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Studies on selenium rich Lead Chalcogenide $Pb_5Se_{95-x}Zn_x$ (X =0, 2.5, 5, and 10) thin films composed of NPs

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ABSTRACT

The as-prepared Se rich (maximum of 95%) samples have been synthesized by melt-quenching method. Thin films of $Pb_5Se_{95-x}Zn_x$ (X =0, 2.5, 5, and 10) have been deposited onto glass substrate (at 100 K), via thermal evaporation method. HRTEM and XRD pattern depict polycrystalline, cubic nanoparticles of average size 21 nm. The particles size has been found to be decreasing with increase in dopent content; this has been verified by FWHM values of the XRD peaks. The stoichiometries of the constituent elements of as-prepared thin films have been confirmed by the EDAX analysis. PL-emission spectra analysis reveals blue shift and peak broadening trends with increase in dopent concentration and laser irradiation time. This is the indication of decrease in particle size with increase in dopent concentration and laser-irradiation time. Thus, defects in as-synthesized lattice are increased which in turn increase the optical band gap. UV/Visible spectroscopy suggests a direct band-gap which increases with increase in Zn content and laser-irradiation time in the deposited thin films.

1. Introduction

Due to many interesting technical applications, lead chalcogenides have been one of the important class of materials [1,2]. PbSe, among the chalcogenides, is a popular material, due to its low band gap of 0.28 eV with large Bohr radius (46 nm). This ensues in strong electron-hole pair confinement and high optical nonlinearity [3]. The development of the multiple exciton generation effect in lead chalcogenides provided an entirely new epitome for low cost and highly efficient technologies for solar cells [4]. The chalcogenides materials can easily be doped to tune the electrical and optical properties. PbSe is also an interesting material for various applications, such as: near-IR luminescence, laser materials thermoelectric devices, sensors, thermoelectronic devices, solar-cells and IR-detectors [5–10]. The lead chalcogenides are found highly applicable in device fabrication due to their high carrier mobility, high dielectric, high transmittance and small optical band gap [11–14].

The structure of thin films and their electronic properties are highly influenced by the synthesis methods and deposition conditions [15–19]. Therefore, all the properties such as: structural, mechanical, electrical and optical can be easily tuned by controlling the physical conditions, compositions and deposition parameters [20,21]. Among all the different methods, thermal evaporation method is very attractive due to its high reliability, controlled deposition rate, easy manipulation, and cost effective for devices fabrication [22]. The band gap of PbSe can be easily tuned by varying the particle size and by doping it with suitable foreign materials [23–27]. This leads to an innovation for fabricating thin films of PbSe with desirable band gap to absorb maximum intensity of the incident solar radiation. Therefore, a lot of investigations have been passed through, proposing wide band-gap PbSe materials. Zhu et al. synthesized PbSe NPs with band gap of 2.15 eV via chemical route [26]. It is evident that the optical band gap of PbSe material alters within a broad range.

The present work focuses on selenium (Se) rich glassy sample of $Pb_5Se_{95-x}Zn_x$ (x=0, 2.5, 5, and 10). We have synthesized the glassy alloys of $Pb_5Se_{95-x}Zn_x$ using melt quenching method and the thin films have been prepared by thermal evaporation method. The structural and optical studies of the thin film of $Pb_5Se_{95-x}Zn_x$ have been investigated.

2. Materials and methods

The bulk samples of Se rich alloys $Pb_5Se_{95-x}Zn_x$ (x=0, 2.5, 5, and 10) were synthesized by the method of melt-quenching. The synthesis of the alloys $Pb_5Se_{95-x}Zn_x$ consist of extremely unadulterated (99.999%) lead(Pb), Selenium(Se) and Zinc(Zn) of Sigma Aldrich (USA). The required quantities of above elements were taken in accordance with their atomic proportion and then filled in quartz ampoules. The interior of the filled ampoules were maintained at a

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pressure of 10^{-6} Torr and then sealed. The sealed ampoules were kept in a programmable muffle furnace, for 16 h at 600 °C through a constant heating rate of 10 °C/min. The heated ampoules were agitated, time and again in order to make a homogeneous material. After completion of the process, they were quickly quenched into ice water. Thin films of the prepared samples were deposited onto ultra cleaned glass substrates by thermal evaporation method. These glass substrates were maintained at 100 K by using liquid nitrogen. The PVD chamber was maintained at a pressure of 10^{-5} Torr. Subsequently, an amount of ambient argon gas was supplied into it, till the pressure became 5 Torr. The pressure was then maintained throughout the deposition process. Since, the properties of thin films are significantly influenced by their thickness [28]; therefore, a thickness monitor (Edward-FTM7) was monitored to measure the thickness of the film until a thickness of 200 nm ± 10% got deposited onto glass substrates maintained at 100 K.

The effect of laser irradiation on the thin films was studied subjected to a He-Ne laser of wavelength 6328 Å, irradiated for 5 min & 10 min respectively. SEM images of the thin films were studied by using high resolution scanning electron microscope (HRSEM-Carl Zeiss Sigma) at 5 kV operating voltage. The purpose was to study the surface and cross-section morphology of as-deposited thin films of $Pb_5Se_{95-X}Zn_X$. Energy dispersive X-ray analysis(EDAX) of the synthesized samples was obtained by using the instrument Bruker (Inc. Germany). High resolution traveling electron microscope (HRTEM) investigations of as-prepared samples were studied at 300 kV by using the instrument Technai (Model-G230S TWIN). X-ray diffraction (XRD) analysis of as-deposited thin films was observed on rotating anode diffractometer using X-ray diffractograms (Rigaku Ultima IV) at wavelength of 1.54056 Å (Cukα1), scanning rate was 5°/min and range was 2θ from 15° −85°. Photoluminescence(PL) emission spectra of the synthesized samples was recorded by using fluorescence spectrophotometer Perkin Elma (Model-LS55). Optical absorbance of the thin films was observed against wavelength, by utilizing a double beam UV/VIS/NIR spectrophotometer (Perkin Elma-Lamda 35).

3. Results and discussion

3.1. Structural studies

Morphology of as-prepared thin film of $Pb_5Se_{85}Zn_{10}$ has been investigated by using High resolution Scanning Electron Microscope (HRSEM). Fig. 1 depicts scanning electron microscope(SEM) images of the thin film. From these images we have observed that as-prepared

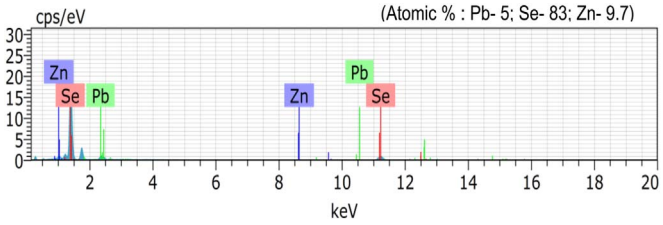

Fig. 2. : EDAX Image of as-deposited $Pb_5Se_{95-x}Zn_x$ thin film with x=10.

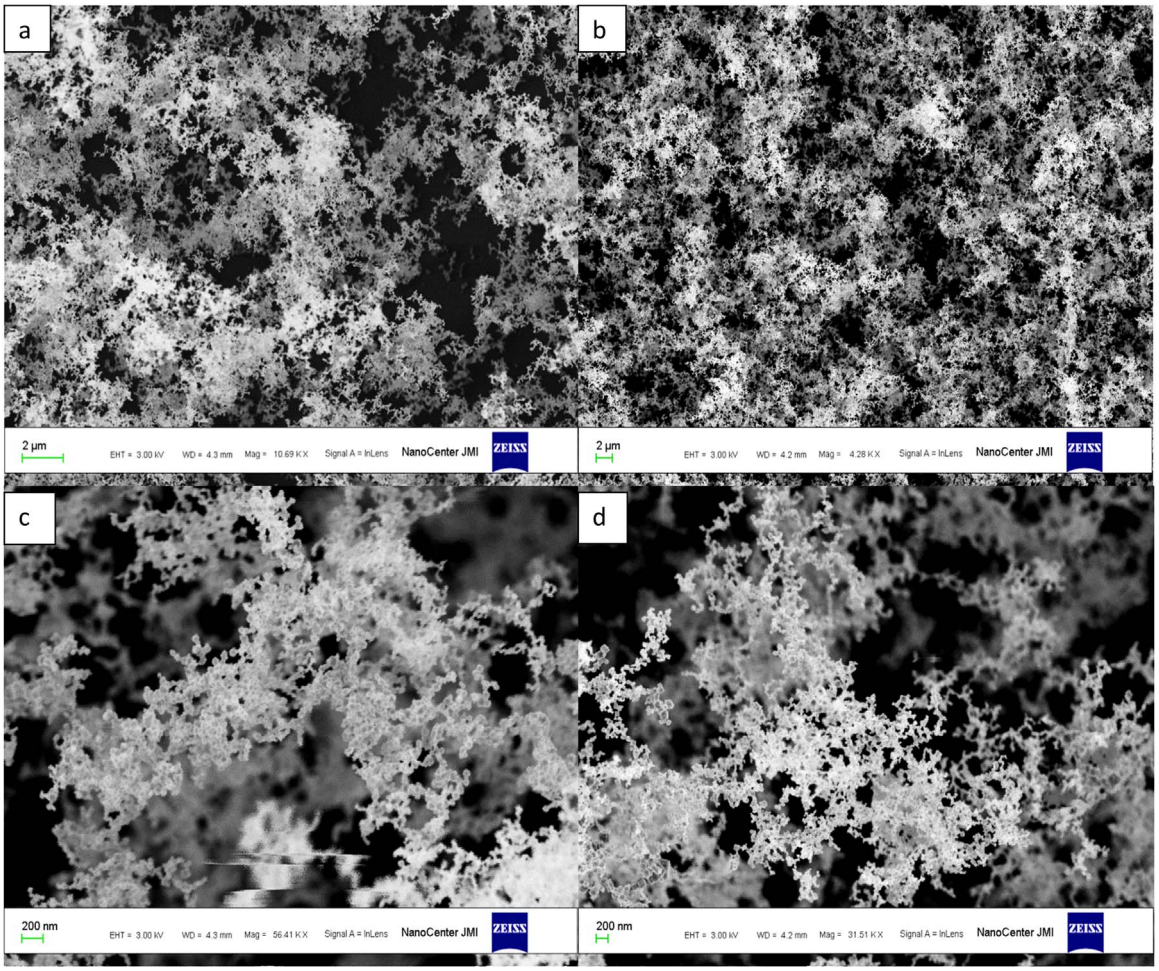

Fig. 1. (a-d): FESEM Images of as-deposited $Pb_5Se_{95-x}Zn_x$ film with x=10.