Structural, Morphological, Optical and PL Studies of Neodymium Doped ZnS Glass Plate by Nebulizer Spray Pyrolysis Method

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Abstract — Herein we have present the preparation of Nd doped ZnS thin films on glass substrate by simple nebulizer spray pyrolysis (NSP) method at 450 °C. XRD, SEM, and UV-Vis Spectrometer were used to analyze the Structural, morphological, and optical behavior of the prepared samples. Nature of polycrystalline hexagonal structure with no secondary phases was confirmed by X-ray analysis. Extra particle creation on the surface of the Nd doped thin film was observed in high magnified SEM images. Room temperature PL studies depicts that the luminescence behavior of the parent sample was enormously changed during the Nd element interstitial with ZnS lattice. Optical band gap value varies from 3.5 eV to 3.58 eV for 3% Nd doped ZnS film ascribed the increasing of film thickness and diminishing of film transparencies.

Keywords — Rare earth, Thin film, Nebulizer spray pyrolysis, Photoluminescence, Band gap.
The Structural properties studied by XPERT SOFTWARE using CuKα (λ=1.5406 nm) radiation. Morphological view of the film was assessed by SEM (Hitachi S-3000H). Transmission and band gap values were analyzed by Shimadzu (UV-3101PC) spectrophotometer. Stylus profile meter (Mitutoyo SJ-301) was used to find the thickness of the Nd:ZnS films. Photoluminescence (PL) were recorded using Perkin Elmer LS55 florescent spectrophotometer.

III. RESULTS AND DISCUSSION

XRD Analysis
Fig.1 shows the XRD patterns of Nd:ZnS thin films. Obtained films have polycrystalline hexagonal structure and matched with JCPDS file No:89-2739. In addition, they have no any other secondary peaks due to neodymium or neodymium oxide when rare earth element was doped with host lattice. From the XRD, it clearly reveals that the high intense peak of pure ZnS is orient along the (102) plane and there is some low intense peak present along (101), (103), (108), (109) and (116) planes. However, when Nd element doped with host ZnS, intensity of the reflection peaks decreases, indicates that decresing of crystal size or increasing of crystal lattice imperfection owing to the higher ionic radius of Nd\(^{3+}\)\ (0.98Å) was not perfectly fit with host Zn\(^{2+}\) lattice of low ionic radius Zn\(^{2+}\) \ (0.74 Å). These results were matched with previous report [10] for Al doped ZnS thin films and confirmed in our SEM image. Moreover, the crystalline size calculated by debye scherer formula [11].

\[
D = \frac{0.9\lambda}{\beta \cos \theta}
\]  

(1)

and crystal imperfections such as dislocation density (\(\delta\)) and micro strain (\(\varepsilon\)) calculated with Williamson and tangent relations [11].

\[
\varepsilon = \frac{\beta \cos \theta}{4}
\]  

(2)

\[
\delta = \frac{1}{D^2}
\]  

(3)

from our XRD data Confirmed the same results.

\[
\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + h k + k^2}{a^2} \right) + \left( \frac{l^2}{c^2} \right)
\]  

(4)

Where, all constants have their usual meanings. The decrement of value of lattice parameters when Nd ions doped with ZnS means changing of crystal growth orientation and evidenced by our XRD intensity variation plot and same result was obtained for K.D.A. Kumar et al [13] when Nd doped with SnO\(_2\). All structural parameters were tabulated given below.

| Nd doping level (%) | Crystallite size (nm) | Dislocation density \((\times10^{15})\mu m^2\) | Strain \((\text{Lines } m^{-2})\) | Lattice Constant |
|---------------------|-----------------------|---------------------------------|--------------------------------|-----------------|
| 0                   | 55                    | 0.321                           | 0.00252                        | 3.805           |
| 3                   | 51                    | 0.377                           | 0.00271                        | 3.778           |

Morphological Studies by SEM
High magnified SEM images shown surface morphology of Pure (fig 2a) and 3% Neodymium (fig 2b) doped ZnS thin films. SEM image of the undoped film visualize that they are homogeneous nature with spherical grains in nanometer range. Whereas, when Nd element was doped with parent film, it is a results of creation of extra particle accumulation on the host lattice; which ascribed the higher ionic radius of Nd\(^{3+}\) ions couldn’t incorporate well to the lower ionic radius of Zn\(^{2+}\) ions in host lattice and makes some imperfection and increment of film thickness. Defects calculation made from XRD data and thickness measurement from Stylus profile meter confirms the above results.

Optical Spectra
Transmittance spectra of synthesized films were portrayed in fig.3. It is seen that the transparency of film decreases when Nd element interstitial with ZnS lattice; which means that scattering of photons increment when thickness of the film increases [14] and it is confirmed by SEM images.

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Using absorption coefficient ($\alpha$), Optical band gap ($E_{g}$) of the prepared films was determined by the Tauc’s formula [12].

$$\alpha h\nu = B(h\nu - E_{g})^n$$  

(5)

Here, ($h\nu$) is the incident photon energy, and ($B$) is constant value. Pure and 3 % Nd doped ZnS film have band gap of value 3.58 and 3.62 eV and they are shown in Fig.4. The average of this band gap value is very close to the value of bulk ZnS (3.60 eV) material and previous report [15].

**PL Spectra**

Photoluminescence (PL) analysis used to determine the quality of the film and radiative transition between the conduction band and the valance band at room temperature. PL spectra of pure and Nd doped films at 325 nm excitation wavelength are displayed in fig 5. In our case, PL Spectrum shows two peaks at 395 and 460 nm. Broad UV emission peak present at 395 nm corresponds to the sulphur vacancies and the same result was reported by sabitha et al for Al:ZnS film [12]. Recombination of electron-hole pairs in zinc vacancies [16] creates high intense visible emission bands at 460 nm. In addition, when Nd element incorporate with host ZnS lattice intensity of the visible emission peak changes enormously; which ascribed the population enhancement in host lattice and easiest energy transfer between the band levels [17].

![Figure 3. Transmittance spectrum](image1)

![Figure 4. Band gap variations](image2)

Table 2 shows the values of transparencies, thickness and band gap of the Nd:ZnS thin films.

| Nd doping level (%) | Transmittance (%) | Thickness (nm) | Band gap (eV) |
|--------------------|-------------------|----------------|--------------|
| 0                  | 83                | 230            | 3.58         |
| 3                  | 78                | 302            | 3.62         |

**IV. CONCLUSION**

Pure and Nd doped ZnS thin films were prepared by low cost NSP technique. Polycrystalline with hexagonal structure of the prepared films were evidenced by XRD. Crystalline sizes, micro strain, lattice parameters of the samples were also calculated from XRD data. Particle in the shape of spherically was shown in SEM images. Band gap values of the films were determined by optical studies. High intense, blue Shift of the PL spectrum obtained from the doped film concludes that they are more suitable for creating new kind of luminescence based devices.

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