# OPTICAL ABSORPTION STUDIES ON $Ni^{+2}$ DOPED PVA CAPPED ZnSe NANOPARTICLES

G. NIRMALA[a], R.V.S.S.N. RAVIKUMAR[b], M. C. RAO[a*]
[a]*Department of Physics, Andhra Loyola College, Vijayawada – 520008, India*
[b]*Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar, India*

ZnSe an important II-VI, n-type direct band gap semiconductor has engrossed substantial consideration due to its applications in light-emitting diodes, lasers, optical instruments, photo detectors and full color display. Zinc Selenide (ZnSe) is an inorganic light yellow binary solid compound. It is an intrinsic semiconductor with a band gap of about 2.70 eV at 25 °C. Poly vinyl alcohol (PVA) is used as a capping agent to stabilize the ZnSe nanoparticles. The optical properties of $Ni^{+2}$ doped PVA capped ZnSe nanoparticles grown at room temperature are studied in the wavelength region of 200-1400 nm. The spectrum of $Ni^{+2}$ doped PVA capped ZnSe nanoparticles exhibit four bands at 1162, 694, 440 and 405 nm (8603, 14405, 22721 and 24654 $cm^{-1}$).The bands observed at 1162, 694 and 405 nm are correspond to the three spin allowed transitions $^3A_{2g}$ (F) $\rightarrow$ $^3T_{2g}$ (F), $^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$ (F) and $^3A_{2g}$ (F) $\rightarrow$ $^3T_{1g}$ (P) respectively. The other band observed at 440 nm is assigned to spin forbidden transition $^3A_{2g}$ (F) $\rightarrow$ $^1T_{1g}$ (G). The small value of the Urbach energy indicates greater stability of the prepared sample.

(Received April 16, 2013; Accepted September 20, 2013)

*Keywords:* ZnSe nanoparticles, Poly vinyl alcohol, $Ni^{+2}$, Optical and Urbach energy.

## 1. Introduction

Nanostructured materials can be utilized in fabricating novel active devices with improved functionalities. The discipline of Nanoscience and nanotechnology has recently become one of the most important areas of knowledge encompassing various scientific disciplines including physics, chemistry, biology and engineering. The word nano is derived from the Greek word “dwarf”. It is the prefix for units of $10^{-9}$. Nanoscience is concerned with the study of the unique properties of matter at its nano level and exploits them to create novel structures, devices and systems for different uses. Particles having size less than 100 nm are generally called nanoparticles. These have strikingly different properties due to their small size and thus are found useful in many applications. The ability to measure and manipulate matter on the nanometer level is making possible a new generation of materials with enhanced mechanical, optical, transport and magnetic properties. Polymers are a large class of materials consisting of many small molecules called monomers that can be linked together to form long chains. A typical polymer may include tens of thousands of monomers. Because of their large size, polymers are classified as macromolecules. Polymers consist mainly of identical or similar units joined together. A small molecule which combines each other to form a giant molecule and the process itself is known as polymerization. Because of the extraordinary range of properties of polymeric, they play an essential and ubiquitous role in everyday life [1, 2].

Polyvinyl alcohol has an excellent film forming, emulsifying and adhesive properties. It is also resistant to oil, grease and solvent. It is odorless and nontoxic. It has high tensile strength and flexibility. PVA is fully degradable and is a quick dissolver. PVA has a melting point of 230°C and 180-190°C for the fully hydrolyzed and partially hydrolyzed grades respectively. It

*Corresponding author: raomc72@gmail.com

decomposes rapidly above 200°C as it can undergo pyrolysis at high temperatures. PVA is close to incompressible. Zinc Selenide is often called an II-VI semiconductor because Zinc and Selenium belong to the 2nd and 6th groups of the periodic table, respectively. ZnSe is a light yellow binary solid compound. It is an intrinsic semiconductor with a band gap of about 2.70 eV at 25 °C. ZnSe rarely occurs in nature. It is found in the mineral stilleite named after Hans Stille. Due to the quantum size effect and the existence of a relatively large percentage of surface atoms ZnSe is one of the most typical and important crystalline materials for both application and research [3]. The ZnSe nanoparticles have wide-ranging applications in laser, optical instruments, etc. because it has a wide band gap (2.69 eV) and transmittance range (0.5–22 m), high luminescence efficiency, low absorption coefficient and excellent transparency to infrared [4-6].

Zinc Selenide nanoparticles were synthesized by Shakir et al. [7] using a microwave irradiation technique at 2.8 GHz using 7N purity Zn and Se powder in stoichiometric ratio as the starting materials. The crystal system and phase was confirmed by powder X-ray diffraction, the crystallite size was calculated using Scherer's formula and found to be ~ 35 nm. Synthesis of ZnSe nanostructures by hydrothermal method was reported by Mollaamin et al. [8]. The effect of different sources of Zn, Se and cetyl tri-methyl-ammonium bromide (CTAB) (cationic) surfactant on the morphology of ZnSe was studied. A simple novel synthetic method for preparing ZnSe/ZnO heterostructured nanowire arrays via the selenization of ZnO nanowires was reported by Lee et al. [9]. A hydrothermally grown ZnO nanowires array on a glass substrate was reacted with selenium vapor to generate 20-30 nm of zinc blend ZnSe nanoparticles on wurtzite ZnO nanowires. A growth mechanism was proposed based on SEM, XRD and TEM analysis to explain the partial chemical conversion of ZnO nanowire surfaces into ZnSe nanoparticles.

## 2. Experimental

4 mL of Zinc chloride ($ZnCl_2$) is added to 2.2g PVA (13,000 g/mol). Volume of the solution is made up to 50 mL by bi-distilled water and the solution is left for 24 hours at room temperature to swell. After that, the solution is warmed up to 60 $^{O}$C and stirred for 4 hours until viscous transparent solution was obtained. One milliliter of Sodium Hydrogen Selenide (NaHSe) was dropped into the solution with gentle stirring. 4 mL of $NiCl_2$ is added to get transparent solution. Solution is casted on flat glass plate dishes. After the solvent evaporation, a thin film containing $Ni^{+2}$ doped PVA capped ZnSe nanoparticles are obtained [10]. The film is washed with de-ionized water to remove other soluble salts before measurements. The Optical absorption spectrum is recorded at room temperature on JASCO V670 spectrophotometer in the wavelength region of 200-1400 nm.

## 3. Results and discussion

The optical properties of $Ni^{+2}$ doped PVA capped ZnSe nanoparticles grown at room temperature are studied in the wavelength region of 200-1400 nm and the Urbach energy is calculated for the prepared samples.

### 3.1 Optical absorption studies

UV-Vis absorption spectrum of $Ni^{+2}$ doped PVA capped ZnSe nanoparticles are recorded at room temperature is shown in Fig. 1 & Fig. 2. The spectrum of $Ni^{+2}$ doped PVA capped ZnSe nanoparticles exhibit four bands at 1162, 694, 440 and 405 nm (8603, 14405, 22721 and 24654 $cm^{-1}$).The bands observed at 1162, 694 and 405 nm are correspond to the three spin allowed transitions $^3A_{2g}$ (F) → $^3T_{2g}$ (F), $^3A_{2g}$ (F) → $^3T_{1g}$ (F) and $^3A_{2g}$ (F) → $^3T_{1g}$ (P) respectively. The other band observed at 440 nm is assigned to spin forbidden transition $^3A_{2g}$ (F) → $^1T_{1g}$ (G) using Tanabe-Sugano diagrams [11-13]. Based on these assignments, energy matrices are solved for different values of inter-electronic repulsion parameters, B, C and crystal field parameter Dq. The values Dq = 870, B = 860 and C = 4020 $cm^{-1}$ give a good fit between the observed and calculated positions of the bands and is given in **Table -1**. The free ion inter-electronic repulsion parameters, B for $Ni^{2+}$ is 1080 $cm^{-1}$ [14]. In the present work the value of B obtained for $Ni^{2+}$ is 860 $cm^{-1}$ which indicates a reduction of about 20% from the free ion value. This suggests that the bonding between transition metal ion and ligand is ionic in nature. In the present investigations $Ni^{+2}$ exhibited distorted octahedral sites in the host lattice.

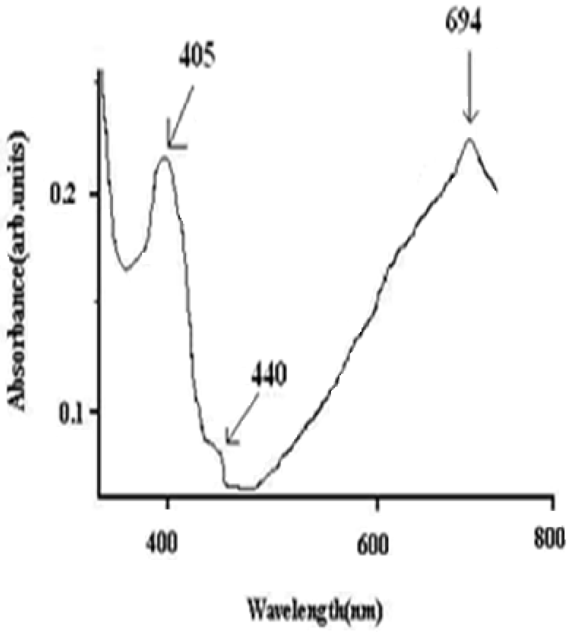


*Fig. 1. Optical absorption spectrum of $Ni^{+2}$ doped ZnSe nanoparticles in the wavelength region of 300-800 nm*

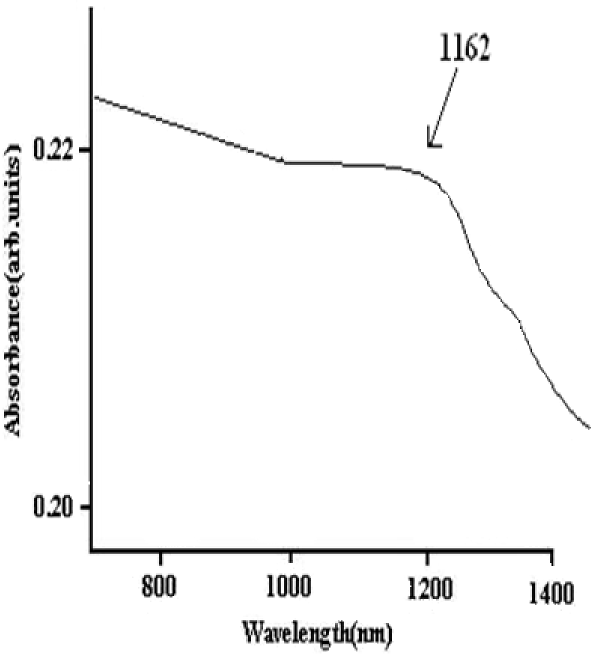


*Fig. 2. Optical absorption spectrum of $Ni^{+2}$ doped ZnSe nanoparticles in the wavelength region of 900-1400 nm*

*Table -1 Observed and calculated band positions for $Ni^{2+}$ doped ZnSe nanoparticles*

| Band Positions | | | |
|---|---|---|---|
| | | Observed | Calculated |
| Transition From $^3A_{2g}$ (F)→ | Wavelength (nm) | Wave number ($cm^{-1}$) | Wave number ($cm^{-1}$) |
| $^3T_{2g}$ (F) | 1162 | 8603 | 8700 |
| $^3T_{1g}$ (F) | 694 | 14405 | 14317 |
| $^1T_{1g}$ (G) | 440 | 22721 | 22767 |
| $^3T_{1g}$ (P) | 405 | 24654 | 24682 |

### 3.2 Urbach energy

The main feature of the absorption edge of crystalline and amorphous materials is an exponential increase of the absorption coefficient α (υ) with photon energy hυ in accordance with the empirical relation [15].

$$\alpha(\upsilon) = \alpha_0 \exp(h\upsilon/\Delta E)$$

Where $\alpha_0$ is a constant, ΔE is the Urbach energy which indicates the width of the band tails of the localized states and υ is the frequency of the radiation. Therefore, Urbach energy can be considered as a measure of disorder in amorphous and crystalline materials [16]. Smaller the value of Urbach energy, greater is the structural stability of the system. The excitation levels at the absorption edges are determined by the random electric fields due to either the lack of long range order or the presence of defects. Urbach energy is calculated by taking the reciprocal of the slope of linear portion in the lower photon energy region of the curve as shown in Fig. 3. The evaluated value of the Urbach energy is 0.043eV [17, 18].

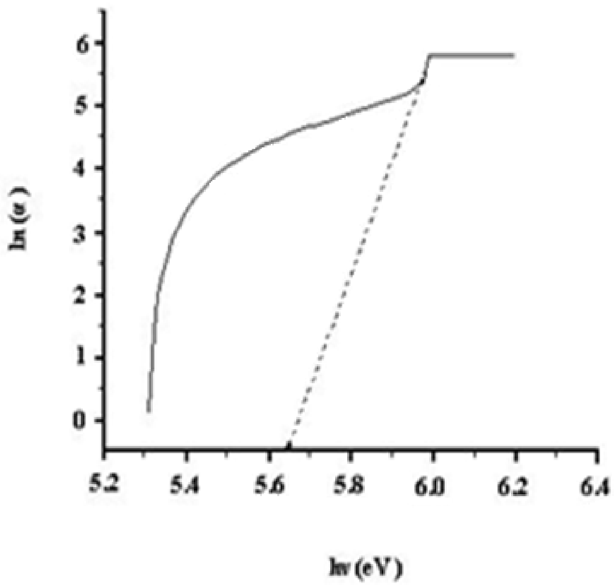


*Fig. 3. Urbach energy plot of $Ni^{+2}$ doped ZnSe nanoparticles*

## 4. Conclusions

From the spectral investigations of $Ni^{+2}$ doped PVA capped ZnSe nanoparticles, the following conclusions are drawn: Optical absorption spectrum reveals the three characteristic spin-allowed bands in the UV-VIS-NIR region. From the optical studies of the $Ni^{+2}$ doped PVA capped ZnSe nanoparticles are described as distorted octahedral in nature for the transition metal ion in the host lattice. The small value of the Urbach energy indicates greater stability of the prepared sample. The incorporation of these nanoparticles into polymer matrices is useful in electroluminescent devices.

## Acknowledgments

The Corresponding author (M. C. Rao) is thankful to UGC for providing the financial assistance through Major Research Project (Link No. F. No. 40-24/2011(SR))

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