Band gap in PbS nanostructured thin films from near-infrared to visible range by in situ Ni-doping


Facultad de Ciencias Químicas, Benemérita Universidad Autónoma de Puebla, C.U. Puebla, Pue. México. P.O. Box 1067, Puebla, Pue., 72001 México

Prep. reg. Simón Bolívar. Atlixco. Pue. BUAP.

Corresponding Author. Tel. (01 222) 2-29-55-00 Ext. 7519.
E-mail: osporti@yahoo.mx

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Band gap in PbS nanostructured thin films from near-infrared to visible range by in situ Ni-doping

1L. A. Chaltel Lima, 1M. Hernández Hernández, 2V. Dorantes-García, 1M. Chávez Portillo, 1A. M, Cervantes Tavera, 1S. Rosas Castilla, 1M. Zamora Tototzintle, 1A. Moreno Rodríguez, 1G. Abarca Ávila, 1*O. Portillo Moreno.

1Facultad de Ciencias Químicas, Benemérita Universidad Autónoma de Puebla, C.U. Puebla, Pue. México. P.O. Box 1067, Puebla, Pue., 72001 México
2Prep. reg. Simón Bolívar. Atlixco. Pue. BUAP.
*Corresponding Author. Tel. (01 222) 2-29-55-00 Ext. 7519.
E-mail: osporti@yahoo.mx

Abstract
The growth of nanocrystalline PbS films by chemical bath deposition (CBD) onto glass at a deposition temperature 80± 2°C is presented in the research. We report on the modification, optical nanostructures due to in situ Ni-doping. The morphological changes of the layers were analyzed using the Scanning Electron microscopy (SEM), and microscopy electronic transmission (TEM). X-ray diffraction (XRD) spectra displayed peaks at the angular positions 2θ = [26.00, 30.07, 43.10, 51.00, 53.48], indicating growth on the zinc blende face. The grain size (GS) determined by XRD of the undoped samples, was found ~36 nm, whereas with the doped sample is found ~32-5 nm, as calculated by employing Scherer’s formula. By TEM, the doped-PbS materials were found crystalline films in the range 3.5-5 nm. Optical absorption (OA), forbidden band gap energy (Eg) shift disclose a shift in the range 2.1-3.8 eV. Finally, Gibbs free energy calculation for the V_{[Ni2+]} doping-PbS process was also established.

Resumen
El crecimiento de películas nanocrystalinas de PbS depositadas mediante la técnica de depósito por baño químico (BBQ) sobre sustratos de vidrio a temperatura de 20± 2°C, es presentada en esta investigación. Reportamos la modificación óptica de las nanoestructuras debido al dopamiento in situ con Ni. Los cambios morfológicos de la capas fueron analizados utilizando microscopía electrónica de barrido (MEB) y microscopía electrónica de transmisión (MET). Los espectros de difracción de rayos (DRX) revelan picos localizados en las posiciones angulares 29 = [26.00, 30.07, 43.10, 51.00, 53.48] indicando crecimiento en fase zinc blenda. El tamaño de grano (TG) es obtenido mediante la fórmula de Scherer’s utilizando los espectros de DRD, para la película no dopada se encontró 36 nm, mientras que las dopadas es de 32-5 nm. De los espectros de absorción Óptica (AO), el ancho de energía de banda prohibida (Eg) muestra corrimiento en el intervalo 2.1-3.8 eV. Finalmente, cálculos en cambios de energía libre de Gibbs en el proceso de dopamiento son establecidos.

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1. Introduction

The ever-increasing interest into deposition of ternary derivative materials, the potential of designing and tailoring both the lattice parameters and the forbidden band-gap energy ($E_g$) by controlling growth parameters [1, 2]. In this regard, many techniques have been successfully employed: successive ionic layer and reaction (SILAR) [3], sol gel methods [4], etc. Most of the studies reported so far have focused in the deposition of ternary derivatives material in thin films as $Cd_{1-x}Zn_xS$ [5], $Cd_{1-x}SCu_x$ [6], $HgCd_{1-x}S$ [7]. Noteworthy is the fact that PbS thin films are promising photovoltaic materials as their variable $E_g$ can be adjusted to match the ideal ~1.5 eV required for achieving a most efficient solar cell [8], likewise size-dependent new physical aspects have generated an ongoing thrust for new practical applications and PbS nanocrystals with grain-size (GS) dimensions in the range 1-20 nm are of technological interest for advanced optoelectronic applications, showing a stronger quantum confinement effect when the crystallite size matches the dimension of Bohr exciton [9]. In this context, there are two situations, called the weak confinement and the strong regimes [10]. In the weak regime the particle radius of the electron-hole pair, but the range of motion of the exciton is limited, which causes a blue shift in the absorption spectrum. When the size of the nanoparticles are below Bohr radius, it's lead to the quantum confinement effect. This confinement induces discrete electronic states in the valence and conduction band of the quantum dots compared to the continuous state of energy in bulk material. If the crystallite size is below the exciton Bohr of the semiconductor, strong quantum confinement occurs. The confinement effect appears as a shift in absorption spectra and the absorption to lower wavelengths, wicks is due to change in the $E_g$ [11,12] and control over assembly through modification of surface functionalization. On the other hand, photovoltaic’s devices are an widely recognized potential application for nanocrystals due, in part, to their high photoconductivity, easy work-up for solutions and also low cost of production. Several schemes for using nanocrystals in solar cells are under active consideration, including nanocrystals-polymer composites [13, 14]. In this regard, growing interest has been devoted to the Pb-chalcogenide family for nanocrystals solar cell applications because they have such large exciton Bohr radii of 18 nm, in the limit where the nanocrystals are only a tenth part or so of the bulk exciton diameter: electrons and holes can then tunnel through a thin surface coating, and therefore strong electronic coupling between particles allows the transport of charge between nanocrystals. The quantized electronic transitions in Pb(S, Se) nanocrystals quantum dots (NQDs) have been reported to provide size-tunable interband absorption and luminescence emission at a broad and technologically important infrared wavelength range, spanning from 0.8-4.0μm [15]. It must be pointed out that the synthesis of ternary $Pb_{1-x}Ni_xS$ nanocrystals remains largely underdeveloped compared to the widely studied cadmium chalcogenide. Thus, on this frame of reference, the aim of this work was to find the optimum conditions for growth of PbS films at different doping levels with $V_{[Ni2+]x}$, employing the chemical bath deposition (CBD) technique in order to investigate structural and optical properties of undoped and doped-PbS films. Surface morphology and composition were determined using a Carl Zeiss Auriga 39-16 coupled with a Bruker energy dispersive analysis of X-Rays (EDAX). The crystalline structure
characterization was carried out by XRD patterns registered in a D8 Discover diffractometer, using the Cu Kα line. The grain size was determined utilizing the Scherer’s formula on XRD patterns. The optical absorption spectra, measured employing a Unicam 8700 Spectrometer, allow to calculate the forbidden band gap energy (Eg) by using the (αhv)² vs. hv plot, where α is the optical absorption coefficient and hν the photon energy. Transmission electron microscopy (TEM) was performed using a Philips CM 300.

2. Chemical reactions and experimental procedure

The reactions for the growth of PbS films doped with Ni²⁺ were determined by employing the cell potential values in basic media reported in the literature [16]. The cell potential and the Gibbs free energy are related through the Nernst equations: ΔG⁰ = - nτε⁰, where n is the number of equivalents, τ is the Faraday constants and ε⁰ are the cell potential, where ΔG⁰ is calculated for the reaction. Numerical value ΔG⁰ provides thermodynamic information on the spontaneity of chemical reactions. Worth-noting is the formation of the coordination complex [M(NH₃)₄]²⁺, which is determinant for the release of M²⁺ ions (M²⁺ = Cd²⁺, Pb²⁺, Zn²⁺, etc.) and their slow recombination with S²⁻ ions that, under these conditions, leads to the spontaneous formations to the MS precipitate in an easily controlled process. The growth of PbS is therefore carried out according to the following steps: (a) by mixing Pb(CH₃COO)₂, KOH and NH₄NO₃, the coordination complex [Pb(NH₃)₄]²⁺ is generated indirectly. (b) The S²⁻ ions are found in the solution and are generated by the thiourea decomposition in alkaline solution. (c) The aforementioned steps allow the slow process at the substrate surface to take place predominantly over direct hydrolysis of thiourea in the bulk of the reaction bath as follow [17].

\[ SC(NH_2)_2 + 3OH^- \leftrightarrow CH_2N_2 + CO_3^{2-} + H_2S + 3H^+ \]  
\[ HPbO_2^- + H_2O + 2e \rightarrow Pb + 3OH^- \quad \Delta G^0 = +104.2KJ \]  

Leading to complex (II)

\[ [Pb(NH_3)_4]^{2+} + 2e \rightarrow Pb + 4NH_3 \quad \Delta G^0 = +180.3 KJ \]  
\[ Pb^{2+} + 2e \rightarrow Pb \quad \Delta G^0 = + 24.31 KJ \]  

Changing the sense of (4) and added with (3)

\[ [Pb(NH_3)_4]^{2+} \rightarrow Pb^{2+} + 4NH_3 \quad \Delta G^0 = +155.99 KJ \]  

The reaction of PbS for the formation of the S²⁻ ion and elemental Pb is therefore

\[ Pb + S^{2-} \leftrightarrow PbS + 2e \quad \Delta G^0 = +179.49 KJ \]  

Addend (5) and (6)

\[ [Pb(NH_3)_4]^{2+} + Pb + S^{2-} \rightarrow PbS + Pb^{2+} + 4NH_3 \quad \Delta G^0 = + 335.48 KJ \]  
\[ S + 2e + 2H^+ \rightarrow H_2S \quad \Delta G^0 = -27.40 KJ \]
Addend (7) and (8)

Changing the sense of (8) and added with (7)

\[
\begin{align*}
\text{[Pb(NH}_3\text{)]}_2^+ + H_2S + S^{2-} & \Leftrightarrow PbS + 4NH_3 + S + 2H^+ + 2e \\
\Delta G^0 &= + 362.88 \text{ KJ} \quad (9) \\

HPbO^- + H_2O + 2e & \Leftrightarrow Pb + OH^- \\
\Delta G^0 &= + 436.61 \text{ KJ} \quad (10)
\end{align*}
\]

Addend (9) and (10)

\[
HPbO^- + H_2O + \text{[Pb(NH}_3\text{)]}_2^+ + H_2S + S^{2-} \Leftrightarrow PbS + 4NH_3 + S + 2H^+ + Pb + OH^- + Pb^{2+} \\
\Delta G^0 &= +799.48 \text{ KJ} \quad (11)
\]

Since \(\Delta G^0 > 0\), and as such, the reaction is not a spontaneous process.

Reversing the direction of the reaction (6), \(\Delta G^0\) changes its sign:

\[
PbS \Leftrightarrow 2e + Pb + S^{2-} \quad \Delta G^0 = -179.4 \text{ KJ} \quad (12)
\]

For sulfur ion

\[
S^{2-} \Leftrightarrow S + 2e \quad \Delta G^0 = +86.272 \text{ KJ} \quad (13)
\]

Adding (4), (5) and (6), the reaction for the PbS is obtained:

\[
Pb + 2S^{2-} + H^+ \Leftrightarrow PbS + HS^- \quad \Delta G^0 = -120.50 \text{ KJ} \quad (14)
\]

\[
PbS + 2e + 2H^+ \Leftrightarrow Pb + H_2S \quad \Delta G^0 = +177.66 \text{ KJ} \quad (15)
\]

\[
Ni^{2+} + 2e \Leftrightarrow Ni \quad \Delta G^0 = +48.250\text{KJ} \quad (16)
\]

\[
Ni + 2OH^- \Leftrightarrow Ni(OH)_2 + 2e \quad \Delta G^0 = -138.96 \text{ KJ} \quad (17)
\]

\[
Ni(OH)_2 \Leftrightarrow Ni^{2+} + OH^- \quad \Delta G^0 = 90.71 \text{ KJ} \quad (18)
\]

Adding (14), and (18), the reaction for the PbS:Ni^{2+} entity is obtained:

\[
Pb + 2S^{2-} + Ni(OH)_2 \Leftrightarrow PbS + HS^- + Ni^{2+} + OH^- \\
\Delta G^0 = -29.79 \text{ KJ} \quad (19)
\]

Based on the Gibbs free energy values obtained from the thermodynamic equilibrium analysis, the Ni^{2+} ionization state probably is present in the volume of PbS under our work conditions comparing the changes in \(\Delta G^0\), which thermodynamically enable to the growth of the PbS:Ni^{2+}.

Deposition includes different limiting physical and chemical processes which determine the kinetic behaviour of the doped PbS. (i) Nucleation stage. It is the initial stage requiring a high activation energy in which reactive centres (nuclei) are formed on the surface on the substrate. (ii) Growth stage. It is the second stage, which is characterized by an enhanced rate of PbS
deposition. (iii) Doped stage. The high rate of deposition is associated with the addition level of doping, with the accelerated growth of PbS doped nuclei formed on the substrate during the nucleation stage. (iv) Termination stage. During this stage, the rate of deposition gradually slows down. This is probably due to a depletion of the reagents in the deposition mixture. Preparation of polycrystalline PbS thin films on glass substrates was performed at a temperature of 80 ± 2°C undoped and doped with V[Ni2+] grown by chemical bath deposition (CBD) and pH = 11.0. The glass substrates were previously immersed in a K2Cr2O7/HCl/H2O solution for 24 h, after which they were rinsed in deionised water and dried in a clean hot–air flow. The growth of PbS films with six different levels of doping V[Ni2+] were obtained by the addition of: 2, 4, 6, 8, 10, 12 mLs in the solutions for PbS growth: Pb(CH3CO3)2 (0.01 M), KOH (0.5 M), NH4NO3 (1.5 M), SC(NH2)2 (0.2 M). The solutions were mixed and the final solution heated at 20°C during 2 h, with the substrate remaining inside the solution. The optimal concentration of the doping solution [V[Ni2+]] Ni(NO3)2 (0.023 M) was determined after several trials, until films had attained good adherence. This solution is routinely added to the reaction mixture during the growth of the PbS films. All the solutions used were prepared with deionised water of resistivity 18.2 MΩ. The samples were labelled as PbSNi0 for the undoped sample and PbSNi2-PbSNi12 for the doped samples. The total volume of the growing-solution consisted of the volume-solution (V Ni2+) for the PbS growth plus the volume-solution V[Ni2+] containing the doping Ni2+ chemical agent: V_{PbS} + V_{Ni2+} = V_{tot}. The relative volume V[Ni2+] changed from 2 to 12. The films were growing obtained were silver-colored, polycrystalline-reflective, with a homogeneous consistency and good adhesion to the substrate.

3. Results and discussion

3.1. Scanning Electron Spectroscopy (SEM)

The Figure 1 displayed a typical EDAX pattern and details of a relative analysis for (a) undoped (b) doped-PbS.

![Figure 1. EDAX patterns (a) undoped-PbS0Ni, (b) doped-PbS12Ni, with 12 mLs](http://www.revista-nanociencia.ece.buap.mx)
The elemental analysis was performed only for Pb, S and Ni, deriving the average atomic percentage of undoped and doped Pb/S. The semi-quantitative analysis of the films was carried out by using the EDAX technique for undoped and doped PbS thin films at different points to study the stoichiometry of the films. In Table I are displayed the atomic concentrations of Pb, S and Ni obtained from Scanning Electron Spectroscopy (SEM).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Pb</th>
<th>S</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbS-Ni0</td>
<td>56.35</td>
<td>43.05</td>
<td>0.0</td>
</tr>
<tr>
<td>PbS-Ni6</td>
<td>70.10</td>
<td>18.38</td>
<td>11.51</td>
</tr>
<tr>
<td>PbS-Ni12</td>
<td>56.29</td>
<td>33.49</td>
<td>10.22</td>
</tr>
</tbody>
</table>

**Table 1.** Atomic concentrations of Pb, S and Ni obtained from EDAX

For the samples the increase in concentration of Ni in PbS films is easily noted, reaching a percent value of Ni = 11.51. In this case, when Ni$^{2+}$ ion enters as a substitute of the Pb$^{2+}$ ion, it is observed that the sample was slightly deficient in S$^{2-}$ ion. Therefore, for the higher $V_{Ni^{2+}}$ values considered here, growth material can probably be estimated as doped semiconductor but actually the material can be regarded as similar to a solid solution of Pb$_{1-x}$Ni$_x$S. It can also be considered how the concentration of Ni in PbS films increase, reaching a percent value of Ni = 11.51. In this case, when the Ni$^{2+}$ ion enters as substitute of the Pb$^{2+}$ ion, probably for the higher $V_{Ni^{2+}}$ values considered here the growth material can also be estimated as a doped semiconductor being the material also as in the aforementioned conditions-similar to a solid solution of Pb$_{1-x}$Ni$_x$S. The micrographs of undoped- and doped-PbS films are showed in Figure 2.
Figure 2. Micrographs obtained from SEM of the films with scales of 1.0 μm and 30 nm for undoped-PbS\textsubscript{Ni0}, PbS\textsubscript{Ni6} and PbS\textsubscript{Ni12} films.

Scale bar at 1.0 μm, and 30 nm respectively were obtained from Scanning Electron Spectroscopy (SEM). The undoped-PbS\textsubscript{Ni}, doped-PbS\textsubscript{Ni6} (with 6mLs), doped-PbS\textsubscript{Ni12} (with 12mLs) films are showed. As can be seen from the uniform surface morphology, such aspect is compact and of polycrystalline nature. The SEM micrographs show that the particle grain size decreases with an increase in V\textsubscript{[Ni2+]} concentration. The granules appeared to be of different sizes and it can be concluded that the doping plays a vital role on the morphological properties of the thin PbS films. The micrographs of the films with doping levels of V\textsubscript{[Ni2+]2, 4, 8 and 10 mLs} are not shown. In such micrographs for the undoped films, crystals as small spheres are observed. A very adherent film with metallic gray-black colored aspect was obtained for undoped and doped films revealing continuous and compact polycrystalline films. Similar morphologies have been reported using a scale of 400 nm by Pentia et. al. with size grain at around 250-300 nm as effect of the reducer Bi\textsuperscript{3+} ion on the deposition by CBD [18].

3.2. Diffraction X Rays (DXR)

Figure 3 shows diffractograms of X-ray (XRD) for doped and undoped films. Such x-ray spectra display peaks located at the following angular positions: 2θ = [26.00, 30.07, 43.10, 51.00, 53.48]. They are related with the reflection peaks of [111], [200], [220], [311], [222] respectively, and all these diffraction peaks can be perfectly indexed to diffractograms of the undoped and doped PbS samples displaying the zinc blende (ZB) crystalline phase according to reference patterns JCPDS 05-0592. The XRD spectra for PbS\textsubscript{Ni2} films indicate that [111] is the orientation of PbS\textsubscript{Ni} grains; the PbS\textsubscript{Ni2} diffraction layer along the [111] plane reveals the highest intensity of a well-defined sharp peak, indicating the high crystallinity of the obtained material.
A maximum value in the intensity peak is reached for the prepared sample, indicating either the existence of a larger number of [111] planes or that the [111] planes have a lower number of defects. The relative intensities for PbS-Ni2 and PbS-Ni4 layers for [111], [200], [220] are nearly equal and all the representative diffraction lines of PbS can be observed. In the PbS-Ni2 film, the [111] reflection has the highest intensity. This phenomenon may be attributed to the doping effect. The low intensity peaks observed in the XRD patterns of the doped PbS-Ni6 to PbS-Ni12 samples indicates that the films are coarsely fine crystallites or nanocrystalline. The broad hump in the displayed pattern is due to an amorphous glass substrate and also possibly due to some amorphous phase present in the PbS-Ni crystallite size of films. These effect are associated with the nanocrystals doped-PbS-Ni with V_{Ni^{2+}} in the regime were the cluster mechanism is dominating (on the contrary to films grown via ion-ion mechanism, were the crystal size was larger), and consist of PbS-Ni nanocrystals embedded in an apparent matrix of PbS. The inset in Figure 3. displays the [111] interplanar distance (ID) for the ZB face, calculated from the 2θ peak positions, vs. V_{Ni^{2+}}. This ID is close to the [111] ID of the ZB phase. First, the ID decreased with V_{Ni^{2+}} due to the presence of Ni^{2+} in substitution sites and, finally, reaching a maximum value in
PbSNi6 film. A possible explanation to this experimental fact can be given as follows: The ionic radii data are \( \text{Pb}^{2+} = 1.21 \, \text{Å} \), \( \text{S}^{2-} = 1.84 \, \text{Å} \) and \( \text{Ni}^{2+} = 0.69 \, \text{Å} \), therefore for a relative low concentration of Ni\(^{2+}\) ions a majority can be located in (i) Pb\(^{2+}\) vacancies sites, which otherwise would be empty (ii) in Pb\(^{2+}\) sites causing the appearance of Pb interstitial, and (iii) in interstitial positions. At this level of \( V_{\text{Ni}^{2+}} \), the PbSNi can be considered a doped material [6]. The incorporation of Ni\(^{2+}\) solubility has been proven to be more effective in Pb chalcogenide than Zn-chalcogenide, a result explained in terms of the cation size.

3.3. Transmission Microscopy Electronic (TEM)

The crystal structure of the PbS undoped and doped films has been studied in more details by TEM. A typical bright plan view obtained by TEM image of the nanoparticle PbS films is show in Figure 4. Scale bar 20 nm (a) Undoped-PbSNi0, (b) Doped-PbSNi6 (c) Doped-PbSNi12. The inset illustrates selected-area electron diffraction (SAED) pattern of plain core (PbS) and core-shell nanocrystals is displayed. Such results revealed that small particles attach together with a common crystallographic orientation, and most of the produced crystals have irregular shapes. The sizes of the clusters are mostly 3.5-5 nm.
Figure 4. TEM images of nanocrystals: (a) Undoped-PbS Ni0 (b) Doped-PbSNi6 (with 6 mLs). (c) y (d) An HRTEM of PbS Ni12 and their respective selected area electron diffraction (SAED) pattern of plain core (PbS) and core-shell nanocrystals.

The micrographs with an electron beam direction close to [111] zone axis in strongly under focused condition and as such, the black/gray contrast in white background represents the PbS nanoparticle in the range 3.5-5 nm. The average grain size (GS) in the films is observed to decrease while doping is increasing. Samples are found to be crystalline by TEM, a feature which is very similar to size calculated from XRD peak width. The ZB phase is detected for all the nanoparticle films from XRD data. The sharp rings presented in SAED patterns are indicative of polycrystalline nature of the films. The SAED patterns were analyzed using the standard
procedure. The SAED pattern with clear spots indicates perfect orientation around [111] plane. The blurring of the diffraction ring in the selected-area electron diffraction (SAED) pattern of core-shell nanocrystals in comparison to that of plain core structures revealed the deposited nanoparticle thin films. From this measurement, it is clear that both undoped and doped films are polycrystalline in nature.

3.4. Optical absorption (OA)

Figure 5 shows a graph of $E_g$ vs $V_{[Ni^{2+}]}$ and in the inferior right part the plot shows the absorption spectrum for the sample PbSNi12. In this plot, it can be observed a $E_g = 2.4$ eV value for the PbSNi0 sample.

![Graph of $E_g$ vs $V_{[Ni^{2+}]}$. The inset illustrates the method to calculate $E_g$ from optical absorption measurements.](image)

**Figure 5.** The band gap energy ($E_g$) as function of $V_{[Ni^{2+}]}$. The inset illustrates the method to calculate $E_g$ from optical absorption measurements.

For PbSCd0 sample, through the intersection of the straight line with the axis of the photon energy, an $E_g$ value is obtained in a similar way to all samples. The confinement effect appears
as a shift in edge of the absorption spectra and the absorption to lower wavelengths, possibly due to the decrease in GS, the decrease in number of defects and the change in color. It is clearly seen from the optical spectrum an absorption edge shift toward a lower wavelength in doped films. The experimentally observed $E_g$ values for the shift indicated an alloying between nanocrystalline PbS. Such increase has been observed by other authors [19, 20]. The $E_g$ for doped samples in the 2.4-3.8 eV range the large experimentally observed $E_g$ in the nanoparticle films theoretically estimated (using Vega–ds law) $E_g$ for bulk shows the extent of quantum size effect in the nanoparticle films. The fundamental optical transition of doped films ($E_g = 0.41$ eV) is not observed in these films, presumably because of complete mixing of PbS with Ni affording an unique ternary intermetallic compound of the Pb$_x$Ni$_{1-x}$S type [1]. It is observed that the size effect on the optical band gap is stronger in nanoparticle films than in PbS nanoparticle of 24-10 nm (average crystallite size) and show an $E_g$: 2.22-2.65 eV [2]. The observed increase in the quantum size effect could possibly be attributed to a decrease in the effective mass [23]. The increased in $E_g$ when increasing the concentration of V in the films is reflected by the presence of an excitonic structure material. Excitonic structures are readily observed in large $E_g$ semiconductors with binding energy such as CdSe [24]. The $E_g$ optical doped films varied from 2.4-3.8 eV, with doping increase of V. A similar shift observed in the position of the excitonic peak towards higher energies in CdSe crystallites has been explained due to a decrease in crystallite size [25]. The redshift of the band gap is associated with the decline of the SG. It is clear that the $E_g$ increase when $V$ increases. As mentioned earlier, we observed a systematic decrease in the crystallite size with increasing concentration. Since the estimated mean crystallite size in this case being approximately half the value of the exciton Bohr radius in PbS, we observe a strong confinement in doped PbSn films. Using already published data, a nanocrystalline size of 4-5 nm corresponding to $E_g = 1-1.25$ eV, 3.8 nm for $E_g = 1.4$ eV, 2.7 nm for $E_g = 2.0$ eV and 2 nm for $E_g = 2.7-3.8$ eV respectively are obtained [22]. Figure 6 shows the average grain size (GS) vs. $V$ for the undoped- and doped PbS samples corresponding to the [111] plane. In this Figure can be observed that GS reduces in the interval 4mLs ≤ $V$ ≤12mLs. It can be seen for the PbSn0, GS ~32 nm, and that the GS decreases for doped samples.
Figure 6. The average grain size (GS) with of the mean peak of XRD patterns vs. $V_{[Ni^{2+}]}$. The inset exhibits the $E_g$ vs GS plot.

The effect of the GS decrease by the doping effect has been reported in films of CdS doped with Cu$^{2+}$ by CBD [6]. A decrease in the degree of order of crystallites is expected to lead to enhanced growth of stable nuclei at the initial stages of growth, followed by impaired grain growth, and hence resulting in smaller grains in the nickel. In the inset of Figure 5, $E_g$ is displayed as function of the GS. For low GS, $E_g$ increases, as GS decreases $E_g$ increase. When GS $\leq 5$ nm, $E_g$ reaches a maximum value. For a larger GS, $E_g$ decreases. Two effects can be considered in such $E_g$ changes: (i) The variation of ID and (ii) the strong quantum confinement.

Conclusions

We have reported the growth of doped-PbS with Ni$^{2+}$ ions affording nanocrystalline films by the chemical bath technique. X-ray spectra show $2\theta = [26.00, 30.07, 43.10, 51.00, 53.48]$, which belong to the ZB phase. The grain size lies in the interval of $\sim 32-5$ nm. The ID for low $V_{[Ni^{2+}]}$ concentrations into the PbS lattice increases and reaches maxima values for intermediates.
V_{[Ni_{2+}]}$. TEM image for nanoparticle films of the undoped- and doped-PbS were obtained, the micrographs with an electron beam direction close [111] zone axis in strongly under focused condition with nanoparticle doped in the range 3.5-5 nm. The average grain size in the films decreases while doping increase. Samples are found to be crystalline by TEM and very similar to size calculated from XRD peak width. Optical absorption spectra are quantified for the PbSCd10 film in which the redshift of band gap is associated with the decrease of the average TG. The $E_g$ of films increased from 2.4-3.8 eV when doping $V_{[Ni_{2+}]}$ is increased. GS reduces in the interval 2mL ≤ $V_{[Ni_{2+}]}$ ≤12mLs and a $E_g$ increase as function of the GS is displayed. When GS ≈ 5 nm, $E_g$ reaches a maximum value; for larger GS, $E_g$ decrease. We deem two effects occur on $E_g$ changes: (i) The variation of ID and (ii) the quantum confinement. The thermal $E_a$ for films was determined from the slope of log $\sigma$ curve versus temperature. This energy was estimated to be 0.15 to 0.5 eV.

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