the melt quenching method. The required chemical amounts were sealed at a vacuum of  $10^{-5}$  Torr inside the quartz ampoule and placed inside a furnace at 500 °C for 30 h. The melt formed inside the ampoule was quenched rapidly in liquid nitrogen to obtain the bulk  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  sample. From the prepared bulk sample,  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films were deposited by employing the thermal evaporation method using an HHV (Smart Coat 3) vacuum coating unit.

About 800 nm thickness of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films was deposited on clean substrates (corning glass) at a rate of 5 Å per second. During the whole deposition process, the pressure inside the deposition chamber was maintained at  $\sim 5 \times 10^{-5}$  Torr, and the substrate temperature was kept at room temperature. The substrate holder was rotated slowly to obtain a homogeneous and uniform film. The film thickness was controlled by the filament current using the current-controlling unit. A crystal sensor is fixed in the deposition chamber to measure the film thickness, which is recorded and displayed on the digital thickness monitor. The thin films were annealed for 1.5 hours at 100, 150, 200, and 250 °C in a hot air oven.

### 2.2. Characterization

The structural properties were studied using a Bruker D8 Advance XRD unit with Cu  $K_\alpha$ -radiation of wavelength  $\lambda = 1.5418$  Å. The XRD data were recorded with a step size of  $0.02^\circ \text{ s}^{-1}$  for the range from  $2\theta = 10^\circ$  to  $70^\circ$ . The change in vibrational mode was determined from Raman spectroscopy (LabRAM HR system) using a 532 nm argon laser source with a CCD detector in backscattering mode. The spectra were recorded from the 50–400  $\text{cm}^{-1}$  range. The spectra calibration was done using the silicon 520  $\text{cm}^{-1}$  line, and 3–4 measurements were taken after calibration at different positions for the same time intervals (40 seconds) to minimize the systematic error. Furthermore, the morphology was imaged using an FESEM (JEOL-JSM-7610F) unit, and the ratio of elemental composition was observed from the EDX unit attached to the FESEM unit. The imaging was done at a voltage of 20 kV during the characterization process.

The transmittance and absorbance spectra of as-prepared and annealed  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films were recorded from the JASCO V-770 UV-Visible spectrophotometer in the wavelength range of 500–2500 nm. The linear and non-linear optical



properties were calculated from the transmission data using various relations.

### 3. Results and discussion

#### 3.1. Structural study by XRD and Raman spectroscopy

The XRD pattern of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  (as-prepared and annealed) thin films is shown in Fig. 1a, which confirms the crystalline nature with the appearance of  $\text{In}_2\text{Te}_3$ ,  $\text{In}_4\text{Se}_3$ , and  $\text{In}_4\text{Te}_3$  phases in the films. The as-prepared film showed crystalline peaks at  $23.95^\circ$  (5 1 1) and  $41.13^\circ$  (8 2 2), corresponding to the cubic phase of  $\text{In}_2\text{Te}_3$  phase (ICSD: 33-1488) and a peak at  $29.46^\circ$  (0 4 0) representing the orthorhombic  $\text{In}_4\text{Se}_3$  phase (ICDS: 48-1575). Among these three crystalline peaks, the former two peaks remain intact with intensity and position. However, the peak intensity of the  $\text{In}_4\text{Se}_3$  peak becomes more intense and prominent with annealing, which is possibly due to thermal energy through annealing. Furthermore, annealing of the  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films results in the appearance of additional peaks at  $23.41^\circ$  (0 1 1) and  $48.56^\circ$  (8 0 0), corresponding to the same orthorhombic  $\text{In}_4\text{Se}_3$  phase (ICDS: 48-1575). The crystalline peaks at  $28.76^\circ$  (3 1 1),  $44.65^\circ$  (3 5 1), and  $51.11^\circ$  (7 3 1) present the orthorhombic  $\text{In}_4\text{Te}_3$  phase (ICDS: 01-071-2085), respectively. It is noteworthy that the intensity, peak number, and sharpness of the peaks are enhanced with annealing, which ensures increased crystallinity through the formation of large crystallites, as confirmed by several studies.<sup>42,43</sup> The formation of more binary In-chalcogen phases might be due to the sufficient kinetic energy of indium, which allows more diffusion of indium with chalcogen lattices (here selenium and tellurium), with annealing temperature and forms bonds with Se and Te atoms.<sup>44</sup> In other words, the defects and unsaturated bonds are annealed out by forming many saturated bonds at boundaries with an increased annealing temperature. Such bonds cause structural variation in annealed  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  films.

Based on the XRD pattern, the average crystallite size ( $D$ ) calculated from the full-width half maxima (FWHM) observed prominent peaks using Scherer's equation:<sup>45</sup>

$$\text{Crystallite size } (D) = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where ' $\lambda$ ' is the Cu  $K_\alpha$ -line wavelength ( $1.54 \text{ \AA}$ ),  $\theta$  is the incidence angle, and  $\beta$  is the FWHM that infers the structural broadening. The  $\delta$  (dislocation density),  $\epsilon$  (lattice strain), and the number of crystallites per unit surface area ( $N_c$ ) were evaluated using the following equations:<sup>46</sup>

$$\text{Lattice strain } (\epsilon) = \frac{\beta \cot \theta}{4}, \quad (2)$$

$$\text{Dislocation density } (\delta) = \frac{1}{D^2}, \quad N_c = \frac{t}{D^3}, \quad (3)$$

where  $t$  has a value of  $\sim 800 \text{ nm}$  (film thickness). The evaluated structural parameters for the different films are presented in Table 1. The ' $D$ ' value increased with annealing for the coalescence of smaller grains. The formed  $\text{In}_2\text{Te}_3$  and  $\text{In}_4\text{Se}_3$  crystallized phases in the as-prepared film possibly act as nucleation points for the heterogeneous growth of other phases at different annealing temperatures.<sup>47</sup> Simultaneously, the  $\delta$  and  $\epsilon$  values decreased, confirming the increase in crystallinity with annealing. The +ve value of residual strain implies that the tensile strain in the film developed owing to the difference in the thermal expansion coefficient of the deposited film and substrate. The  $N_c$  value decreased with annealing temperature because of the change in structure for the coalescence of smaller crystallites.<sup>48</sup>

Table 1 Structural parameters of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films

Structural parameters	$D$ (nm)	$\delta \times 10^{15}$ ( $\text{m}^{-2}$ )	$\epsilon$	$N_c$ ( $\text{nm}^{-2}$ )
As-prepared	9.55	0.0109	0.014	0.91
Annl 100 °C	12.90	0.0060	0.011	0.37
Annl 150 °C	13.17	0.0057	0.010	0.35
Annl 200 °C	14.43	0.0047	0.008	0.26
Annl 250 °C	18.68	0.0028	0.005	0.12

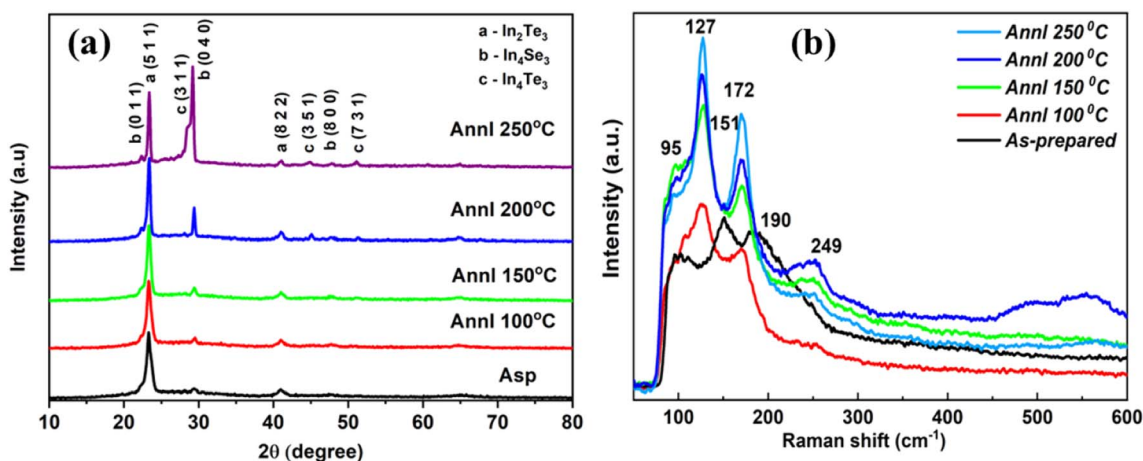


Fig. 1 (a) XRD pattern and (b) Raman spectra of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films.

Raman spectroscopic analysis is an effective method for studying the structural aspects of non-crystalline compounds. The nature of the chemical bonds, atomic arrangements, and structural changes in vibrational levels induced by external energy were viewed through Raman analysis. The Raman data of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin film are presented in Fig. 1b, which depicts different peaks ranging from 50 to  $600\text{ cm}^{-1}$  for the as-prepared and annealed films. The as-deposited  $\text{In}_{10}\text{Se}_{70}\text{Te}_{10}$  thin film has peaks at 95, 151, and  $190\text{ cm}^{-1}$ , corresponding to the In-Se phase.<sup>49–51</sup> Annealing led to the appearance of extra peaks at 127, 172 and  $249\text{ cm}^{-1}$  with variation in intensity. The peak at  $127\text{ cm}^{-1}$  is related to the  $\gamma\text{-In}_2\text{Se}_3$  phase.<sup>51</sup> The latter two Raman peaks were attributed to the Te-Te<sup>52</sup> bond vibration and  $\text{Se}_n$  rings.<sup>50,53</sup> The intensity increase in the Raman peaks and low shift towards higher wavenumbers with annealing might be due to annealing-induced structural changes inside the matrix.

### 3.2. Morphology study using FESEM and EDX

For imaging the microstructure and morphology study of any material, FESEM is one of the most important tools. The morphological structure of the  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  (as-prepared and annealed) thin films was analysed by FESEM images, as shown in Fig. 2. The morphological images at a scale of 200 nm illustrate the uniformity of the films. The annealing-induced morphological changes were clearly observed in the granular structure of the annealed films. The particle size was calculated using ImageJ software (version-Java 1.8.0\_172), with statistical analysis, as presented in Fig. 3. With an increased annealing temperature, the average particle size increased, as demonstrated in Fig. 3.

Elemental analysis was performed using EDX, which showed the presence of In, Te, and Se components (Fig. 4) in the annealed and as-prepared films. The distinct peaks refer to the relevant components, and the composition of the various samples is closely the same within a 2% error of the estimated one. The uniform distribution of constituent elements through elemental mapping obtained from EDX for the as-deposited  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  film is shown in Fig. 5, and the  $250^\circ\text{C}$  annealed film is shown in ESI Fig. S1.†

### 3.3. Optical property study

**3.3.1. Transmittance, optical density, extinction coefficient and skin depth.** The variation in transmittance with wavelength for  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  (both in as-prepared and annealed) thin films is presented in Fig. 6a, which infers an increase in transmission power upon annealing. The transmittance value increased from 35% (as-prepared) to 76% for the  $250^\circ\text{C}$  annealed film at a 1900 nm wavelength. This increase in the transmittance value is due to the increase in crystallinity with annealing.<sup>54</sup> The enhanced transmission is also owing to the decrease in surface scattering with annealing.<sup>55,56</sup> The transparency is found to be more in the infrared region, which allows such films for potential use in infrared systems, such as fiber optics.<sup>57</sup> The observed interference pattern in the film is due to the interference between the substrate and film surface.

The optical absorbance provides valuable information related to the bandgap and band structure of both crystalline and amorphous materials. There is a shift in the absorption edge to the lower wavelength side, which is due to the thermal bleaching effect, thus inferring an increase in bandgap energy

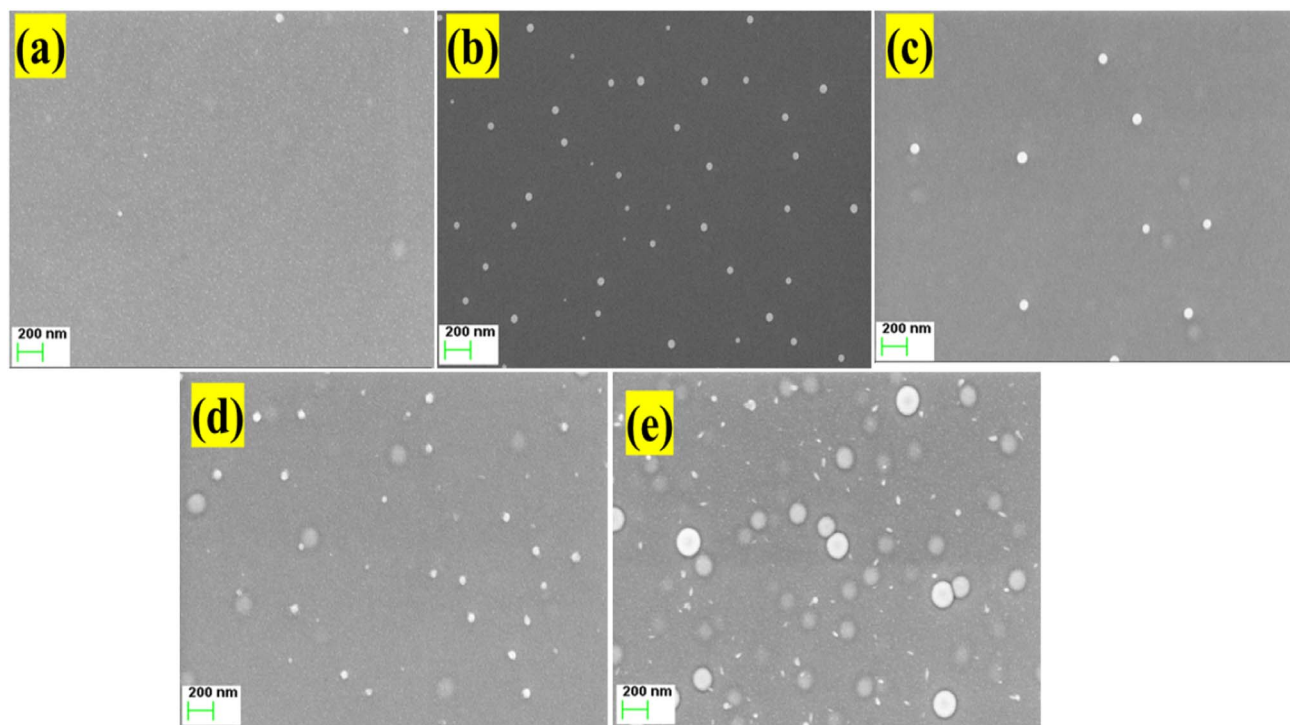


Fig. 2 FESEM images for surface morphological analysis of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films.





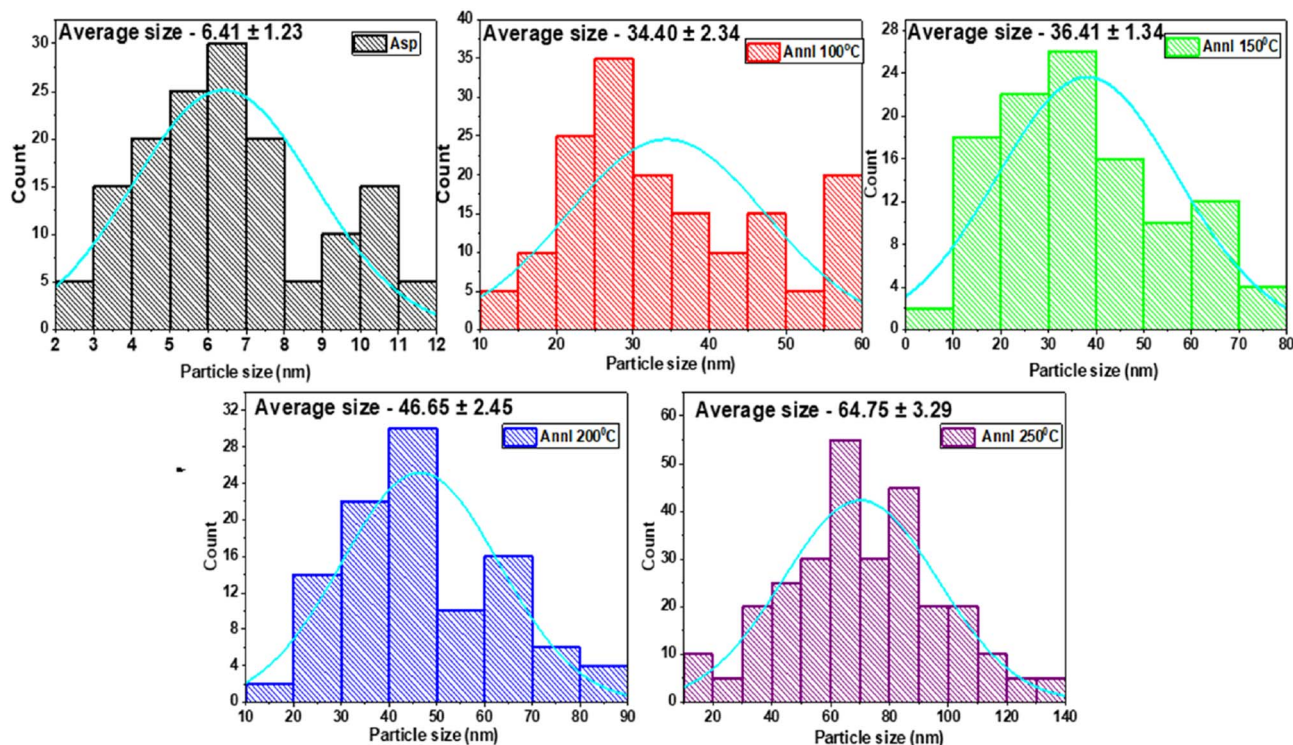


Fig. 3 Particle size distribution of the  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films.

with annealing.<sup>58</sup> The optical absorption edge appears because of the electronic transition in the semiconductor.<sup>58,59</sup> Here, the absorption edge region lies in the range of 750–1200 nm, and the coefficient ( $\alpha$ ) was determined from the absorbance value using the following equation:

$$\alpha = \frac{\text{absorbance}}{\text{thickness}} = \frac{A}{t}, \quad (4)$$

where 'A' and 't' are the absorbance and film thickness, respectively. The absorption coefficient measures the rate of reduction in electromagnetic radiation intensity while

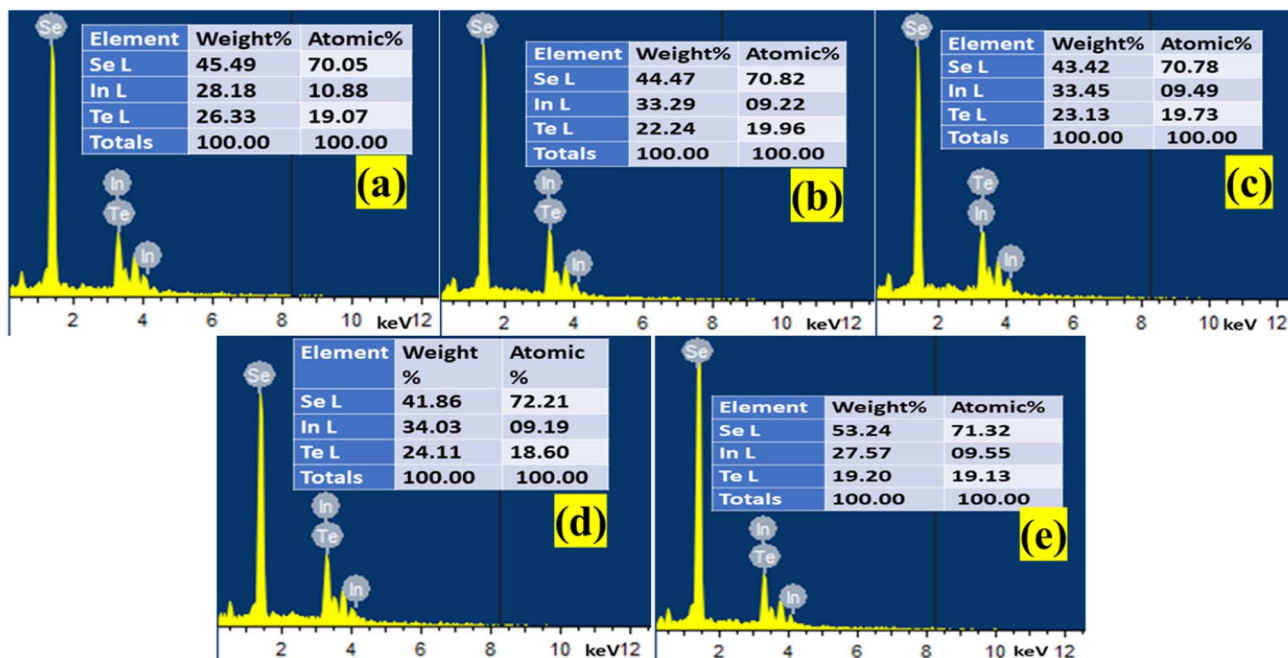


Fig. 4 EDX spectra for compositional analysis of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films.

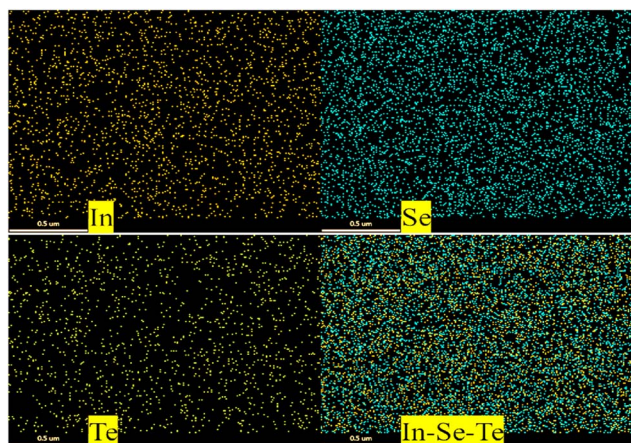


Fig. 5 EDX mapping of the elements in the as-prepared  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  film.

penetrating through a material medium. The greater the absorption of light by the material, the higher the absorption coefficient.<sup>59</sup> The change in ' $\alpha$ ' with wavelength under various annealing conditions is shown in Fig. S2.† The ' $\alpha$ ' values are in the order of  $10^4 \text{ cm}^{-1}$ , which decreased with annealing and increased with photon energy. The presence of such absorption

edges makes them a potential candidate for optical filter materials.<sup>60</sup>

Thermal annealing at and above  $T_g$  minimizes the structural imperfections, resulting in few available states for photon absorption within the band gap. The local structure in the film changes because of the bond breaking and rearrangements due to annealing. This results in a shift in the absorption edge and substantial reconfiguration at the atomic and molecular levels, ultimately changing the optical parameters of the film.<sup>61</sup>

The extinction coefficient ( $k$ ) represents the polarization ability of the material, which is dependent on ' $\alpha$ ' using the following formula:<sup>56</sup>  $k = (\alpha\lambda/4\pi)$ . The ' $k$ ' infers the interaction between the electric field of the incident waves and the film. The ' $k$ ' value decreased with wavelength, as shown in Fig. 6b for the annealed and as-deposited one. This behaviour is owing to the decrease in ' $\alpha$ ' with an increase in ' $\lambda$ '. The heat treatment annealed out the unsaturated defects and produced a large number of saturated bonds after annealing. The density of the localized state change because annealing modifies the ' $k$ ' value.<sup>62</sup> The as-prepared  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  sample showed crystallinity with the appearance of  $\text{In}_2\text{Te}_3$  and  $\text{In}_4\text{Se}_3$  phases. The increase in the annealing temperature led to an increase in crystallinity. This might be due to the annealing process that provides sufficient energy to the atoms, enabling them to

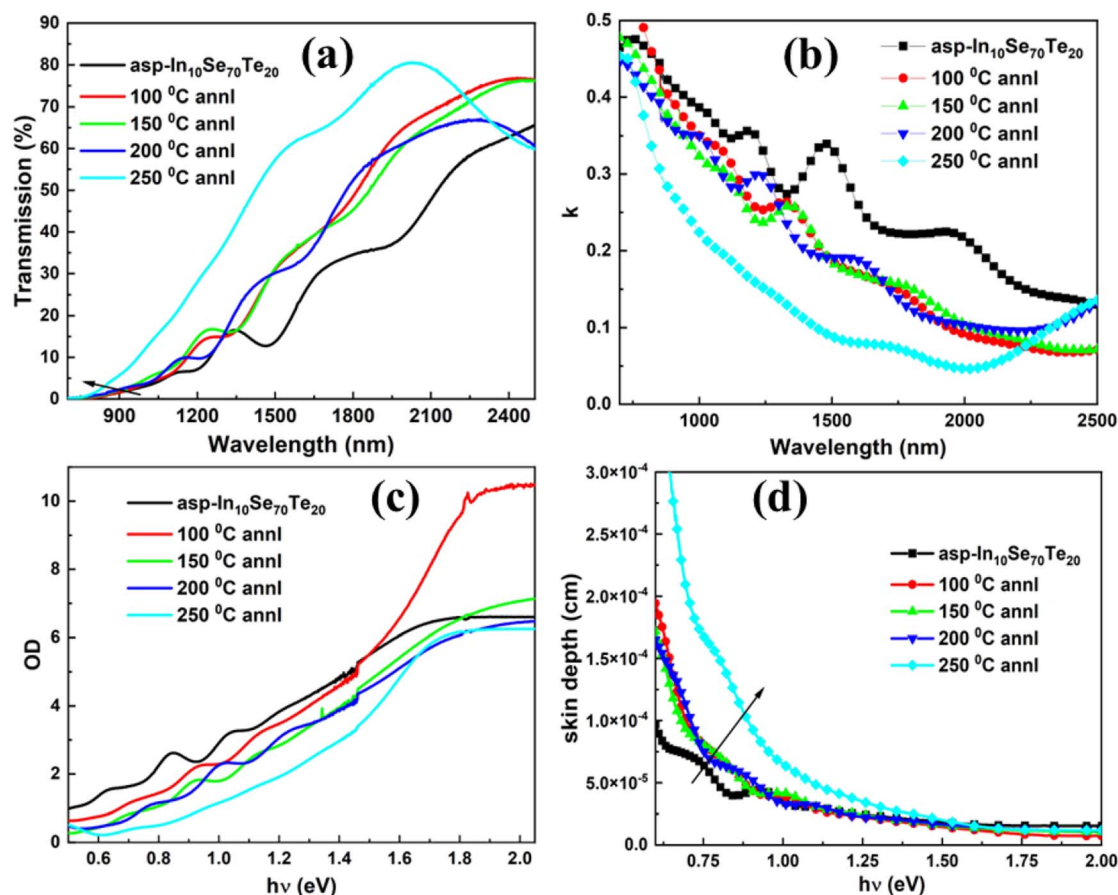


Fig. 6 Change in (a) transmittance, (b) extinction coefficient with wavelength, (c) optical density and (d) skin depth with energy of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films.





migrate from their relative equilibrium position. Consequently, grain growth increases, and lattice dislocation decreases. This causes an increase in lattice perfection and lattice growth.<sup>63,64</sup> This causes changes in the optical properties by improving the transmittance and shifting the absorption edges. The blue shifting in the absorption edge reduced the absorption coefficient, representing light absorption through the material medium. The extinction coefficient, refractive index, and non-linear parameters are all related to the absorption coefficient. Therefore, these parameters showed a reducing pattern with annealing temperature.

The absorption capability of the film is also represented by another optical quantity so called optical density (OD). It signifies the degree to which a refractive medium retards transmitted light rays. Fig. 6c depicts the change in OD ( $= \alpha \times t$ , where ' $t$ ' is the film thickness and ' $\alpha$ ' is the absorption coefficient), which decreased with an increase in annealing temperature. In thin films, OD is due to the refraction and scattering of light, measuring the velocity of light in the material.<sup>65</sup> The absorbance is very low (below 2%) at a lower  $h\nu$ , which leads to an enhancement in the transmittance of electromagnetic waves in a low absorbance regime. This behavior is responsible for the high IR transmission in In-Se-Te chalcogenide thin films. The decrease in OD value accounts for the increase in the velocity of light inside the material with annealing. The material concentration decreased, resulting in an increase in optical transparency as obtained in the transmission spectra.

The penetration depth, so-called skin depth ( $\delta$ ), is measured as the length scale at which the absorbance of incident photon becomes  $1/e$  of its value inside the film surface. The value of  $\delta$  is calculated from  $1/\alpha$ .<sup>65</sup> It is clear from Fig. 6d that the skin depth increased with annealing at lower photon energy but decreased because of a lower value at high photon energy. The cut off energy ( $E_{\text{cutoff}}$ ) is defined as the photon energy at which  $\delta$  is having nearly zero value for all the investigated samples. The  $E_{\text{cutoff}}$  value is 1.75 eV for the investigated films. The cut off wavelength ( $\lambda_{\text{cutoff}}$ ) is the wavelength corresponding to the cut off energy, and its value is  $\sim 708$  nm for the investigated films.

**3.3.2. Optical bandgap, Tauc parameter, and Urbach energy.** The optical absorption phenomena at the fundamental edge are discussed using the concept of a band-to-band transition. Absorption occurs by absorbing photons with energy equal to or more than the band gap. The electronic transition probability across the forbidden gap measures the absorption coefficient, which is the number of absorbed photons per incident photon. The optical bandgap of the material can be determined by the absorption coefficient. Using the absorption coefficient, photon energies are approximately equal to the bandgap energies of chalcogenides. In the first region, there is a weak absorption region ( $\alpha < 1 \text{ cm}^{-1}$ ), where the absorption depends on the synthesis, purity of material and temperature history. The second region ( $10 < \alpha < 10^4 \text{ cm}^{-1}$ ) corresponds to the Urbach region, where the absorption occurs in between localized and extended states. In the third region, a higher absorption coefficient ( $\alpha > 10^4 \text{ cm}^{-1}$ ) was observed in the Tauc region.<sup>59</sup> The optical bandgap due to structural randomness was calculated using the following Tauc equation:<sup>66</sup>

$$\alpha h\nu = C(h\nu - E_g)^p, \quad (5)$$

where ' $C$ ' and ' $p$ ' are the Tauc parameter and exponent, respectively. The term ' $p$ ' refers to the transition-mode power factor, which decides the type and nature of electronic transition in the gap. It has different values, such as  $p = 2$  (indirect allowed),  $1/2$  (direct allowed),  $3$  (indirect forbidden) and  $3/2$  (direct forbidden) transitions.<sup>56,61</sup> The investigated thin film absorption data fits for  $p = 2$ , suggesting the indirect allowed transition type. Fig. 7a-e shows the plot of  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$  and depicts the indirect allowed transition. The straight-line fitting of the linear portion, which cuts the  $X$ -axis, gives the  $E_g$  value (Table 2).

The  $E_g$  value of the as-prepared  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  film was 0.418 eV, which increased to 0.645 eV upon annealing at 250 °C temperature. The  $E_g$  values for the other films are shown in Table 2, which shows an increasing trend with annealing. The enhancement in  $E_g$  value with annealing is explained by the Mott and Davis theory.<sup>67</sup> A large number of saturated bonds are formed by annealing unsaturated bonds at the above crystallization temperature. Such a decrease in unsaturated defects causes a reduction in the density of localized states in the gap and ultimately enhances the band gap.<sup>68</sup> In other way, according to the chemical bond approach, the formation of greater bond energy-based bonds such as In-Se ( $53.64 \text{ kcal mol}^{-1}$ ), Se-Te ( $44.18 \text{ kcal mol}^{-1}$ ) and In-Te ( $33.05 \text{ kcal mol}^{-1}$ ) occurs at first, followed by low energy-based bonds Te-Te ( $33 \text{ kcal mol}^{-1}$ ) and Se-Se ( $44 \text{ kcal mol}^{-1}$ ).<sup>49,69,70</sup> The local structure in the film changed by bond breaking and bond arrangement due to annealing the thin films. Therefore, the low-energy bonds along with some dangling bonds were annealed with the formation of stronger bonds In-Se and In-Te bonds. This behaviour was also satisfied by the XRD and Raman studies. The formation of stronger saturated bonds in place of dangling bonds results in the reduction of the density of defect states over the gap region and enhances the band energy. Such effects bring changes in the absorption edge shift and reorganization at the atomic and molecular levels, modifying the optical parameters. According to Surbhi *et al.*, the temperature dependency of the bandgap in semiconductors is often related to an increase in interatomic separation as the magnitude of atomic vibration rises with an increase in thermal energy, which leads to an increase in the electron-lattices interactions.<sup>71</sup>

The parameter  $C$  is an indicator of the degree of structural disorder for semiconducting materials. The value of  $C$  was evaluated from the slope of the fitting, as shown in Fig. 7a-e. The low value of  $C$  depicts more structural disorders.<sup>72</sup> Thus, the higher  $C$  value (see Table 2) for the annealed films than for the as-deposited ones infers a reduction in structural disorder with annealing. Liu and colleagues studied the annealing-induced absorption and photoluminescence (PL) study of PbS QDs, which showed that an increase in annealing duration led to improved absorption and PL response.<sup>73</sup> However, in our case, the annealing duration was kept at a fixed duration, *i.e.* 1.5 h, with varying temperatures in the range of 100–250 °C. Such variation in annealing temperature led to a reduction in the ' $\alpha$ ' of the material. Similarly, Gami *et al.* synthesized (6,6)-phenyl



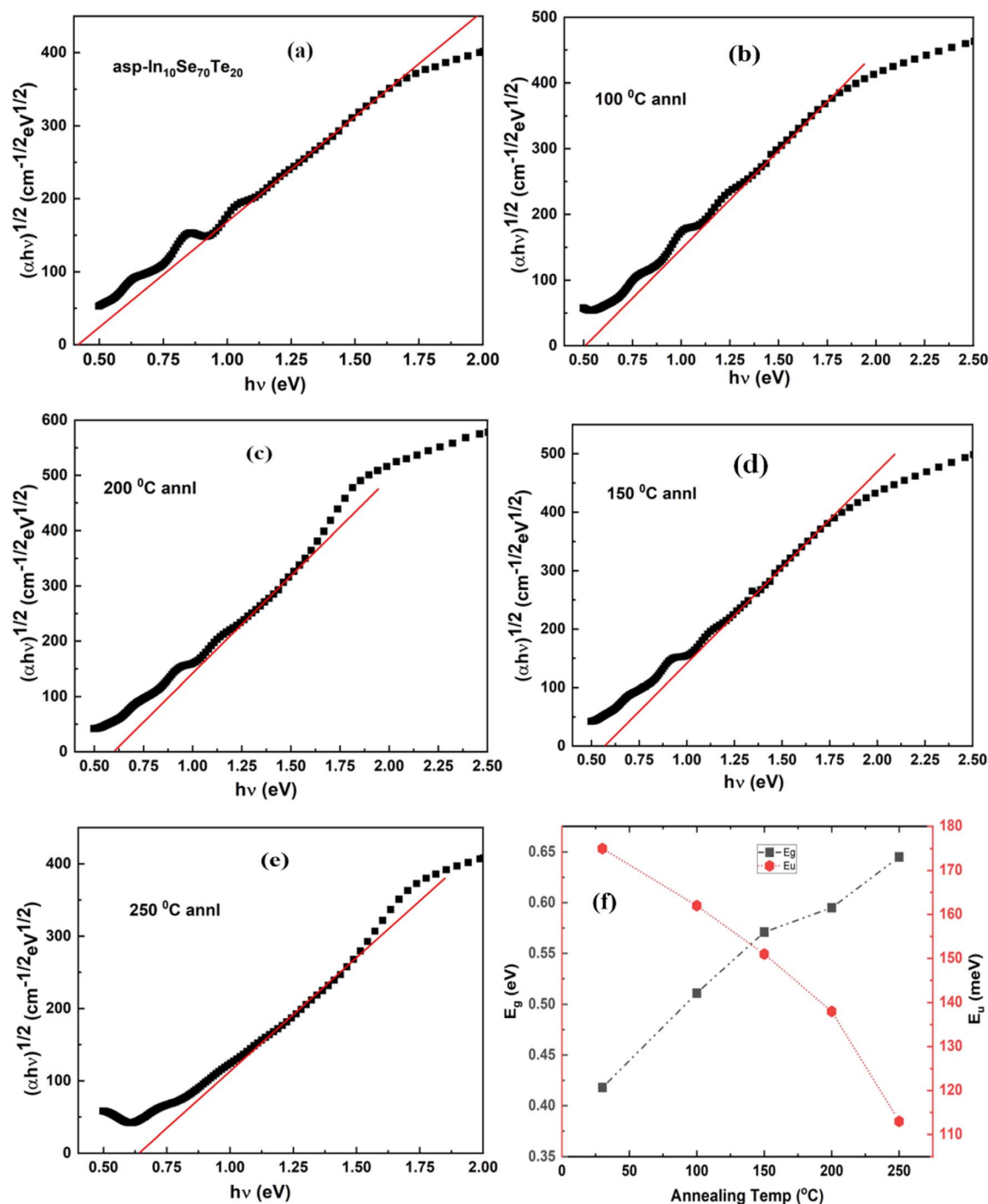


Fig. 7 (a–e) Optical bandgap of as-deposited and annealed  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  films and (f) variation of  $E_g$ , which is the Urbach energy with annealing temperatures.

C61 butyric acid methyl ester (PCBM)/Zinc(II) octaethylporphyrin (ZnOEP) thin film using the spin coating method. By varying the PCBM/ZnOEP thin film layer thickness, the  $E_g$  value was reduced, which is due to the creation of defects by the PCBM film. Thus, the Tauc parameter ( $B$ ) was reduced, indicating that the PCBM content influenced the disorder of ZnOEP/PCBM.<sup>74</sup> Surbhi *et al.* investigated the optical response of  $\text{Te}_{1-x}(\text{GeSe}_{0.5})\text{Sc}_x$  ( $x = 0, 0.05, 0.1$ , and  $0.15$ ) (TGSS) thin films,

which showed enhancement in the  $E_g$  with Sc doping. Here, the Tauc parameter ( $A$ ) showed a reduction pattern as Sc increases, signifying the influence of doping in the TGSS film. This competition could be utilized for optical storage applications. The observed  $E_g$  range in TGSS is 1.18 eV–1.27 eV, which is slightly close to the currently observed values. Therefore, this In–Se–Te film might also be a possible application for optical storage applications.<sup>75</sup> Furthermore, Dongol *et al.* investigated





Table 2 Variation in optical parameters of In<sub>10</sub>Se<sub>70</sub>Te<sub>20</sub> thin films

Optical parameter	As-prepared	100 °C	150 °C	200 °C	250 °C
$E_g$ (eV)	0.418 ± 0.03	0.511 ± 0.01	0.571 ± 0.01	0.595 ± 0.04	0.645 ± 0.02
$C^{1/2}$ (cm <sup>-1/2</sup> eV <sup>-1/2</sup> )	208	229	241	256	301
$E_U$ (meV)	175	162	151	138	113
$\sigma \times 10^{-2}$ (steepness parameter)	14.8	15.98	17.15	18.76	22.92
$S_{e-p}$	4.504	4.172	3.887	3.554	2.909
$E_d$ (eV)	0.1192	0.0804	0.0420	0.0371	0.0311
$E_o$ (eV)	1.438	1.440	1.467	1.476	1.511
$f = E_o E_d$	0.1714	0.1157	0.0616	0.0547	0.0469
$M_{-1}$	0.0828	0.0558	0.0286	0.0251	0.0205
$M_{-3}$	0.0400	0.0269	0.0132	0.0115	0.00897
$n_0$	1.041	1.027	1.0142	1.0126	1.010
$\varepsilon_\infty$	1.0836	1.0547	1.0286	1.0253	1.0201
$\lambda_o$ (nm)	734.01	721.05	701.81	685.34	667.25
$S_0$ (nm <sup>2</sup> × 10 <sup>-8</sup> )	12	6.6	4.3	3.7	3.5
$\varepsilon_L$	7.669	6.582	5.208	3.608	2.255
$N/m^* \text{ (m}^{-3} \text{ kg}^{-1}) \times 10^{39}$	9.2	7.96	6.44	4.21	3.01
Plasma frequency $\omega^2 (\times 10^{11})$	8.67	8.74	8.94	9.13	9.65
$\eta_{opt}$	2.225	2.233	2.240	2.241	2.242
$\chi^1$ (esu) × 10 <sup>-3</sup>	6.65	4.35	2.27	2.01	1.60
$\chi^3$ ( $h\nu \rightarrow 0$ ) × 10 <sup>-22</sup> (esu)	3324	608.7	45.13	27.74	11.14
$n_2^T$ (esu)	$1.2 \times 10^{-17}$	$2.23 \times 10^{-18}$	$1.67 \times 10^{-19}$	$1.03 \times 10^{-19}$	$4.15 \times 10^{-20}$
$n_2^F$ (esu)	$2.38 \times 10^{-20}$	$1.05 \times 10^{-20}$	$2.77 \times 10^{-21}$	$2.15 \times 10^{-21}$	$1.36 \times 10^{-21}$

the annealing-induced optical properties of Ge<sub>20</sub>Se<sub>65</sub>S<sub>15</sub> thin films, which showed a reduction pattern in the absorption coefficient with an increment in  $E_g$  from 2.07 eV to 2.13 eV. Such behavior is due to the creation of more numbers of saturated bonds in place of unsaturated bonds. Here, the Tauc parameter ( $B$ ) value showed an increased trend, indicating a lower structural disorder with annealing. Such annealing-induced optical tuning in the Ge<sub>20</sub>Se<sub>65</sub>S<sub>15</sub> thin film could be effectively used in photonic device fabrication.<sup>76</sup>

The presence of impurities and defects in the film results in a weak absorption region in which ' $\alpha$ ' shows exponential variation with  $h\nu$ . Such an absorption edge indicates the existence of a localized state in the gap. The band tailing is due to random fluctuations in internal fields, causing structural disorders.<sup>77</sup> The energy corresponding to this region is called the Urbach energy ( $E_U$ ), which is evaluated from Urbach's relation:<sup>78</sup>

$$\alpha(h\nu) = \alpha_0 e^{\frac{h\nu}{E_U}}, \quad (6)$$

where  $\alpha_0$  is the value of the absorption coefficient at the bandgap point.  $E_U$  value (given in Table 2) is determined as the reciprocal of the slope of the straight-line fitting between  $\ln(\alpha/\alpha_0)$  versus  $h\nu$  graph.  $E_U$  represents the width band tails in localized states that indicate the amount of disorder in the semiconductor. According to Surbhi *et al.*, the change in the  $E_U$  is related to the density of defect states in the regime of the bandgap.<sup>75</sup> The decrease in  $E_U$  value from 175 meV (as-prepared) to 113 meV for the 250 °C annealed film indicates a reduction in the density of defect states over the band gap. Thus, annealing results in a decrease in disorder and defects inside the matrix. The decrease in  $E_U$  value and increase in  $E_g$  value under different annealing conditions are shown in Fig. 7f.

The broadening in the absorption edge is represented by the steepness parameter ( $\sigma$ ), which is because of excitation due to electron-phonon or excitation-phonon interaction. This parameter is evaluated by the relation<sup>77</sup>  $\sigma = KT/E_U$ , where  $T$  is temperature,  $E_U$  is the Urbach energy, and  $K$  is the Boltzmann constant. The obtained  $\sigma$  values are presented in Table 2 and shown in Fig. 8a, depicting an increase in  $\sigma$  with annealing. This confirms the increase in the optical bandgap due to the broadening of the gap.

The interaction strength between electrons and phonons is represented by  $S_{e-p}$ . The knowledge of lattice expansion and the increase in lattice constants is obtained from  $S_{e-p}$ . The increase in  $S_{e-p}$  value infers the increase in lattice dimensions and *vice versa*. The  $S_{e-p}$  value is calculated by  $S_{e-p} = 2/3\sigma$ ,<sup>77</sup> as demonstrated in Table 2. Considering that increasing the lattice dimensions leads to decreasing the band-gap energy, the decrease in the  $S_{e-p}$  value with annealing results in an increase in the  $E_g$  value, as shown in Fig. 8b.

The decreased  $S_{e-p}$  values are in good correlation with the increased  $E_g$  value because of their inverse relationship with each other. Because of the peculiar optical properties of In-Se-Te thin films, they are considered for many optoelectronic applications and devices, such as photonic circuits, photovoltaics, signal preparing, solar cells, optical fibers, photolithography, and optical recorders.

**3.3.3. Refractive index and dispersion parameters.** Refractive index ( $n$ ) is an indicator of light dispersion and is useful for non-linear phenomena. This is one of the important optical parameters required for strong optical field confinement, which allows for small waveguide bend radii and enhanced optical intensities.<sup>59</sup> It depicts useful information related to both the linear and non-linear parameters of the sample. The value of ' $n$ '



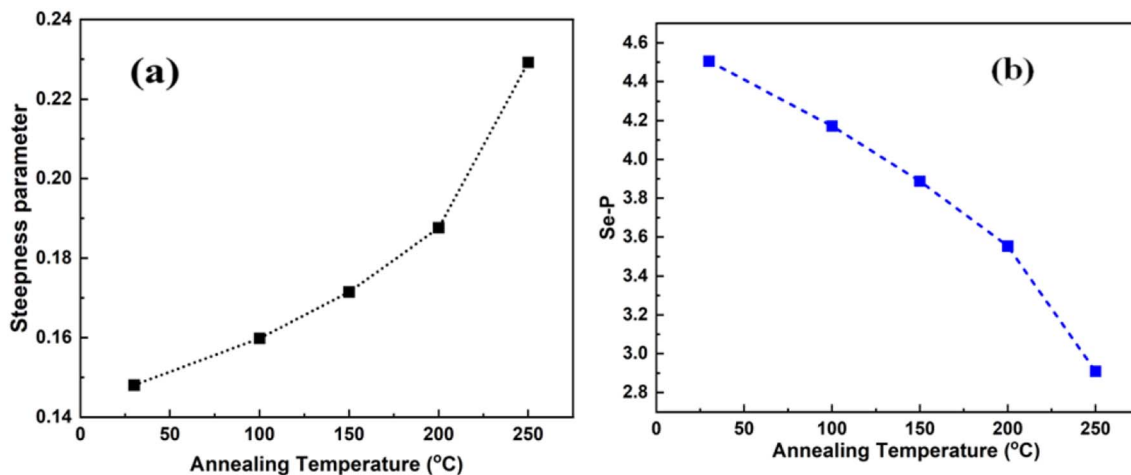


Fig. 8 (a) Increase in steepness parameter and (b) decrease in  $S_{e-p}$  value at different annealing temperatures.

was calculated from the transmission data using the following formula:<sup>79</sup>

$$n = \left( \frac{1}{T-1} \right)^{1/2} + \frac{1}{T}. \quad (7)$$

Fig. 9a shows the refractive index change at different ' $\lambda$ ', showing the normal dispersion behaviour of the film. The value of ' $n$ ' decreased with annealing temperature with a simultaneous increase in  $E_g$ . In the lower wavelength regime, the ' $n$ ' value is large, whereas in the upper wavelength region, it

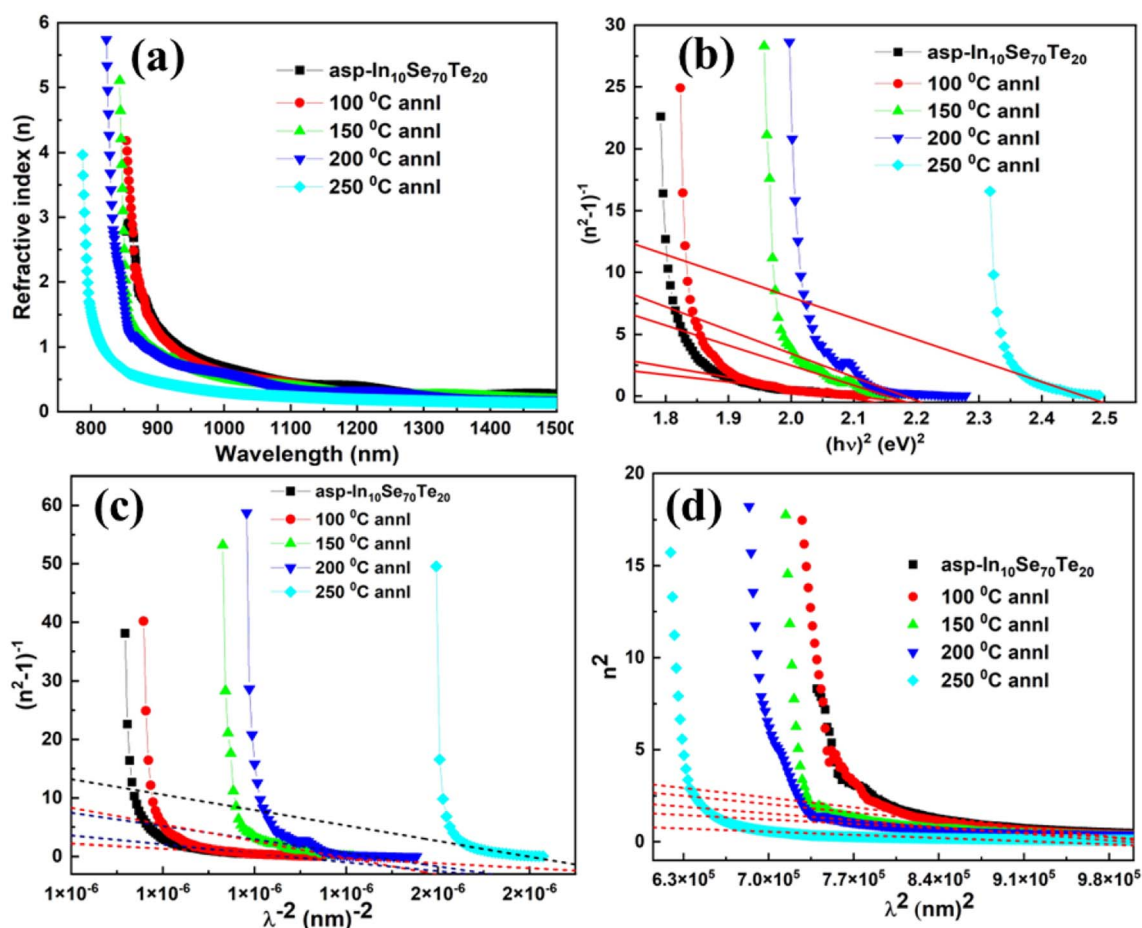


Fig. 9 (a) Variation in ' $n$ ', (b)  $(n^2 - 1)^{-1}$  vs.  $(h\nu)^2$  graph, (c)  $(n^2 - 1)^{-1}$  vs.  $(\lambda)^{-2}$  graph and (d)  $n^2$  vs.  $\lambda^2$  graph of In<sub>10</sub>Se<sub>70</sub>Te<sub>20</sub> thin films.



decreases to a saturated value. The absorption capability is more at higher frequencies for which the speed of light decreases and the  $n$ -value increases. The optical field confinement is more at a high value of ' $n$ ', which maintains the small waveguides to bend inside the fibre. Thus, the optical intensities increase for which the material becomes more efficient and useful for non-linear interactions.<sup>80</sup>

The variation in refractive index is associated with the change in bandgap by Moss rule, *i.e.*,  $E_g n^4 \sim \text{constant}$ .<sup>81</sup> The valence band is formed by lone pair orbitals, and the anti-bonding orbital forms the conduction band. With the increase in annealing temperature, there is excitation of bonding states and lone-pair electrons to the antibonding states. The vacancy created by this process is filled by the outer electrons and leads to the increase in lone-pair, holes and bonding orbitals, resulting in the formation of vacancy.<sup>61</sup> Such bond rearrangement favors the local structure to change and reduces ' $n$ ' and ' $k$ ' values at higher annealing temperatures.

The dispersion parameters play an important role in designing various spectral dispersion and optical communication devices. Single oscillator ( $E_o$ ) and dispersion ( $E_d$ ) energy are two essential parameters for optical devices. The  $E_d$  is independent of  $E_o$  because  $E_d$  depends on the dielectric loss, whereas  $E_o$  does not depend on the dielectric loss. The Wemple-DiDomenico model is related to  $E_o$ ,  $E_d$  and  $h\nu$ .  $E_o$  is regarded as the average energy gap that gives information on the band structure, while  $E_d$  carries the average inter band optical transition strength, in which the  $E_d$  value decreased because of the annealed films. It is related to structural parameter change in the material, such as coordination number ( $N_c$ ), ionicity ( $\beta = 0.37$  eV), the effective number of valence electrons per anion ( $N_e$ ) and anion valency ( $Z_a$ ) of the material by  $E_d = \beta N_c Z_a N_e$  (eV).<sup>76</sup> The structural disorder and physical properties of the material are associated with ' $E_d$ '. The decreased value of  $E_d$  for the present case with annealing infers less structural disorder.

The single effective oscillator model provides an in-depth physical interpretation of the measured parameters. The model is presented by the following equation:<sup>54</sup>

$$(n^2 - 1)^{-1} = \frac{E_o^2 - (h\nu)^2}{E_o E_d} = \frac{E_o}{E_d} - \frac{(h\nu)^2}{E_o E_d}. \quad (8)$$

The calculations of  $E_o$  and  $E_d$  were performed from the graph between  $(n^2 - 1)^{-1}$  vs.  $(h\nu)^2$ , as depicted in Fig. 9b. The  $E_o$  and  $E_d$  values are evaluated from the slope and intercept of the fitting, as depicted in Table 2. It is noticed that  $E_o$  increased while  $E_d$  decreased with an increase in the annealing of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  film. The lattice dielectric constant ( $\epsilon_\infty$ ) and static refractive index ( $n_0$ ) were calculated using the following formula:<sup>45,54</sup>

$$\epsilon_\infty = 1 + \frac{E_d}{E_o}, \quad n_0 = \sqrt{1 + \frac{E_d}{E_o}}. \quad (9)$$

The quantity  $f = E_o E_d$  refers to the oscillator strength of the material, which decreased with an increase in annealing, as shown in Table 2. It is found that  $\epsilon_\infty$  decreased with annealing of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  film.

The two moments of spectra first-order ( $M_{-1}$ ) and third-order ( $M_{-3}$ ) were evaluated by  $E_o$  and  $E_d$  using the following equations:<sup>45,52</sup>

$$M_{-1} = E_d/E_o \text{ and } M_{-3} = M_{-1}/E_o^2. \quad (10)$$

The values of both  $M_{-1}$  and  $M_{-3}$  decreased with the annealing of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  films, as shown in Table 2.

At the lower frequency region, the ' $n$ ' value satisfies the following Sellmeier's dispersion model:<sup>45,76</sup>

$$(n^2 - 1)^{-1} = \frac{1}{s_0 \lambda_0^2} - \frac{1}{s_0 \lambda^2}. \quad (11)$$

The straight-line fitting of  $(n^2 - 1)^{-1}$  vs.  $(\lambda)^{-2}$  (Fig. 9c) evaluates the value of ' $s_0$ ' (strength of the oscillator) and  $\lambda_0$  (oscillator wavelength). The decreases in  $\lambda_0$  and  $s_0$  values with annealing of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  films are shown in Table 2.  $\lambda_0$  is inversely proportional to  $E_o$ , and  $E_o$  is directly proportional to  $E_g$ , which leads to  $\lambda_0 \propto 1/E_g$ . Consequently,  $\lambda_0$  decreased due to the improvement in the crystallinity and change in the surface morphology of the films.<sup>82</sup>

**3.3.4. High-frequency dielectric constant ( $\epsilon_L$ ) and dielectric parameters and plasma frequency.** The ' $\epsilon_L$ ' and carrier concentration per effective mass ( $N/m^*$ ) were calculated from the variation of ' $n$ ' with ' $\lambda$ ' using the following equation:<sup>54,57</sup>

$$n^2 = \epsilon_L - \left( \frac{e^2}{4\pi^2 c^2 \epsilon_0} \right) \left( \frac{N}{m^*} \right) \lambda^2. \quad (12)$$

The plot between  $\lambda^2$  and  $n^2$ , as presented in Fig. 9d, evaluates the value of  $N/m^*$  and  $\epsilon_L$  from its intercept and slope. The  $N/m^*$  decreased from  $9.2 \times 10^{39} \text{ m}^{-3} \text{ kg}^{-1}$  of the as-prepared film to  $3.01 \times 10^{39} \text{ m}^{-3} \text{ kg}^{-1}$  for the 250 °C annealed film. This shows the microstructural changes in the film, as shown in Fig. 2. The change in the orientation of dipoles present in chalcogenide films led to variations in  $\epsilon_L$ . Although both the values of  $\epsilon_L$  and  $\epsilon_\infty$  are very close to each other, the decrease in both values upon annealing films is due to the increase in polarization.<sup>83</sup> The lower value of  $\epsilon_\infty$  compared to  $\epsilon_L$  is due to the contribution of free charge carriers to the polarization process, which has also been observed in other studies.<sup>84</sup>

The value of the plasma frequency ( $\omega_p$ ) is evaluated using the following Drude relation:<sup>85</sup>

$$\frac{N}{m^*} = \left( \frac{\epsilon_0 \epsilon_\infty}{e^2} \right) \omega_p^2$$

Or

$$\omega_p = \left[ \left( \frac{e^2}{\epsilon_0 \epsilon_\infty} \right) \frac{N}{m^*} \right]^{1/2}. \quad (13)$$

The calculated  $\omega_p$  values for the films are listed in Table 2. At the plasma frequency, the oscillation of free charge carriers achieves its peak. There is no other resonance except the plasma frequency, and the radiation of the material travels in the





dielectric material and is reflected in the lower frequency. Here,  $\omega_p$  increased with thermal annealing for the studied films.

The dielectric constant is the built-in property of a semiconductor that defines the behavior under an applied electric field. The complex dielectric constant has both real ( $\epsilon_r$ ) and imaginary ( $\epsilon_i$ ) parts,  $\epsilon^* (= \epsilon_r + i\epsilon_i)$ . Additionally, in terms of ' $n$ ' and ' $k$ ', it is expressed as  $\epsilon^* = (n + ik)^2$ . The dielectric loss tangent ( $\tan \delta$ ) was evaluated from  $\epsilon_r$  and  $\epsilon_i$ . The  $\epsilon_r$  gives an idea of the de-acceleration of incident energy during propagation inside the films. The ' $\epsilon_i$ ' accounts for the loss of energy and is called the damping factor. This parameter measures the energy loss and dissipation inside the material during the passing of light waves inside it.<sup>85</sup> The ratio  $\epsilon_i/\epsilon_r$  evaluates the loss factor, and these parameters are evaluated using the following formulas:<sup>85</sup>

$$\epsilon_i = 2nk \text{ and } \epsilon_r = n^2 - k^2. \quad (14)$$

Fig. 10a and b show the variation in  $\epsilon_r$  and  $\epsilon_i$  with  $h\nu$ , and both parameters decreased with the annealing of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  films. The comparatively high value of  $\epsilon_r$  than  $\epsilon_i$  is due to the changes in ' $n$ ' and ' $k$ '. The figures clearly show that the ' $\epsilon_1$ ' is seven times greater than the ' $\epsilon_2$ '. This is because  $n \gg k$  in the ' $1$ ' case, whereas in the ' $\epsilon_2$ ' case, the low ' $k$ ' value reduced the imaginary part to less than 5.

The dielectric loss factor measures the energy absorbed by the material when the electromagnetic wave passes inside it. This parameter also depicts the phase difference in the loss of energy at a fixed frequency (Fig. 10c). The value of ' $\tan \delta$ ' is more for the annealed film at high photon energy. The nature of change in  $\tan(\delta)$  is similar to the ' $k$ ' value, which infers the dominating nature of dielectric loss in this electromagnetic regime over optical absorption. The quality of oscillation so-called quality factor ( $Q$ )<sup>85</sup> is the inverse of  $\tan(\delta)$ , i.e.  $Q = \epsilon_r/\epsilon_i$ . The  $Q$  factor is found to decrease with the annealing of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  films, as shown in Fig. 10d.

The moving electron loses energy while moving within the sample during its motion owing to plasma oscillations, which are excited in a sea of conduction band electrons. The degree of such loss of energy is associated with the optical features of any material. The energy loss functions are essential quantities for shedding light on damping on the surface or within the films. The average free path of the inelastic electron during its travel inside the sample is measured by such an energy loss function. Thus, it is essential to calculate the volume energy losses (VELF) and surface energy loss function (SELF). The VELF and SELF are evaluated using  $\epsilon_r$  and  $\epsilon_i$  as follows:<sup>82,85</sup>

$$\text{VELF} = \frac{\epsilon_i}{\epsilon_r^2 + \epsilon_i^2}, \quad \text{SELF} = \frac{\epsilon_i}{(\epsilon_r + 1)^2 + \epsilon_i^2}. \quad (15)$$

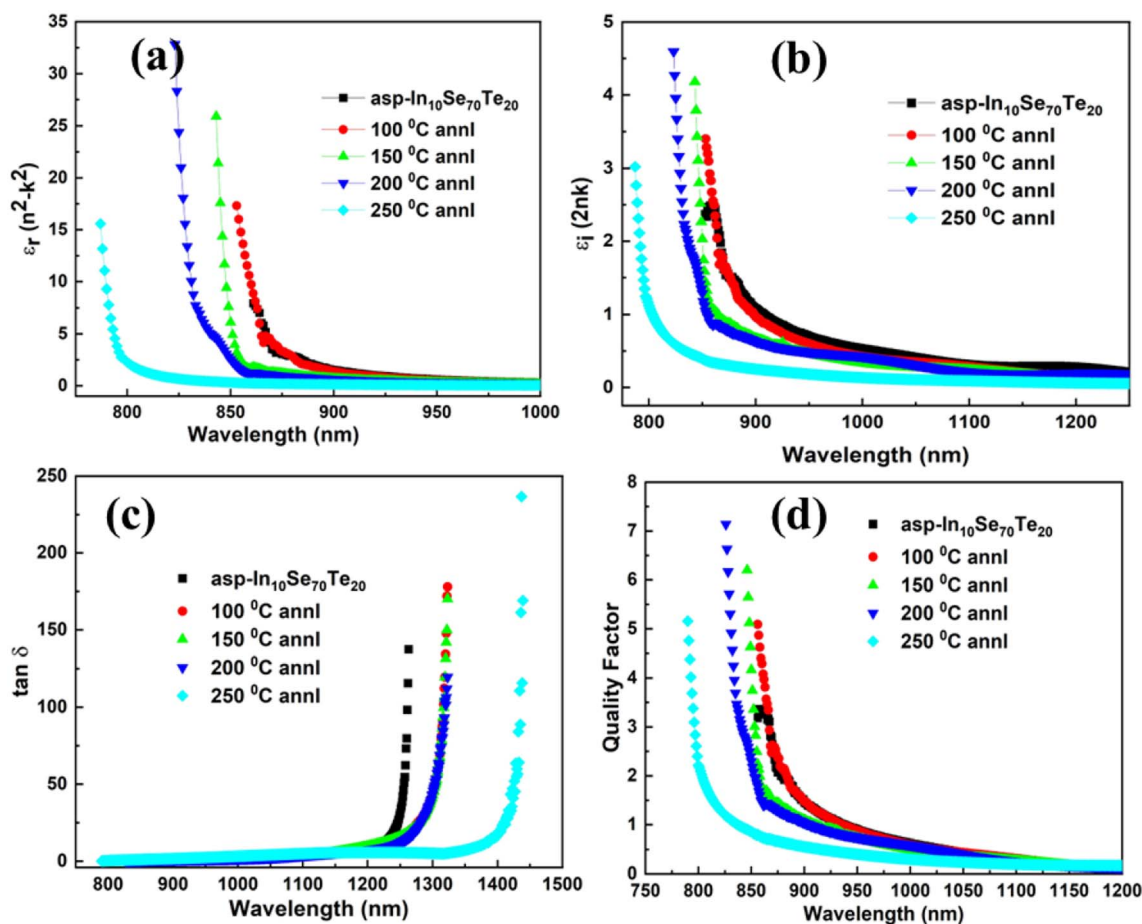


Fig. 10 (a)  $\epsilon_r$  vs.  $h\nu$ , (b)  $\epsilon_i$  vs.  $h\nu$ , (c)  $\tan(\delta)$  vs.  $h\nu$  plot and (d) quality factor vs.  $h\nu$  plot for as-prepared and annealed  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films.



Both VELF and SELF define the absorption of energy of a material that signifies losses and is also related to a single transition of electrons in the semiconductor. The variation in VELF and SELF with  $\lambda$  is given in Fig. 11a and b, from which it is evident that VELF increased with annealing whereas SELF decreased with annealing.

**3.3.5. Optical conductivity and optical electronegativity ( $\eta_{\text{opt}}$ ).** The optical response of the sample is measured from its optical conductivity ( $\sigma$ ) value. The amount of light propagation through the medium in a certain wavelength regime is obtained from ' $\sigma$ '. The study of the complex ' $\sigma$ ' of films is essential owing to their functional applications. The ' $\sigma$ ' value is dependent on  $\varepsilon_r$  and  $\varepsilon_i$ . The ' $\sigma$ ' value infers the electronic state density within the bandgap of the material.<sup>86</sup> The complex ' $\sigma$ '  $\sigma^* = \sigma_r(\omega) + i\sigma_i(\omega)$  has both real and imaginary components. The  $\sigma_i(\omega) = \omega\varepsilon_o\varepsilon_r$  and  $\sigma_r(\omega) = \omega\varepsilon_o\varepsilon_i$ , where  $\omega$  is the angular frequency. Fig. 11c and d show the variation in real and imaginary optical conductivities with photon energy. There is a rapid increase in both  $\sigma_i(\omega)$  and  $\sigma_r(\omega)$  as energy increases. This increment in both optical conductivities is explained by an increment in the absorption coefficient at a higher energy or lower wavelength. This behaviour has also been observed in other studies.<sup>75</sup> Both values decreased upon annealing the  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  films.

The degree of polarization so called electrical susceptibility ( $\chi_c$ ) is denoted as follows:<sup>87</sup>

$$\chi_c = \frac{1}{4\pi} [n^2 - k^2 - n_0^2] = \frac{1}{4\pi} [\varepsilon_r - n_0^2]. \quad (16)$$

The value of  $\chi_c$  is shown in Fig. S3,<sup>†</sup> which indicates the decreasing trend with annealing and a higher value at a high value of  $h\nu$ .

The presence of lone pairs is linked with polarization by optical electronegativity ( $\eta_{\text{opt}}$ ). The value of  $\eta_{\text{opt}}$  in terms of  $n_o$  is given as follows:<sup>86,87</sup>  $\eta_{\text{opt}} = \left(\frac{C}{n_o}\right)^{1/4}$ , where  $C = 25.54$ . The evaluated  $\eta_{\text{opt}}$  values increased with annealing for  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  films, as shown in Table 2. Because  $\eta_{\text{opt}}$  is related to the refractive index, the optical electronegativity also affects the non-linear parameters.

**3.3.6. Non-linear optical properties.** The non-linearity in the films originates when the high-intensity electromagnetic wave incident on it and is governed by the Kerr effect:  $\Delta n_o = n_2 \times I$ , where  $I$  is the optical intensity and  $n_2$  is the non-linear refractive index. The origin of non-linearity is due to the interactions of electronic polarization, which affects the bond length of the material.<sup>45</sup> The idea of non-linear optical entities of a material determines the propagation characteristics of light through it. The polarization  $P$  is expressed as follows:<sup>38</sup>

$$P(t) = \varepsilon_0[\chi^1 E(t) + \chi^2 E(t)^2 + \chi^3 E(t)^3 + \dots], \quad (17a)$$

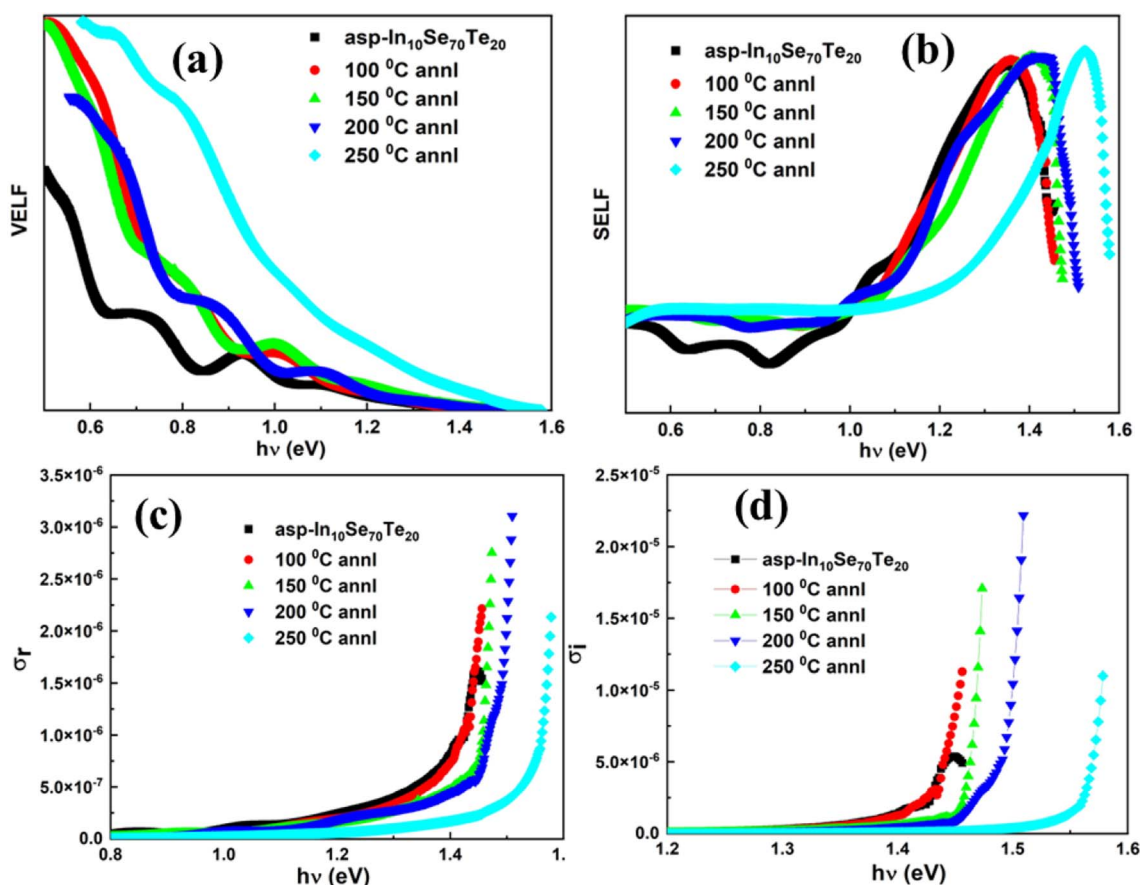


Fig. 11 (a) Change in VELF, (b) SELF with  $h\nu$ , (c) variation in  $\sigma_r$  and (d)  $\sigma_i$  with  $h\nu$  for  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  films.



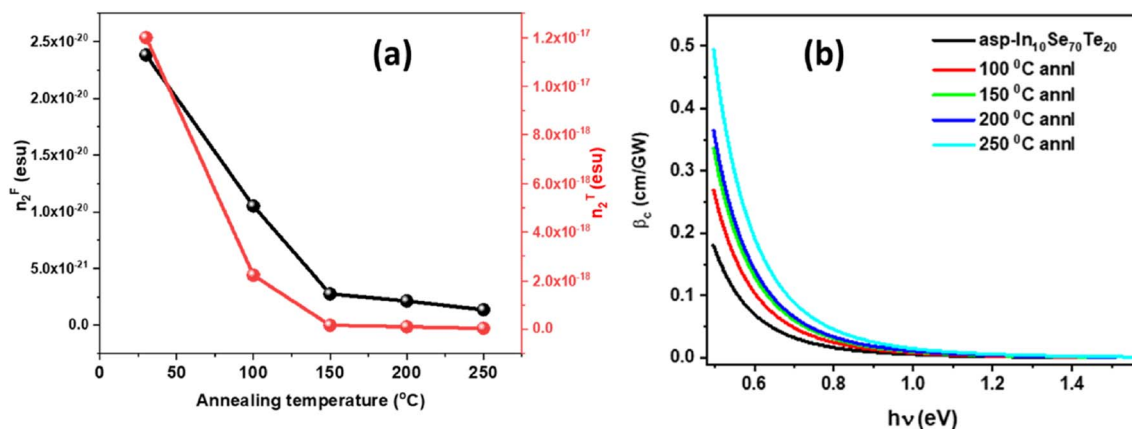


Fig. 12 (a) Variation in  $n_2^F$  and  $n_2^T$  and (b)  $\beta_c$  with energy in  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films.

where  $E(t)$  and  $\epsilon_0$  are the electric field strength and permeability in free space. Electrical susceptibility has linear susceptibility ( $\chi^1$ ) and non-linear susceptibility ( $\chi^2$ ,  $\chi^3$ ). The materials with inversion symmetry have the even order terms as zero for the non-linear susceptibility *i.e.*  $\chi^2 = 0$ . The linear susceptibility  $\chi^1$  is given by the following formula:<sup>88</sup>

$$\chi^1 = \frac{n_0^2 - 1}{4\pi} \quad (17b)$$

where ' $n_0$ ' is the linear refractive index. The values of  $\chi^1$  are presented in Table 2, which shows the decreased value with annealing of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  films. Miller's generalised rule<sup>88</sup> was used to obtain third-order non-linear optical susceptibility ( $\chi^{(3)}$ ):

$$\chi^{(3)} = A(\chi^{(1)})^4 \quad (17c)$$

where  $A$  is  $1.7 \times 10^{-10}$  esu. The values of  $\chi^{(3)}$  for different annealed films are listed in Table 2, which also decreases with annealing. The polarized atoms with lone pairs (chalcogens) affect  $\chi^3$  value, but the presence of heavy atoms with easily polarized electron clouds (*e.g.* In) is even more suitable. This monotonic decrease in non-linear susceptibility is caused by a change in material structure caused by annealing-induced enhancement in crystallization and crystallite size.

The nonlinear refractive index is calculated from  $\chi^{(3)}$  using the Tichy and Ticha formula:<sup>88</sup>

$$n_2^T = \frac{12\pi\chi^{(3)}}{n_0} \quad (17d)$$

The value of  $n_2^T$  is found to decrease with the annealing of  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  films, as shown in Table 2. The  $n_2^T$  value for the as-prepared  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  film decreased from  $1.2 \times 10^{-17}$  esu to  $4.15 \times 10^{-20}$  esu for 250 °C annealing. Fornier and Snitzer correlated the  $n_2^F$  and linear refractive index of the material using WDD parameters as follows:<sup>89</sup>

$$n_2^F = \frac{(n^2 + 2)(n^2 - 1)}{48\pi Nn} \frac{E_d}{(E_0)^2} \left( \frac{x_{32}^2}{x_{2g}^2} - 1 \right), \quad (17e)$$

where  $n$  is the refractive index,  $N$  is the density of polarizable constituents, and subscripts g, 2 and 3 to  $x$  denote the ground state (g) and excited states (2 and 3), respectively. Considering the three-level system for this model, the quantity  $((x_{32}^2/x_{2g}^2) - 1) = 1$  and  $n$  as static refractive index  $n_0$ , the above equation becomes<sup>89</sup>

$$n_2^F = \frac{(n_0^2 + 2)(n_0^2 - 1)}{48\pi Nn_0} \frac{E_d}{(E_0)^2}. \quad (17f)$$

The estimated  $n_2^F$  using the Fornier and Snitzer models is presented in Table 2. The  $n_2^F$  showed a lower value compared to  $n_2^T$ . The comparative plot presented in Fig. 12a showed that both  $n_2^F$  and  $n_2^T$  follow the same trend as that of the linear refractive index, *i.e.*, overall decreased with an increase in annealing temperature. Furthermore, the change in  $E_g$ ,  $\chi^3$  and  $n_2$  under different annealing conditions is shown in Fig. S4.† The number of homopolar bonds decreased with an increase in heteropolar ones, thus decreasing the defects in the band structure. Therefore, the reduction in the density of defects and the decrease in the variety of defects account for the decrease in non-linearity with annealing. Lowering of  $\chi^{(3)}$  and  $n_2$  upon annealing is suitable for solid-state laser and UV non-linear materials.<sup>90</sup>

Two-photon absorption (TPA) is one of the most fundamental mechanisms that describes the procedure of induced absorption inside materials. This mechanism happens only when the energy of incident light is in the range of  $E_g/2 < h\nu < E_g$ . This TPA mechanism is described by the non-linear absorption coefficient ( $\beta_c$ ), which can be calculated using a simple empirical relation by Sheik Bahae *et al.*:<sup>75,91,92</sup>

$$\beta_c(\nu) = \frac{3100 \sqrt{21} \left[ \left( \frac{2h\nu}{E_g} \right) - 1 \right]^{\frac{3}{2}}}{n^2 E_g^3 \left[ \frac{2h\nu}{E_g} \right]^5} \text{ cm GW}^{-1}. \quad (17g)$$

The  $\beta_c$  value showed greater magnitude at a lower energy and was then reduced. Fig. 12b shows the same pattern of  $\beta_c$  as the





non-linear parameters, *i.e.*, increased with annealing temperature.

## 4. Conclusions

The findings from this study showed that annealing induced an increase in crystallinity and a decrease in dislocation density in  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  thin films. The particle size increased from 9.55 nm of the as-deposited one to 18.68 nm for the 250 °C annealed film. The structural change is due to the annealing out of the unsaturated bonds and defects in the film with heat energy, increasing the structural order. The  $\text{In}_2\text{Se}_3$  and  $\text{In}_2\text{Te}_3$  phase formation from the  $\text{In}_{10}\text{Se}_{70}\text{Te}_{20}$  film was confirmed by XRD and Raman studies. Surface morphological modification was noticed from the FESEM images, and the elemental mapping study showed a uniform distribution of elements in the film. The indirect allowed bandgap is found to be increased by 0.227 eV for the 250 °C annealed film from the as-deposited one. Such an increase in  $E_g$  is due to the increase in crystallinity and decrease in defects caused by annealing. The steepness parameter increased, and the  $S_{e-p}$  value decreased with annealing. The effect of annealing temperature is observed on the dispersion and the non-linear parameters. The ' $k$ ' and ' $\alpha$ ' values decreased by making the film more transparent upon annealing. The decrease in refractive index satisfies the Moss rule and results in an increase in  $E_o$  value by 0.073 eV and a decrease in  $E_d$  value by 0.0881 eV due to annealing. The oscillator strength, first and third moments of spectra, dielectric constant carrier concentration and oscillator wavelength decreased upon annealing. Simultaneously, plasma frequency increased from 8.67 to 9.65, and optical electronegativity increased with annealing temperature. Electrical susceptibility decreased along with optical conductivity. The non-linear refractive index decreased from  $1.2 \times 10^{-17}$  esu (as-prepared) to  $4.15 \times 10^{-20}$  esu (250 °C), as did the non-linear susceptibility with annealing. The observed changes in the linear and non-linear optical parameters with annealing temperature are suitable for optoelectronic and non-linear optics.

## Author contributions

S. Giri: writing – original draft, software, data curation, investigation. P. Priyadarshini: experiment, data curation. D. Alagarasan: experiment, investigation. R. Ganesan: visualisation, investigation. R. Naik: conceptualization, methodology, writing – review & editing, supervision.

## Data availability

The data that support the findings of this study are available from the corresponding author upon reasonable request.

## Conflicts of interest

There are no conflicts of interest for this manuscript.

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