Synthesis and characterization of nanoparticle thin films of a-(PbSe)$_{100-x}$Cd$_x$ lead chalcogenides

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Abstract

We report the synthesis of amorphous (PbSe)$_{100-x}$Cd$_x$ (x = 5, 10, 15, and 20) nanoparticle thin films using thermal evaporation method under argon gas atmosphere. Thin films with a thickness of 20 nm have been deposited on glass substrates at room temperature under a continuous flow (50 sccm) of argon. X-ray diffraction patterns suggest the amorphous nature of these thin films. From the field emission scanning electron microscopy images, it is observed that these thin films contain quite spherical nanoparticles with an average diameter of approximately 20 nm. Raman spectra of these a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles show a wavelength shift in the peak position as compared with earlier reported values on PbSe. This shift in peak position may be due to the addition of Cd in PbSe. The optical properties of these nanoparticles include the studies on photoluminescence and optical constants. On the basis of optical absorption measurements, a direct optical bandgap is observed, and the value of the bandgap decreases with the increase in metal (Cd) contents in PbSe. Both extinction coefficient (k) and refractive index (n) show an increasing trend with the increase in Cd concentration. On the basis of temperature dependence of direct current conductivity, the activation energy and pre-exponential factor of these thin films have been estimated. These calculated values of activation energy and pre-exponential factor suggest that the conduction is due to thermally assisted tunneling of the carriers.

Keywords: Amorphous lead chalcogenides, Nanoparticle thin films, Raman spectra, Photoluminescence, Optical bandgap, dc conductivity

Background

Metal chalcogenides, especially zinc, cadmium, and lead, have a lot of potential as efficient absorbers of electromagnetic radiation [1-3]. In recent years, there has been considerable interest in lead chalcogenides and their alloys due to their demanding applications as detectors of infrared radiation, photoresistors, lasers, solar cells, optoelectronic devices, thermoelectric devices, and more recently, as infrared emitters and solar control coatings [4-6]. A lot of work has also been focused on the fundamental issues of these materials possessing interesting physical properties including high refractive index [6-8].

There have been many theoretical and experimental studies on lead chalcogenides (PbS, PbSe, and PbTe) [9,10]. These chalcogenides are narrow, direct bandgap semiconductors (IV-VI groups) and crystallized at ambient condition in the cubic NaCl structure. They possess ten valence electrons instead of eight for common zinc blende and wurtzite III-V and II-VI compounds. They also exhibit some unusual physical properties, such as anomalous order of bandgaps, high carrier mobility, and high dielectric constants. All these unique properties of these semiconductors have inculcated great interest in the fundamental studies of these materials. Thin film semiconductor compounds, especially lead chalcogenide, and their alloys have drawn a lot of attention due to their technological importance and future prospects in various electronic and optoelectronic devices [11-13].

Nano-chalcogenides continue to attract the attention of researchers and engineers as a very large group of interesting solids in which unusual physical and chemical phenomena are revealed and as the materials that open new roads in science and technology. The nonlinear optical properties of these materials have attracted much attention because of their large optical nonlinearity and short response time. The size, shape, and surface
characteristics have a strong influence on the physical properties of nanomaterials. Therefore, much attention has been paid in controlling these parameters to manipulate the physical properties of nanomaterials. Nanostructure formation has been explored for many kinds of materials, and this leads to an interesting topic also for lead chalcogenides. Lead chalcogenide possesses unique characteristics which are different from those in oxide and halide glasses, i.e., molecular structures and semiconductor properties. However, studies on lead chalcogenides at nanoscale are still at their early stages, and accordingly, overall features of these nanostructures have not been discovered.

Several workers reported the electrical and optical properties of PbSe in bulk form [14-17]. Many studies on PbSe films synthesized by chemical techniques are available in the literature [18-22]. There are also few reports on PbSe films and PbSe nanostructured thin films deposited by thermal evaporation technique [23-26]. Ma et al. [27] deposited polycrystalline PbSe thin films on Si substrates by thermal reduction method with carbon as the reducing agent. Kumar et al. [28] have studied the electrical, optical, and structural properties of PbSe$_{1-x}$Te$_x$ thin films prepared by vacuum evaporation technique. Lin et al. [29] reported the fabrication and characterization of IV-VI semiconductor Pb$_{1-x}$Sn$_x$Se thin films on gold substrate by electrochemical atomic layer deposition method at room temperature. Pei et al. [30] studied the electrical and thermal transport properties of lead-based chalcogenides (PbTe, PbSe, and PbS) with special emphasis on the lattice and the bipolar thermal conductivity. Gad et al. [31] have studied the optical and photoconductive properties of Pb$_{0.5}$Sn$_{0.5}$Se nanostructured thin films deposited by thermal vacuum evaporation and pulse laser technique.

Recently, in a joint article from one of us [32], the structural, optical, and electrical properties of polycrystalline cadmium-doped lead chalcogenide (PbSe) thin films are reported. They also studied the optical bandgap, optical constants, and temperature dependence of direct current (dc) conductivity of these thin films in polycrystalline form. In the present work, we have synthesized the materials, i.e., (PbSe)$_{100-x}$Cd$_x$ in amorphous form using melt quenching technique and the prepared thin films containing nanoparticles using thermal evaporation method. Here, all the calculated experimental parameters are reported on the amorphous thin films containing nanoparticles of (PbSe)$_{100-x}$Cd$_x$.

**Methods**

The source material (PbSe)$_{100-x}$Cd$_x$ with $x = 5, 10, 15$, and $20$ were synthesized by direct reaction of high purity (99.999%) elemental Pb, Se, and Cd using melt quenching technique. The desired amounts of the constituent elements were weighed according to their atomic percentage and then sealed in quartz ampoules under a vacuum of $10^{-6}$ Torr. The bulk samples of (PbSe)$_{100-x}$Cd$_x$ were prepared in steps. Initially, we have prepared PbSe in amorphous form, then doped with cadmium, and finally synthesized the (PbSe)$_{100-x}$Cd$_x$ in amorphous form using melt quenching. The sealed ampoules containing the samples PbSe and Cd were kept inside a programmable furnace, where the temperature was raised up to $923$ K at the rate of $4$ K/min and then maintained for $12$ h. During the melt process, the ampoules were agitated frequently in order to intermix the constituents to ensure homogenization of the melt. The melt was then quenched rapidly in ice water.

Thin films of (PbSe)$_{100-x}$Cd$_x$ with a thickness of $20$ nm were deposited on glass substrates at room temperature under argon pressure of $2$ Torr using an Edward Coating Unit E-306 (Island Scientific, Ltd., Isle of Wight, England, UK). The thickness of the films was measured using a quartz crystal monitor (Edward model FTM 7). The earthed face of the crystal monitor was facing the source and was placed at the same height as the substrate. Evaporation was controlled using the same FTM 7 quartz crystal monitor.

The surface morphology of these thin films was studied by field emission scanning electron microscopy (FESEM). We have dispersed these samples in acetone solution, and a drop of solution is dispersed on carbon tape. The morphology of these dispersed particles was also studied. This suggested that the dispersed nanoparticles are aggregated with the average diameter of $20$ nm. The X-ray diffraction (XRD) patterns of (PbSe)$_{100-x}$Cd$_x$ chalcogenide thin films were recorded using an X-ray diffractometer (Ultima-IV, Rigaku Corporation, Tokyo, Japan). The copper target (Cu-K$_\alpha$, $\lambda = 1.5406$ Å) was used as a source of X-rays. These measurements are undertaken at a scan speed of $2^\circ$/min for the scanning range ranging from $10^\circ$ to $70^\circ$. Thin films composed of nanoparticles were used for measuring optical and electrical parameters. For optical studies, we recorded the Raman spectra, photoluminescence, optical absorption, reflection, and transmission of these thin films containing nanoparticles. Optical absorption and reflection of these thin films were measured by UV–vis spectrophotometer (UV-1620PC, Shimadzu Corporation, Nakagyo-ku, Kyoto, Japan). Raman spectrum is recorded by a Raman spectrophotometer (DXR, Thermo Fisher Scientific, Waltham, MA, USA), and photoluminescence had been measured by a spectro-fluorophotometer (RF-5301PC, Shimadzu). To study the electrical transport properties, dc conductivity of these thin films was measured as a function of temperature. The resistance of these nanoparticle thin films was measured for a temperature range of $293$ to $473$ K. To measure the
Results and discussion
The morphological studies of these thin films show the presence of high yield of nanoparticles on the surface (Figure 1a). To understand the shape and size of these nanoparticles, we have further undertaken the morphological studies of the dispersed solution of these nanoparticles. Our studies suggest that these nanoparticles are aggregated with an average size of approximately 20 nm, and the particles are quite spherical (Figure 1b). Figure 2 presents the XRD pattern of these nanoparticle thin films. The XRD spectra do not show any significant peak for the thin films of all the studied alloy composition, thereby suggesting the amorphous nature of these nanoparticles synthesized in this study. Raman spectra of (PbSe)\(_{100-x}\)Cd\(_x\) nanoparticles for different concentrations of cadmium are shown in Figure 3. Several Raman bands are observed at 116, 131, 162, 218, 248, 289, 383, and 822 cm\(^{-1}\). The weak peak observed at 116 cm\(^{-1}\) probably originates from the surface phonon (SP) mode, which is close to the reported value of 125 cm\(^{-1}\) for the SP mode in the case of PbSe nanoparticles [33]. The peak at around 131 cm\(^{-1}\) is assigned to the lattice mode vibration. It is an elementary transition, and the energy of this lattice phonon is 16.2 MeV. Murali et al. [33] observed a Raman peak at 135 cm\(^{-1}\) for the PbSe thin films. It is designated as lattice phonon (LO) mode. Similarly, the peaks observed at 162, 218, and 248 cm\(^{-1}\) may be attributed to 2LO(X), LO(L) + LA(L) and 2LO(A) vibration bands, respectively [34]. The peak observed at around 289 cm\(^{-1}\) is closer to the reported value of 279 cm\(^{-1}\), which is to be associated with two phonon scattering (2LO) [35]. The high-frequency peak that appeared at 822 cm\(^{-1}\) is in accordance with the polar theory, which is close to the reported value of 800 cm\(^{-1}\) for PbSe films possibly corresponding to the ground state energy of the polar on the study of Appel [36]. It is observed from the Raman studies that this alloy also contains some phases of CdSe, and a peak at 383 cm\(^{-1}\) has been observed. This peak is near the reported value of 410 cm\(^{-1}\), corresponding to the CdSe LO phonon mode [37,38]. Here, it is clear that all the observed Raman peaks show a wavelength shift on adding Cd to the PbSe system. In the case of the present system of (PbSe)\(_{100-x}\)Cd\(_x\) nanoparticles, this shift in wavelength on low as well as on high sides may be associated with the shape of dispersion of LO phonon with a maximum wavelength at the zone center, which decreases as the phonon vector moves toward the zone edges. It is also suggested that the optical phonon line will also get broadened on reducing the size to nanoscale dimensions. This broadening may also originate from the disorder present in these nanoparticles.

The room-temperature photoluminescence (PL) spectra of these thin films of a-(PbSe)\(_{100-x}\)Cd\(_x\) nanoparticles as a function of incident wavelength is presented in Figure 4. The spectrum shows the emission peak under PL excitation wavelength at 300 nm within the range of 300 to 600 nm. We have observed the emission peak at 360 and 380 nm and a broad peak at 425 nm for a-(PbSe)\(_{100-x}\)Cd\(_x\) nanoparticles. These peaks show a shift to the lower wavelength side as the metal (Cd) concentration increases. It is suggested that this shift in the emission peaks toward the lower wavelength side may be attributed to the narrowing of the bandgap of a-(PbSe)\(_{100-x}\)Cd\(_x\) nanoparticles with the increase in cadmium concentration. This shows clearly an agreement with our results on the variation of optical bandgap with metal (Cd) content, which decreases with the increase in Cd content. It is also observed that these peaks show a broad full width at half maximum, which suggests the effect of size reduction to nanoscale in the present samples. Arivazhagan et al. [39] studied the effect of thickness on the vacuum-deposited PbSe thin film. They reported that the emission peak centered at 380, 386, 388, and 405 nm for the films of thickness 50, 100, 150, and 200 nm, respectively. This suggests that the peak shows a blueshift with the decreasing film thickness. In our case, we have deposited the films of 20-nm thickness. Therefore, the peak observed at 360 nm shows a further blueshift due to
to the decrease in film thickness (20 nm) as compared with that of the reported results of 50-nm-thick PbSe films. A new peak originating at 380 nm may be due to the addition of Cd to PbSe. These peaks show a blueshift with the increase in Cd content. Several workers [40] showed an emission peak at 420 nm under the PL excitation at 300 nm for nanocrystalline PbSe. In our case, we have also observed the emission peak at 425 nm for the thin films of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles, which shows a slight red shift as compared with that of the reported results. This may be due to the disorder (amorphous nature) present in the films. This peak also shows a slight blueshift with the increase in Cd content. Therefore, the peak observed at 425 nm agrees well with that of the reported results [40].

![Figure 2 XRD patterns at various concentrations of Cd in thin films of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles.](image)

![Figure 3 Raman spectra at various concentrations of Cd in thin films of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles.](image)
The understanding of optical and electrical processes in lead chalcogenide materials in nanoscale is of great interest for both fundamental and technological points of view. In recent years, owing to their very interesting physical properties, this particular material has raised a considerable deal of research interest followed by technological applications in the field of micro/optoelectronics. Significant research efforts have been focused to the study of the optical and electrical properties of this compound in thin film formation because the optimization of device performance requires a well-established knowledge of these properties of PbSe and metal-doped PbSe thin films. Here, we have studied the optical absorption, reflection, and transmission of amorphous thin films of \((\text{PbSe})_{100-x}\text{Cd}_x\) nanoparticles as a function of the incident wavelength in the range of 400 to 1–200 nm.

The optical absorption studies of materials provide a simple approach to understand the band structure and energy gap of nonmetallic materials. Normally, the absorption coefficient is measured in the high and intermediate absorption regions to study the optical properties of materials. It is one of the most important means of determining the band structures of semiconductors. On the basis of measured optical density, we use the following relation to estimate the values of the absorption coefficient [4]:

\[
\text{Absorption coefficient } (\alpha) = \frac{\text{OD}}{t}, \quad (1)
\]

where OD is the optical density measured at a given layer thickness \((t)\).

On the basis of the calculated values of absorption coefficient, we have observed that the value of absorption coefficient increases with the increase in photon energy for all the studied thin films of \(a-(\text{PbSe})_{100-x}\text{Cd}_x\) nanoparticles. During the absorption process, a photon of known energy excites an electron from a lower to a higher energy state, corresponding to an absorption edge. In the case of chalcogenides, we observe a typical absorption edge, which can be broadly attributed to one of the three processes: (1) residual below-gap absorption (2) Urbach tails, and (3) interband absorption. Highly reproducible optical edges are being observed in chalcogenide glasses. These edges in chalcogenides are relatively insensitive to the preparation conditions, and only the observable absorption [41] with a gap under equilibrium conditions accounts for the first process. A different type of optical absorption edge is observed in amorphous materials, and absorption coefficient increases exponentially with the photon energy near the energy gap. A similar behavior has also been observed in other chalcogenides [42]. This optical absorption edge is known as the Urbach edge and is given as follows:

\[
\text{Absorption coefficient } (\alpha) \sim \exp\left[A(h\nu - h\nu_0)\right]/k_BT, \quad (2)
\]

where \(A\) is a constant of the order of unity, \(\nu\) is the frequency of the incident beam \((\omega = 2\pi\nu)\), \(\nu_0\) is the constant corresponding to the lowest excitonic frequency, \(k_B\) is the Boltzmann constant, and \(T\) is the absolute temperature.
The calculated values of the absorption coefficient for thin films of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles are of the order of approximately $10^5$ cm$^{-1}$, which is consistent with the reported results [43,44]. The calculated values of absorption coefficient ($\alpha$) are given in Table 1. It is observed that $\alpha$ shows an overall increasing trend with the increase in the metal (Cd) concentration. It is suggested that bond breaking and bond rearrangement may take place when there is increasing cadmium concentration, which results in the change in local structure of these lead chalcogenide nanoparticles. This includes subtle effects such as shifts in the absorption edge, and more substantial atomic and molecular reconfiguration which is associated with changes in the absorption coefficient and absorption edge shift.

In the case of amorphous semiconductors, the fundamental absorption edge follows an exponential law. Above the exponential tail, the absorption coefficient obeys the following equation [4]:

\[ (\alpha \theta)^{1/m} = B(\theta - E_g)^{-x} \]

where $B$ is a constant, $E_g$ is the optical bandgap, and $m$ is a parameter that depends on both the type of transition (direct or indirect) and the profile of the electron density in the valence and conduction bands. The values of $m$ can be assumed to be 1/2, 3/2, 2, and 3, depending on the nature of electronic transition responsible for the absorption: $m = 1/2$ for allowed direct transition, $m = 3/2$ for forbidden direct transition, $m = 2$ for allowed indirect transition, and $m = 3$ for forbidden indirect transition.

The present systems of a-(PbSe)$_{100-x}$Cd$_x$ obey the role of direct transition, and the relation between the optical gap, absorption coefficient $\alpha$, and the energy ($\theta$) of the incident photon is given as follows:

\[ (\alpha \theta)^2 = B(\theta - E_g) \]

The variations of $(\alpha \theta)^2$ with photon energy ($\theta$) for a-(PbSe)$_{100-x}$Cd$_x$ nanoparticle films are shown in Figure 5. Using this figure, the intercept on the x-axis gives the value of direct optical bandgap $E_g$ and the calculated values of $E_g$ for a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles are given in Table 1. It is clear from the table that $E_g$ decreases with the increase in Cd concentration in this system of nanoparticles. This decrease in optical bandgap may be explained on the basis of ‘density of state model’ proposed by Mott and Davis [45]. According to this model, the width of the localized states near the mobility edges depends on the degree of disorder and defects present in the amorphous structure. In particular, it is known that unsaturated bonds together with some saturated bonds are produced as the result of an insufficient number of atoms deposited in the amorphous film [46]. The unsaturated bonds are responsible for the formation of some defects in the films, producing localized states in the amorphous solids. The presence of high concentration of localized states in the band structure is responsible for the decrease in optical bandgap on increasing dopant (Cd) concentration in these amorphous films of (PbSe)$_{100-x}$Cd$_x$ nanoparticles. This decrease in optical bandgap may also be due to the shift in the Fermi level whose position is determined by the distribution of electrons over the localized states [47].

The values of refractive index ($n$) and extinction coefficient ($k$) have been calculated using the theory of reflectivity of light. According to this theory, the reflectance of light from a thin film can be expressed in term of the Fresnel’s coefficient. The reflectivity [48-50] on an interface is given as follows:

\[ n = \left[ (1 + R) + \{ (1 + R)^2 - (1 - R)^2 (1 + k^2) \}^{1/2} \right] / (1 - R) \]

where the value of $k$ has been calculated by using the following formula:

\[ k = (\alpha \lambda)/(4\pi) \]

with $\lambda$ is the wavelength.

Figures 6 and 7 show the spectral dependence of the extinction coefficient and refractive index for a-(PbSe)$_{100-x}$Cd$_x$ thin films. It is observed that the values of these optical constants ($n$ and $k$) increase with the increase in photon energy. A similar trend has also been observed for thin films of other various amorphous semiconductors [51,52]. The values of $n$ and $k$ for different concentrations of Cd are given in Table 1. It is evident from the table that, overall, the value of these optical constants increases with the increase in dopant concentration. This can be understood on the basis of density of defect states. It is well known that chalcogenide thin films contain a high concentration of unsaturated defects.
bonds or defects. These defects are responsible for the presence of localized states in the amorphous bandgap [53]. In our case, the addition of Cd in the PbSe alloy results in the increased number of unsaturated defects. Due to this increase in the number of unsaturated defects, the density of localized states in the band structure increases, which consequently leads to the increase in values of refractive index and extinction coefficient with the addition of metal (Cd) content.

For the study of electrical transport in amorphous semiconductors, especially chalcogenide glasses, dc conductivity is one of the important parameters. The dc conductivity of chalcogenide glasses depends on the combination of starting components, synthesis conditions, rate of melt annealing, purity of starting components, thermal treatment, and on some other important factors. The electrical conduction process in amorphous semiconductors is generally governed by the three mechanisms namely (1) the transfer of charge carriers between delocalized states in the conduction band ($E > E_c$) and valence band ($E < E_v$), (2) transitions of charge carriers in the band tails, and (3) the hopping of charge carriers between delocalized states in

Figure 5 Temperature dependence of dc conductivity. It is in the range of 297 to 400 K at various concentrations of Cd in thin films of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles.

Figure 6 $(\alpha h\nu)^2$ against photon energy $(h\nu)$ for thin films of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles.
bands near the Fermi level ($E_F$). To explain the conduction mechanism in amorphous semiconductors, studies on temperature dependence of conductivity is reported by various workers [54-57]. It is understood that conduction in chalcogenide glasses is intrinsic [58,59] and that the Fermi level is close to the midway of the energy gap. Intrinsic conduction of amorphous semiconductors is determined by carrier hopping from the states close to the edge of the valence band to localized states near the Fermi level or from the state near the Fermi level to the conduction band. The suitable conduction mechanism is decided depending on the predominant process. In the case of chalcogenide glasses, the Fermi level is somewhat shifted from the middle of the energy gap toward the valence band [60].

In the present work, we have also studied the temperature dependence of dc conductivity of thin films of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles over the temperature range of 297 to 400 K. From the variations of dc conductivity with temperature, it is found that the experimental data for the entire temperature range is fitted well with the thermally activated process model. To elucidate the conduction mechanism in the present sample of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles, we have applied the thermally activated process for the temperature region of 297 to 400 K.

The plot of $\ln \sigma_{dc}$ versus $1000/T$ for the temperature range of 297 to 400 K is presented in Figure 8. The graph is a straight line, indicating that the conduction in this system is through a thermally activated process. The conductivity is, therefore, expressed by the usual relation given as follows [4]:

$$\sigma_{dc} = \sigma_0 \exp\left(-\Delta E_c/k_B T\right), \quad (7)$$

where $\sigma_0$ represents the pre-exponential factor, and $\Delta E_c$ is the dc activation energy which is calculated from the slope of $\ln \sigma_{dc}$ versus $1000/T$ plot.

Using the slope and intercept of Figure 8, we have calculated the value of $\Delta E_c$ and $\sigma_0$, respectively.

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Figure 7 Variation of extinction coefficient ($k$) with incident photon energy ($h\nu$) in thin films of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles.

Figure 8 Variation of refractive index ($n$) with incident photon energy ($h\nu$) in thin films of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles.
calculated values of $\Delta E_c$ and $\sigma_0$ for different compositions of cadmium in a-(PbSe)$_{100-x}$Cd$_x$ nanoparticle thin films are shown in Table 1. On the basis of these calculated values, it may be suggested that the conduction is due to the thermally assisted tunneling of charge carriers in the extended states for the temperature range of 297 to 400 K of our sample a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles. However, it is important to mention that activation energy alone does not provide any information as to whether conduction takes place in the extended states above the mobility edge or by hopping in the localized states. This is due to the fact that both of these conduction mechanisms may take place simultaneously. The activation energy in the former case represents the energy difference between mobility edge and the Fermi level, $E_c - E_F$ or $E_F - E_V$ and in the latter case, it represents the sum of the energy separation between the occupied localized states and the separation between the Fermi level and the mobility edge. It is evident from Table 1 that dc conductivity increases as the concentration of Cd increases, whereas the value of activation energy decreases with the increase in Cd contents in our lead chalcogenide nanoparticles. An increase in dc conductivity with a corresponding decrease in activation energy is found to be associated with a shift of the Fermi level for the impurity-doped chalcogenide [46,61]. It also shows that the Fermi level changes after the incorporation of Cd. However, it has also been pointed out that the increase in conductivity could be caused by the increase in the portion of hopping conduction through defect states associated with the impurity atoms [62].

A clear distinction between these two conduction mechanisms can be made on the basis of the pre-exponential factor value. For conduction in extended states, the value of $\sigma_0$ reported for a-Se and other Se alloys in thin films is of the order $10^9 \Omega^{-1}$ cm$^{-1}$ [62]. In the present sample of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles, the value of $\sigma_0$ is of the order $10^7 \Omega^{-1}$ cm$^{-1}$. Therefore, extended state conduction is most likely to take place. An overall decrease in the value of $\sigma_0$ is observed with the increase in Cd contents in the PbSe system, which may be explained using the shift of Fermi level on adding Cd impurity. Therefore, the decrease in the value of $\sigma_0$ may be due to the change in Fermi level on adding Cd in the PbSe System.

**Conclusions**

Thin films of amorphous (PbSe)$_{100-x}$Cd$_x$ nanoparticles have been synthesized using thermal evaporation technique. The average diameter of these nanoparticles is approximately 20 nm. Raman spectra of these a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles revealed the presence of PbSe phases in as-synthesized thin films, and the observed wavelength shift in the peak position as compared with that of reported values on PbSe may be due to the addition of Cd impurity. PL spectra suggest that the peaks show a shift to the lower wavelength side as the metal (Cd) concentration increases, which may be attributed to the narrowing of the bandgap of a-(PbSe)$_{100-x}$Cd$_x$ nanoparticles with the increase in cadmium concentration. A direct optical bandgap is observed, which decreases on increasing cadmium concentration. This may also be due to the increase in the density of defect states, which results in the extension of tailing of bands. The value of refraction index and extinction coefficient increases with increasing photon energy for all samples of a-(PbSe)$_{100-x}$Cd$_x$. From temperature dependence of dc conductivity measurements, it may be concluded that conduction is taking place through the thermally activated process over the entire range of investigation. The pre-exponential factor shows an overall decreasing trend with increasing Cd content. The decrease in $\sigma_0$ may be due to the change in the Fermi level on the addition of Cd in the lead chalcogenide system. Finally, the suitability of these nanoparticles of lead chalcogenides for various applications especially in solar cells can be understood on the basis of these properties.

**Competing interests**

The authors declare that they have no competing interests.

**Authors’ contributions**

Both authors - MAA and ZHK - participated equally in the experiments performed to accomplish this work and in the preparation of this manuscript. Both authors read and approved the final manuscript.

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