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PHOTOLUMINESCENCE STUDIES OF CHEMICAL BATH DEPOSITED NANOCRYSTALLINE PbS AND $Zn_xPb_{1-x}S$ (x=0.02) THIN FILMS

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Nanocrystalline PbS and $Zn_xPb_{1-x}S$ (x = 0.02) thin films have been deposited on glass substrates by chemical bath deposition (CBD) method. The as deposited thin films were found to be crystalline having cubic phase structure. The photoluminescence properties of the undoped and Zn doped PbS thin film have been studied. The $Zn_xPb_{1-x}S$ film shows four emission peaks at 386, 418, 517 and 595 nm wavelengths, excited at $\lambda = 290$ nm and one emission peak at $\lambda = 693$ nm is observed for the undoped PbS thin film when excited at 524 nm.

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1. Introduction

The study of optical properties of nanocrystalline solids have become the topic of great interest from the theoretical and experimental research point of view. It is known that nanocrystalline semiconductors exhibit the “quantum confinement effect’’ and possess many superior properties as compared to bulk counterparts. As a consequence of quantum confinement, the continuum of states in the conduction and valance band are broken down into discrete states with an energy spacing relative to the band edge, which is approximately inversely proportional to the square of the particle radius [1], resulting in widening of the band gap as compared to the bulk. This is normally observed by a blue shift in the optical absorption spectra. The absorption edge of lead sulphide (PbS) exhibits a large blue shift when the size of the crystallite size is reduced to nanometre scale [2-5]. The structural and optical properties of pure nanocrystalline PbS thin films have been widely reported in the literature. However, detailed studies on optical properties of Zn doped PbS thin films have not been reported in the literature to the best of our knowledge. In this paper, a detailed study on structural and photoluminescence properties of chemical bath deposited undoped and Zn doped PbS nanostructured thin films is reported. This study was aimed to gain into inside the material properties of the systems for their practical applications in electronic devices such as photovoltaic cells, light emitting devices, light detector etc.

2. Experimental procedure

The source materials used for fabrication of undoped lead sulphide (PbS) thin films were lead acetate, $Pb(CH_3COO)_2$ and thiourea $(NH_2)_2CS$. $Pb(CH_3COO)_2$ solution was prepared by dissolving the required amount of it in distilled water. To the above solution, dilute ammonium hydroxide(NH_4OH) solution was added drop wise, keeping it constantly stirred, till we get a final solution with pH value of 11.

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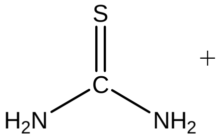
To the above solution, we added equimolar solution of thiourea and the mixture was stirred well for some time to get homogeneous solution. Then the glass substrates were kept overnight by immersing inside the above solution with the help of a specially designed substrate holder after which PbS thin films were obtained. Then the thin films were washed with deionised water and allowed to dry in a desiccator. The unwanted film on one side of the substrate was removed by treating the surface with dilute HCl acid and cleaned by a cotton swap rinsed with distilled water taking precaution that the dil. HCl does not disturb the film on the other side of the substrate. The starting materials used for fabrication of nanocrystalline $Zn_xPb_{1-x}S$ (x=0.02) thin films were lead acetate $Pb(CH_3COO)_2$, zinc acetate $Zn(CH_3COO)_2$, and thiourea $(NH_2)_2CS$. Thin films were prepared by following the same procedure that was used for preparing undoped PbS thin film as described above. The stepwise chemical reaction mechanisms involved in the fabrication of the samples are as follows [6]:

Reaction mechanism for undoped PbS thin film:

Step I.

$$Pb(CH_3COO)_2 \longrightarrow Pb^{2+} + 2CH_3COO^{1-}$$

Step II.



$$+ \ OH^- \longrightarrow CH_2N_2 + H_2O + SH^-$$

Step III.

$$SH^- + OH^- \longrightarrow S^{2-} + H_2O$$

Step IV

$$S^{2-} + Pb^{2+} \longrightarrow PbS\downarrow$$

deposited on glass

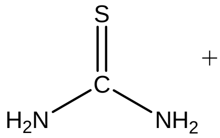
Reaction mechanism for doped PbS thin film:

Step I.

$$Zn(CH_3COO)_2 \longrightarrow Zn^{2+} + 2CH_3COO^{1-}$$

$$Pb(CH_3COO)_2 \longrightarrow Pb^{2+} + 2CH_3COO^{1-}$$

Step II.



$$+ \ OH^- \longrightarrow CH_2N_2 + H_2O + SH^-$$

Step III.

$$SH^- + OH^- \longrightarrow S^{2-} + H_2O$$

Step IV.

$$(1-x)Pb^{2+} + xZn^{2+} + S^{2-} \longrightarrow Zn_xPb_{1-x}S\downarrow$$

deposited on glass

The structural characterization of the samples was carried out by using PANalytical X' Pert Pro X-ray diffractometer at the Department of Physics, Manipur University. The optical properties of the samples were studied by using Perkin Elmer LS55 Fluorescence Spectrometer facility available in the Department of Chemistry, Manipur University.

3. Results and discussion

3.1 Structural Properties

Fig.1 shows the XRD pattern of as-deposited PbS and $Zn_XPb_{1-X}S$ (x=0.02) films deposited at room temperature. In the case of as-deposited PbS films, we observe sharp peaks at $2\theta \approx 25.9°$, 29.9°, 43.0°, 50.9° and 53.4°. The observed peak positions are consistent with the fcc cubic phase structure of PbS [7, 8]. With the addition of Zn, the peak intensities decrease considerably. This can be attributed to doping induced structural disorder in the films [9].

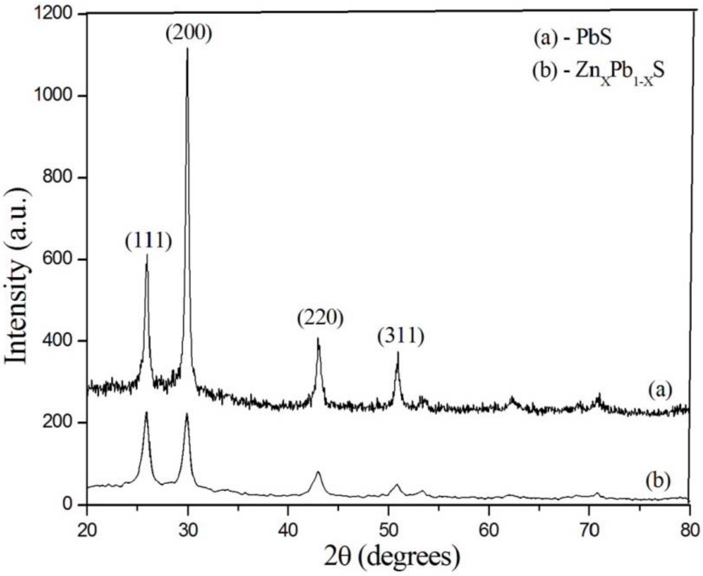


Fig.1. XRD patterns of (a) PbS thin film sample and (b) $Zn_XPb_{1-X}S$ *thin film sample*

With doping of Zn, the broadening of the peaks is quite obvious from Fig. 1. There are two main possible causes for the peak broadening. The first is the increase in heterogeneity of the films due to the occupation of Zn into the host lattice. A second cause could be the decrease in the particle size (D). When Zn^{+2} occupies more and more sites of Pb^{2+} in the host lattice, internal strain would arise and the crystal structure of ZnPbS solid solution becomes unstable. In order to stabilize the crystal structure, there would be a spontaneous size reduction of the particles which might release the strain. As the Zn concentration is increased, the diffraction peaks become broader due to a reduction in the size [10]. The crystalline sizes of the film were calculated from the XRD spectra using the Scherer's relation

$$D = \frac{k\lambda}{\beta cos\theta} \tag{1}$$

where k is a constant equal to 0.94, λ is the wavelength of the x-ray used (CuK_α radiation, λ = 1.5418 Å), β is the full width at half maximum (FWHM) of the dominant x-ray diffraction peak in radian [11] and θ is the diffraction angle of the dominant peak. The average crystallite size of PbS film was found to be 29 nm while that of the $Zn_xPb_{1-x}S$ thin film was found to be 15 nm. The decrease in crystallite size of $Zn_xPb_{1-x}S$ may be due to the replacement of some the larger size lead ions (1.21Å) by smaller size zinc ions (0.74Å). Similar results are reported for Mn-doped CdS films [12,13].

3.2 Photoluminescence Properties

The room temperature PL emission spectra of the nanocrystalline PbS thin film is shown in Fig. 2. The emission peak was observed at wavelength 693 nm when the sample was excited at 524 nm. It has been reported in the literature that PbS is weakly luminescent at room temperature [14]. However, the low emission peak at 693 nm (red region) is shifting from the infrared region of bulk value 3200 nm [15]. This may be attributed to quantum confinement effect in our samples. It has been also reported that ZnS shows strong photoluminescence effect [16]. Thus, by doping PbS with Zn may improve its photoluminescence properties. Therefore, we have studied the photoluminescence properties of Zn doped PbS thin films.

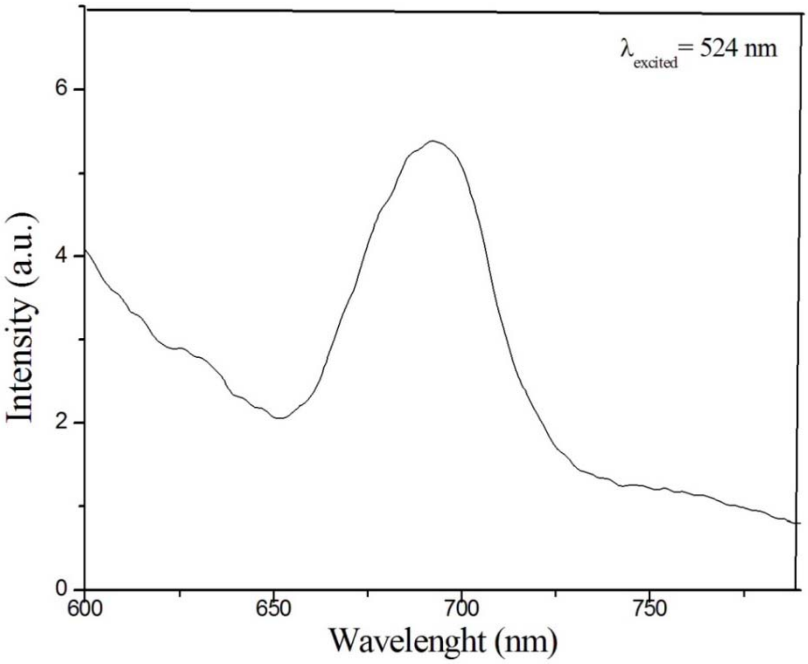
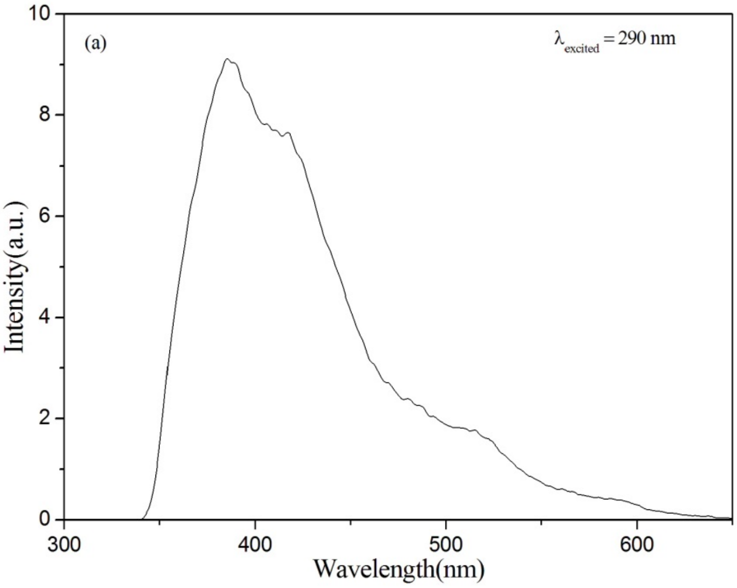


Fig. 2. PL emission spectra of nanocrystalline PbS thin film

The spectrum in Fig. 3(a) shows that the luminescence peaks ascribed to the nanocrystalline $Zn_xPb_{1-x}S$ (x=0.02) thin film sample is not symmetrical, but has a tail towards longer wavelengths. To investigate this, the spectrum excited at 290 nm was fitted with multiple Gaussian profiles. Fig. 3(b) shows that four Gaussian peaks are necessary to provide an acceptable fit, with peak wavelengths of 386 nm, 418 nm (corresponding to the ZnS emission), 517nm and 595 nm [15].The latter two wavelengths correspond to different transitions from the PbS. From the first two wavelengths, the shorter wavelength 386 nm is ascribed to a direct band to band transition of nanocrystalline ZnS and the second broad peak centred at 418 nm is attributed to the presence of sulphur vacancies in the lattice [17]. This emission results from the recombination of photo generated charge carriers in shallow traps [18, 19]. The remaining two peaks centred at longer wavelengths 517 nm and 595 nm are due to the transitions in nanocrystalline PbS. The shorter wavelength emission is ascribed to a direct recombination and the longer wavelength to a recombination through shallow surface states.[20,21,22,23].



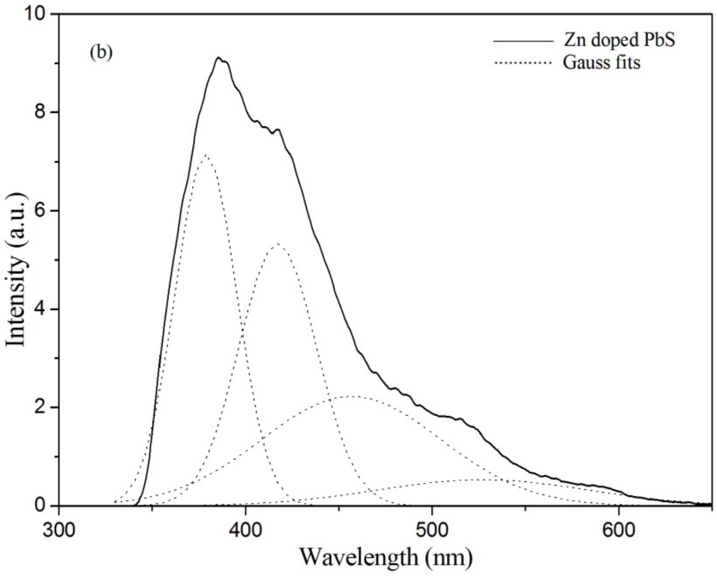


Fig. 3. (a) PL spectra of the nanocrystalline $Zn_xPb_{1-x}S$ (x=0.02) thin film sample excited at wavelength 290 nm; (b) The 290-nm excited emission spectrum fitted with multiple Gaussian profiles.

4. Conclusion

Nanocrystalline PbS and $Zn_xPb_{1-x}S$ (x=0.02) thin films having average crystallite sizes of 29 and 15 nm were prepared by chemical bath deposition method. The films showed cubic phase structures and the crystallite size was found to decrease by Zn doping. Lead sulphide thin films doped with Zn shows better photoluminescence properties as compared to undoped PbS thin films.

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