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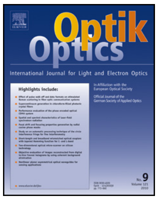

On the optical properties of lead chalcogenide nanoparticles

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ABSTRACT

Lead chalcogenide (PbS, PbSe) nanoparticles are prepared for two equimolar concentrations (0.25 and 0.5) by simple and low cost sol–gel method at room temperature. The obtained Pb(S,Se) nanoparticles were characterized by XRD, FTIR, SEM and Optical analysis. The XRD pattern confirm the Pb(S,Se) nanoparticles have face-centered cubic structure and crystallinity found to be increased as increase ($0.5\,\text{mol}\,\text{L}^{-1}$) the concentration. Average crystallite size is found be around 62–69 nm and 66–70 nm for PbS and PbSe, respectively. The FTIR spectra confirms the presence of stretching and bending vibrations of Pb—S at 615, 976, 1096 and 1366 cm^{-1} and Se—O—Se vibrations at 656, 736 and 852 cm^{-1}. In the SEM images, coalescence between grains, homogeneous agglomeration form with spherical particles has shown which is found to be less than 0.5 μm. The band gap energy of PbS is found to be 1.6 eV and 2.1 eV for PbSe.

1. Introduction

Nanocrystalline semiconductor have been focused of scientific research in the past two decades because of their special properties such as a large surface-to-volume ratio, increased activity, special electronic properties; and unique optical properties as compared those of the bulk materials [1]. Recent advances in the synthesis, manipulation and analysis of nanoparticles from a large variety of semiconductor materials have been reached, so it is possible to obtain nanoparticles whose spectral response can be modulated [2]. PbE, (E = S, Se, Te) that are a special class of IV–VI narrow-band-gap (0.2–0.4) semiconductors [3]. These materials shows strong quantum confinement effect due to its large Bhor radius [4] compared with II–VI compounds (CdTe, CdS, CdSe). The quantized electronic transitions in Pb(S, Se) nanocrystal quantum dots (NQDs) have been reported that it provide size-tunable absorption and luminescence emission at a broad and technically important infrared wavelength range, spanning 0.8–4.0 μm [5].

The combination of such properties makes PbE suitable for efficient electroluminescent devices such as tunable near-infrared detectors [6], solar cell materials [7], thermoelectric cooling materials [8], and light—emitting diodes [9] and as Pb^{2+} ion selective sensors [10]. PbE has been prepared by various methods such as microwave [11–13], sonochemical [14–16], hydrothermal [17–20] precipitation [21,22] greener chemical method [23] wet chemical technique [24], pulse sonochemical synthesis [25] photochemical method [26] and mechanochemical method [27]. Among these, the sol–gel method is simple, low temperature process, no requirement of sophisticated instruments and minimum materials. Hence; in this paper, PbS and PbSe nanoparticles were prepared at room temperature under constant atmospheric pressure without any kind of toxic reagents by sol–gel method.

2. Materials and methods

The following precursors such as lead nitrate ($Pb(NO_3)_2$); sodium sulfide ($Na_2S{\cdot}xH_2O$), selenium dioxide (SeO_2), Sodium hydroxide (NaOH), hydrazine hydrate ($N_2H_2{\cdot}H_2O$), ethylenediaminetetraacetic acid (EDTA) and double distilled water were used.

To prepare PbS, equimolar ($0.25\,\text{mol}\,\text{L}^{-1}$ and $0.5\,\text{mol}\,\text{L}^{-1}$) ratio of $Pb(NO_3)_2$ and Na_2S were mixed with distilled water separately and were stirring for 1 h using magnetic stirrer. Then the former solutions were mixed together and again, stirred vigorously about 1 h at room temperature. Consequently, a black precipitate was obtained by proper filtration which was thoroughly washed using distilled water and dried at room temperature for 24 h. To prepare PbSe, equimolar ($0.25\,\text{mol}\,\text{L}^{-1}$ and $0.5\,\text{mol}\,\text{L}^{-1}$) ratio of $Pb(NO_3)_2$ and SeO_2 were made solution by mixing with each 10 mL of distilled water and 10 mL of hydrazine hydrate, respectively. Consequently, the $Pb(NO_3)_2$ solution was complexed with each 10 mL of $0.4\,\text{mol}\,\text{L}^{-1}$ EDTA, and $0.4\,\text{mol}\,\text{L}^{-1}$ NaOH solution and it was allowed vigorous stirring for 1 h. Next, SeO_2 solution was added slowly in to the former complex solution and again stirred

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vigorously for 1 h. Final, the obtained precipitate by proper filtering, which was thoroughly washed with double distilled water and dried at room temperature for 24 h.

The structural characteristics of the Pb(S, Se) nanoparticles were carried out by analyzing the X-ray diffraction (XRD) patterns using Cu $K\alpha$ radiation in the range of $2\theta = 10–80°$ in an X' Pert PRO diffractometer (PANalytical, Netherlands). FTIR spectra of the samples were recorded using Perkin Elmer (Spectrum Two) Fourier Transform Infrared Spectrometer (FTIR) in range of 4000–450 cm^{-1} with resolution of 4 cm^{-1}. JEOL-Scanning Electron Microscopy (SEM) (JSM—5610 LV) was used to record the micrographs of the samples. Optical absorption studies were carried out using a (Ultra Violet) UV–vis spectrometer (UV2202) in the wavelength range of 300–800 nm.

3. Results and analysis

3.1. XRD analysis

The XRD patterns of PbS prepared for equimolar (0.25 mol L^{-1} and 0.5 mol L^{-1}) concentration are shown in Fig. 1(a) and (b) indicates that intense peaks at $2\theta = 26.01°$, $30.11°$, $43.09°$, $51.04°$, $53.43°$, $62.55°$, $68.93°$, $70.88°$, and $78.96°$ corresponding to the reflections of (1 1 1), (2 0 0), (2 2 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (4 2 0) and (4 2 2), respectively, of fcc PbS (JCPDS Card no. 05-0592) with lattice parameter $a = 5.923$ Å.

Further, no other peaks found in the diffraction pattern indicate pure PbS particles. In higher concentration (0.5 mol L^{-1}), the intensity of the fcc characteristic peaks drastically increased as well as brodering of peaks than low Pb concentration. It is an important notice that, increase the Pb concentration does not make any structural changes in the diffraction pattern and no other characteristic peaks were found implying purity of the PbS particles even increase the concentration. The results are in well agreement with the earlier reports by Patel et al. [6] and Ding et al. [11].

The XRD pattern of PbSe prepared with 0.25 mol L^{-1} and 0.5 mol L^{-1} are shown in Fig. 2(a) and (b) indicates diffraction peaks at $2\theta = 25.21°$, $29.16°$, $41.70°$, $49.31°$, $51.71°$, $60.40°$, $66.55°$, $68.45°$ and $76.05°$ corresponding to planes of (1 1 1), (2 0 0), (3 1 1), (2 2 2), (4 0 0), (3 3 1), (4 2 0) and (4 2 2), respectively, of fcc PbSe rock-salt structure (JCPDS 06-0354). In higher concentration (0.5 mol L^{-1}), the intensity of the characteristic peaks gets increased in comparison to low concentration (0.25 mol L^{-1}). On comparing with PbS, the diffraction angle of the characteristics peaks shifted to lower angle which may be due to due to bigger size of Se ions that may shrink the crystal structure. The result is in agreement well with the earlier reports by Xiaofeng et al. [13] and Borhade et al. [17]. However, some additional peaks appear at $2\theta = 26.71°$, $27.97°$, $32.44°$ and $39.82°$ perhaps which is due to the formation of $PbSeO_3$ as an impurity (JCPDS Card no.: 73-0575) and peaks at $2\theta = 26.77°$ and 47.93 are related to the presence of NaOH and $NaNO_3$, respectively. The results are well also in agreement with the earlier report on PbSe by Shimko et al. [22] and Roman-Trujillo et al. [2].

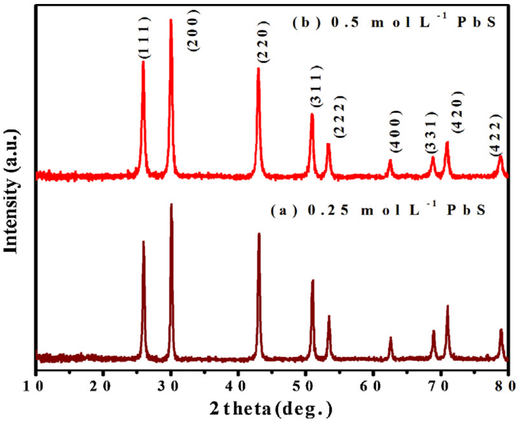

Fig. 1. XRD pattern of PbS prepared for (a) 0.25 mol L^{-1} and (b) 0.5 mol L^{-1}.

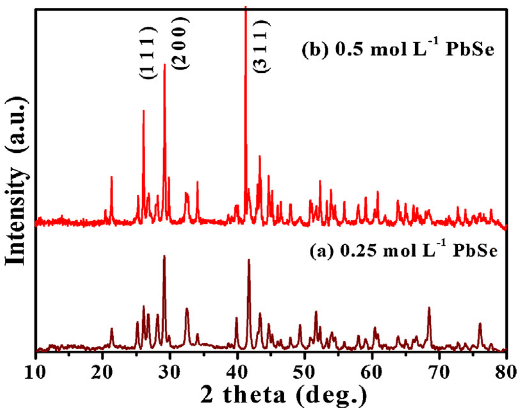

Fig. 2. XRD pattern of PbSe prepared for (a) 0.25 mol L^{-1} and (b) 0.5 mol L^{-1}.

Average crystallite size of the Pb(S,Se) was calculated using the Debye–Scherre formula ($D = K\lambda/\beta\cos\theta$), where D is the crystallite size, K is the Scherrer constant ($K = 0.9$), λ is wavelength of the X-ray source, β is full-peak width at half maximum intensity and θ is the peak position. The average crystallite size of PbS and PbSe are given in Table 1.

The crystallite size of the prepared nanoparticles can also be calculated using the Williamson Hall (W–H) plot through the relation ($\beta\cos\theta = (k\lambda/D) + 4\sigma\sin\theta$) [28], where D is the grain size and σ is the strain. A plot drawn for in x-axis $4\sin\theta$ vs $\beta\cos\theta$ along the y-axis for Pb(S,Se) nanoparticles as shown in Fig. 3. From the linear fit of the data, the crystallite size is estimated from the y-intercept and the result also given in Table 1. The dislocation density δ which represents the amount of defects in the film and it was determined from the formula $\delta = 1/D^2$ [29,30]. The dislocation densities and particle size for prepared samples were also given in Table 1.

Crystallite size found to be decreased with increase of concentration (0.5 mol L^{-1}) in both PbS and PbSe particles. The small dimensions and high monodisparity of PbS and PbSe are intriguing. The small dimension of PbSe may be relates to nucleation and

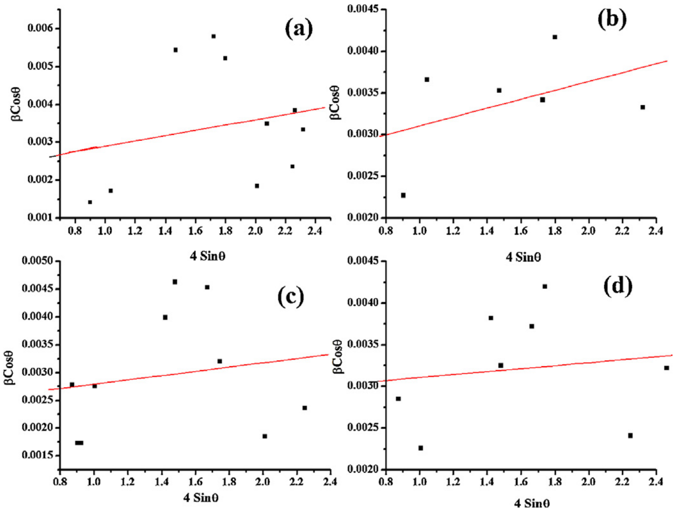

Fig. 3. W–H plot for (a) 0.25 mol L^{-1} PbS, (b) W–H plot for 0.5 mol L^{-1} PbS, (c) W–H plot for 0.25 mol L^{-1} PbSe and (d) W–H plot for 0.5 mol L^{-1} PbS.