Cu^{2+} Doped PVA-Capped CdSe Polymer Applications to Blue LED

B. Sekhar[1], Sk. Muntaz Begum[2], L. V. Krishna Rao[3], R. V. S. S. N. Ravikumar[4]

[1, 2, 3]Depepartment of Physics, Acharya Nagarjuna University, Nagarjuna Nagar-522510, A.P., India

[4]Department of Physics, Sir C R Reddy College, Eluru-534007, A.P., India

Abstract: *Cu^{2+} doped CdSe polymer was prepared by using poly vinyl alcohol (PVA) at room temperature. The prepared sample was characterized by Powder X-ray diffraction, optical absorption, Photoluminescence, EPR and FT-IR studies. X-ray diffraction pattern showed the cubic zinc blende crystalline phase of CdSe and the average size of the grains is in the order of 23 nm. Optical absorption spectrum exhibited a broad band at 832 nm which is the characteristic of Cu^{2+} in distorted octahedral symmetry. EPR results indicate that Cu^{2+} ion enters the host lattice as tetragonally elongated octahedral site. By correlating optical and EPR data, the evaluated bonding parameters suggested that the bonding between the doped ion and ligands is partially covalent. Luminescence spectrum gives the emission bands in UV and blue region. The calculated CIE chromaticity coordinates from emission spectrum are located in blue region. FT-IR spectrum exhibits the molecular vibrations of PVA in CdSe.*

Keywords: A. Polymers; B. Chemical synthesis; C. X-ray diffraction; D. Crystal field, D.EPR

1. Introduction

Inorganic semiconductor materials of nano-dimensions have drawn considerable attention of researchers in recent years because of their size-tunable optoelectronic properties, which are attributed to the quantum confinement effect when compared to bulk semiconductor [1]. Cadmium chalcogenide semiconductors exhibit excellent chemical, optical, electrical and sensing properties and has been widely used for the fluorescent detection of various gases. CdSe has become quite interesting and important because of its major applications in solar cells and other optoelectronic devices due to its optimum band gap (~1.75 eV), high absorption coefficient and n-type of conductivity [2-4]. The 1.7 eV direct band gap together with the high absorption coefficient guarantee a high sensitivity through the visible part of the spectrum. Due to high photosensitivity of CdSe it has been used as a photoconductive device [5,6]. CdSe along with some additive in it forms an important class of semiconductor materials which finds applications in low cost devices such as LED's, solar cells, photodetectors, lasers etc. [7,8]. Ellis and co-workers found that n-CdSe in single crystal state can be used as a "luminescent litmus test" to sense the presence of a variety of Lewis acids and bases [9]. The structural, electrical, optical and other characteristic properties of host lattice can be improved by deliberate addition of 'impurity' atoms in it so that materials having desired properties can be produced [10].

Transition metal doped CdSe semiconductor is regarded as near ideal fluorophores based on particle-size tunable optical properties (efficient broad band absorption and narrow-band emission) [11] and attract extensive interest due to unique spintronic [12, 13], excitonic luminescence [14], electrochemical [15] and magnetic properties [16]. In general, impurity occupation and structure properties can be investigated by means of optical absorption and electron paramagnetic resonance (EPR) studies. Cu is a well-known doping impurity in II–VI semiconductors. These materials, however, cannot be applied singly under most circumstances

and thereby need to be incorporated into other materials, especially polymers to acquire necessary processability and strength. PVA is used as a polymer in Cu^{2+} doped host lattice. Polyvinyl alcohol (PVA), a polymer containing many hydroxyl groups, is water-soluble with excellent properties, such as elasticity, high hydrophilicity, low permeability, good film forming ability and is found in wide industrial and agricultural applications [17,18–20].

Recently some of the authors reported the physical and optical characterization of different transition metals (Mn^{2+}, Fe^{3+}, Co^{2+}, Cu^{2+}) doped PVA capped ZnSe nanoparticles [21-24]. But in the literature no CdSe polymers with PVA were reported for to identify the site symmetry and nature of the bonding by correlating Optical and EPR studies, in view of this the prepared sample is characterized by X- ray diffraction, Optical, PL, EPR and FT-IR spectroscopy analysis for suitable application to LED devices.

2. Experimental Section

2.1 Materials

Cadmium Chloride ($CdCl_2.2H_2O$), Polyvinyl alcohol (PVA), Sodium Hydrogen Selenide (NaHSe), Copper Chloride ($CuCl_2.2H_2O$) are used as starting materials without further purification. All the chemicals used are of analytical grade. Double distilled water is used as a solvent in the experiment.

2.2 Preparation of Sample

Cadmium Chloride ($CdCl_2. 2H_2O$), 50 mM was added to 2.2 g PVA (13,000 g/mol) and the volume of each solution was completed to 50 mL by bi-distilled water. Each solution was left for 24 hours at room temperature to swell and then the solution was warmed up to 60 ^{0}C and stirred for 4 hours until viscous transparent solution was obtained. One millilitre of NaHSe (50mM) was dropped to each solution with gentle stirring to obtain red transparent solution [25] and then 0.01 mol % $CuCl_2$ solutions was added to it to get

transparent solution. Each solution was casted on flat glass plate dishes. After the solvent evaporation, a thin film containing Cu^{2+} doped PVA capped CdSe was obtained. The prepared film was washed with deionized water to remove other unsoluble salts before measurements.

2.3 Physical measurements

Using PAN alytical X'pert pro-X-ray diffractometer with CuK_α radiation source, X-ray diffraction pattern of the sample is recorded. The optical absorption spectrum is recorded using JASCO V-670 Spectrophotometer in the range from 600-1200 nm. Photoluminescence spectrum is recorded at room temperature on Horiba Jobin-Yvon Fluorolog-3 spectrofluorimeter with Xe continuous (450W) and pulsed (35W) lamps as excitation sources. EPR spectrum is recorded at room temperature on JES-FA series EPR Spectrometer operating at X–band microwave frequency. Bruker FT-IR Spectrophotometer is used for recording the FT-IR spectrum in the region from 500-4000 cm^{-1}.

3. Results and Discussion

3.1 X-ray diffraction studies

XRD pattern of Cu^{2+} doped PVA-capped CdSe is shown in figure 1. XRD is used to determine the degree of crystallinity of CdSe and PVA. An intense peak is observed at a scattering angle $(19 < 2\theta < 20)$ which corresponds to PVA [26]. The crystalline nature of PVA results from the strong intermolecular interaction between PVA through intermolecular hydrogen bonding. The other diffraction peaks observed at $2\theta = 41.29^o$, $49.78°$ corresponds to (220) and (311) plane reflections of cubic CdSe which is consistent with the JCPDS NO: 65-2891.

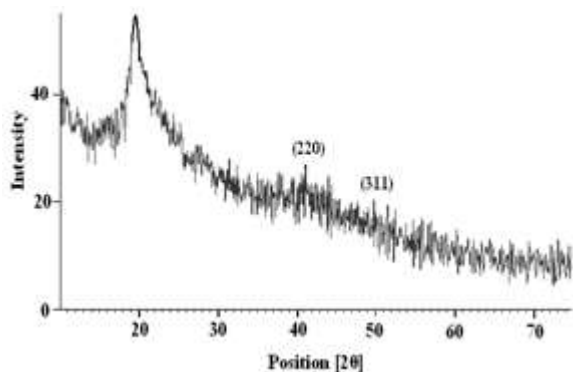**Figure 1:** Powder X-Ray diffraction pattern of Cu^{2+} doped CdSe polymer

Moreover, the Debye-Scherrer's equation is used to estimate the particle size of CdSe depending on the full-width at half-maximum of diffraction peaks, as the particle size increases the broadening increases [27].

$$D = (K \lambda / \beta Cos\theta)$$

Where K is a constant (shape factor, about 0.9), λ is the wavelength of X-ray radiation (1.5405Å), β is the full width at half maximum (FWHM) intensity of the diffraction line and θ is the diffraction angle. Based on the FWHM, the average crystallite size is estimated to be 23 nm.

3.2 Optical Properties

The optical properties of CdSe polymer are studied through optical absorption and photoluminescence measurements. figure 2 represents the optical absorption spectrum of Cu^{2+} doped PVA-capped CdSe polymer. It shows the broad absorption band at 832 nm which is characteristic of distorted octahedral symmetry [28, 29]. The broad band is assigned to $^2B_1 \rightarrow {}^2B_2$ transition of Cu^{2+} ion. The peak energy of this band corresponds directly to the ligand field strength 10 Dq. In case of Cu^{2+} doped ZnSe polymer, three characteristic bands are observed which gives tetragonally distorted octahedral site symmetry [24].
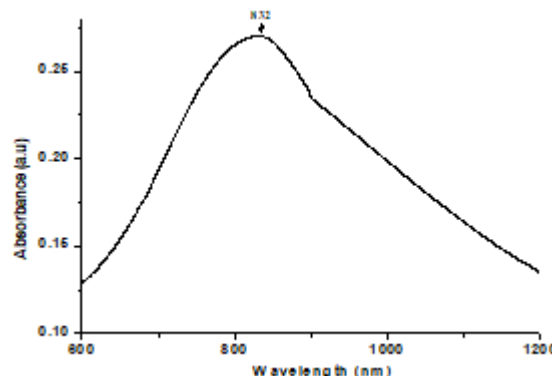

Figure 2: Optical absorption spectrum of Cu^{2+} doped CdSe polymer.

Photoluminescence (PL) measurement is a sensitive non-destructive technique to investigate the intrinsic and extrinsic defects in a semiconductor. It provides abundant information on the energy states of impurities and defects, even at very low densities, which is helpful for understanding structural defects in semiconductors [30]. The normalized room temperature Photoluminescence spectrum of Cu^{2+} doped PVA-capped CdSe polymer by exciting at a wavelength of 310 nm is shown in figure 3. The influence of the surface on photoluminescence is attributed to the trap states [31]. These trap states are caused by defects such as vacancies, local lattice mismatches or dangling bonds [32]. The excited electron or hole may be trapped by the local energy states of these defects and reduce the irradiative recombination of luminescence [33]. In the present study the emission bands are observed at 352, 410 and 468 nm which correspond to UV and blue regions.
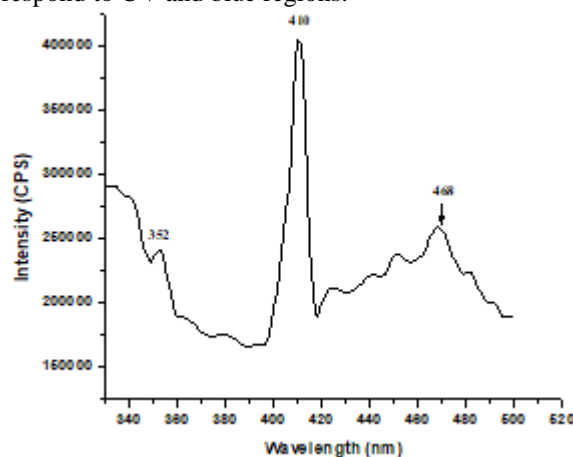

Figure 3: Photoluminescence spectrum of Cu^{2+} doped CdSe polymer.

When compared to Cu^{2+} doped ZnSe, significant red shift is observed in the PL spectrum of Cu^{2+} doped CdSe. The UV emission is attributed to the radiative recombination of a hole in the valence band and an electron in the conduction band [34,35]. The emission band observed at 468 nm is attributed to the recombination of excitons resulting in blue emission from the recombination of photon-generated holes with charge states [36].
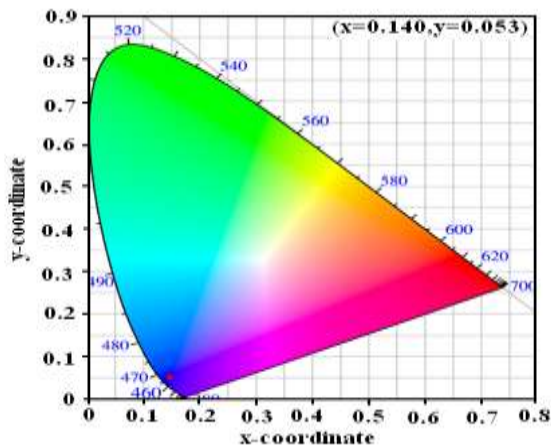

Figure 4: CIE chromaticity diagram of Cu^{2+} doped CdSe polymer.

In general, the colour of any light source can be represented on the (x, y) coordinate in colour space (CIE chromaticity diagram) [37, 38] and is calculated in CIE coordinate calculator by using PL emission spectrum. The CIE chromaticity coordinates of Cu^{2+} doped CdSe is shown in the figure 4. The colour of the sample is located in the blue region and the CIE coordinates are observed at (x = 0.140, y = 0.053). The calculated CIE coordinates are close to the standard NTSC values (x = 0.146, y = 0.057). These coordinates are also close to the edge of CIE diagram which indicates the high colour purity of the prepared sample [39].

3.3 EPR studies

The EPR spectrum of Cu^{2+} doped PVA-capped CdSe polymer, recorded at room temperature is shown in figure 5. It reveals two sets of well resolved lines, one each in low and mid fields, corresponding to spin Hamiltonian parameters in the parallel and perpendicular directions of the applied magnetic field, i.e. $g_\parallel$ and $g_\perp$. The spin-Hamiltonian and hyperfine splitting values are evaluated from the recorded EPR spectrum is as follows: $g_\parallel$ = 2.328, $g_\perp$ = 2.1115, $A_\parallel$ = 134 x 10^{-4} cm^{-1} and $A_\perp$ = 72 x 10^{-4} cm^{-1}.
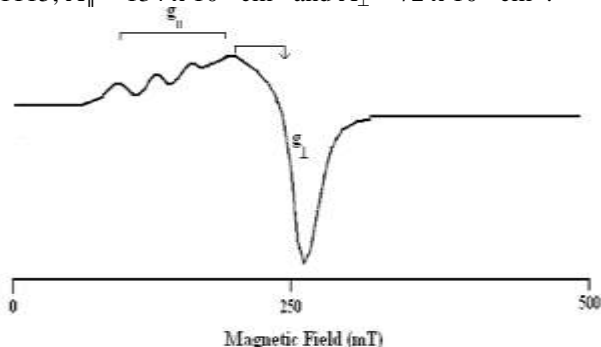
Figure 5: EPR spectrum of Cu^{2+} doped CdSe polymer.

From the EPR spectrum it is observed that $g_\parallel > g_\perp > 2.0023$ which suggests that Cu^{2+} ions are subjected to tetragonally elongated distortion. The covalency parameter α^2 for the in-plane σ-bonding is evaluated using the expression given by Kivelson and Neiman [40].

$$\alpha^2 = A_\parallel / P + (g_\parallel - g_e) + 3/7 \, (g_\perp - g_e) + 0.04$$

The value of α^2 thus evaluated is 0.785. Another parameter $\alpha`$ can be evaluated from the normalization conditions on the ground state β_1 orbital as

$$\alpha` = (1 - \alpha^2)^{1/2} + \alpha S$$

where S is the overlap integral between $d_{x^2-y^2}$ orbital and normalized ligand orbital. The value of S is 0.076 is used for oxygen ligands in the present investigation [40]. $\alpha`$ is a parameter for normalization of $\beta_1$ orbital and indicates the extent of overlap between $d_{x^2-y^2}$ orbital of the central metal ion and the normalized ligand orbital. The evaluated value of $\alpha`$ is 0.531. This intermediate parameter is also used to evaluate another important parameter β_1^2 which is a direct measure of the covalency of the in-plane π-bonding between copper and its ligands. The β_1^2 is more sensitive to variations in covalency than α^2 and is therefore better indicator of the covalent character. β_1^2 is evaluated by using the expression [41]

$$\alpha^2 \beta_1^2 = (g_\parallel - 2.0023) \, \Delta E / 8\lambda_o$$

ΔE is the transition energy between $^2B_1 \rightarrow \, ^2B_2$ and λ_o is the spin–orbit coupling constant (-828 cm^{-1}). The evaluated value of β_1^2 is 0.7503. The normalized covalency of Cu^{2+} ions for in-plane bonding of σ or π symmetry can be expressed as [42].

$$\Gamma_\sigma = 200 \, (1-S) \, (1- \alpha^2) / (1-2S) \, \%$$
$$\Gamma_\pi = 200 \, (1- \beta_1^2) \, \%$$

Generally, the covalency of in-plane σ-bonding Γ_σ decreases, while the covalency of in-plane π-bonding Γ_π increases. In the present case the evaluated values of $\Gamma_\sigma = 47$ % and $\Gamma_\pi = 50$ %. Thus the calculated values of all covalency parameters indicates tetragonally distorted octahedral site for Cu^{2+} ions.

3.4 FT-IR studies

Figure 6 represents the FT-IR spectrum of Cu^{2+} doped PVA-capped CdSe polymer in the wavenumber range 500-4000 cm^{-1}. The bands observed at 3751 and 3370 cm^{-1} are attributed to ν (OH) stretching frequency, indicates the presence of hydroxyl groups [43, 44]. Absorptions for asymmetrical stretching vibration and symmetrical stretching vibration of $-CH_2-$ occur at 2924 and 2855 cm^{-1} respectively [45]. The bands at 2375 and 1518 cm^{-1} are due to the C=O stretching mode arising from the absorption of atmospheric CO_2 on the surface [46]. Absorption peaks at 1715 and 1654 cm^{-1} are attributed to C=O, C=C stretching mode [45]. The absorption band occurring 1427 cm^{-1} is due to bending vibrations of CH_2 groups respectively. The band at 1243 cm^{-1} corresponds to C-O stretching of acetyl groups

present on the PVA backbone. The band at about 1084 cm^{-1} is assigned to ν (C–O) stretching vibration [47]. A band observed at 1025 cm^{-1} is assigned to C-O stretching and O-H bending vibrations. A band
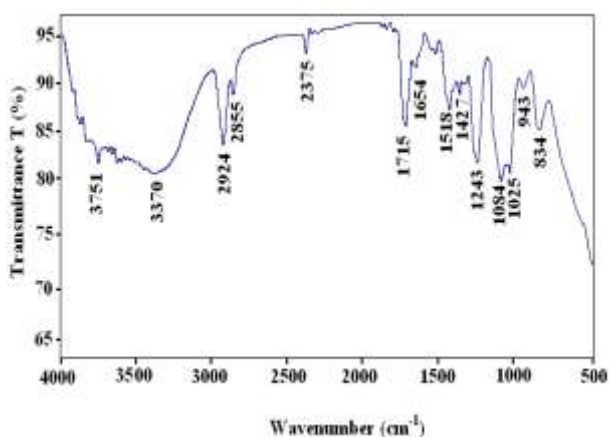

Figure 6: FT-IR spectrum of Cu^{2+} doped CdSe polymer.

observed at 943 cm^{-1} is assigned to C–C stretching vibration [48]. The band at 834 cm^{-1} corresponds to stretching vibration of C-C group.

4. Conclusion

From the results and discussion of Cu^{2+} doped PVA-capped CdSe polymer, the following conclusions are drawn:
X- ray diffraction pattern indicates cubic zinc blende structure of CdSe and the average grain size is evaluated as 23 nm which confirms the prepared sample is in nano size.The optical absorption spectrum confirms the tetragonally distorted octahedral coordination of Cu^{2+} ions in the host lattice. From the EPR spectral studies, spin-Hamiltonian and hyperfine splitting parameters are evaluated. The g-values (g$_\parallel$ > g$_\perp$) indicates tetragonally elongated octahedral site for Cu^{2+} ion. By correlating EPR and optical results, the evaluated parameters indicate the partial covalency of in-plane σ (α^2) and in-plane-π bonding (β_1^2) between copper ions and its ligands. PL spectrum exhibits emission bands in UV and blue region and appropriate CIE chromaticity coordinates (x = 0.140, y = 0.053) with bright blue emission, hence it is considered that Cu^{2+} doped CdSe can be used for fabrication of blue-LEDs and other display devices. FT-IR spectrum exhibits the molecular vibrations of polyvinyl alcohol.

5. Acknowledgements

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