ISSN : 0974 - 7494 Volume 8 Issue 4

Nano Science and Nano Technology

An Indian Journal

Full Paper

NSNTAIJ, 8(4), 2014 [148-152]

Spectroscopic studies on Ni^{2+} doped PVA assisted ZnSe nanoparticles

G.Nirmala[1], K.Ravindranadh[1], R.V.S.S.N.Ravikumar[2], M.C.Rao[1]*

[1]Department of Physics, Andhra Loyola College, Vijayawada - 520008, (INDIA)

[2]Department of Physics, Acharya Nagarjuna University, Nagarjuna Nagar, (INDIA)

E-mail : raomc72@gmail.com

ABSTRACT

Semiconductor nanoparticles have been attracting widespread scientific and technological interest due to their unique size-tunable optical and electronic properties as well as their potential applications. Polymers are used as stabilizers during the preparation of semi conductor nanoparticles. Poly vinyl alcohol is a semi crystalline, water soluble and low electrical conductivity polymer. Zinc selenide of II-VI group semiconductor is one of the most typical and important crystalline material for both application and research of quantum dots. Ni^{2+} doped ZnSe nanoparticles were prepared using Poly vinyl alcohol as assisting agent. Spectroscopic techniques such as XRD and FT-IR studies have been carried out. The particle size is calculated by powder X-ray diffraction and it is around 12.8 nm. FT-IR spectrum exhibited bands, which are attributed to O–H, C–H, C = C and C = O groups of stretching and bending vibrations. The physical parameters like density, refractive index, molar refractivity, ionic concentration, electronic polarizability, polaron radius, inter ionic distances and Urbach energy are measured for the prepared samples.

KEYWORDS

ZnSe nanoparticles;
Poly vinyl alcohol;
Ni^{2+};
XRD;
FT-IR;
Physical properties.

INTRODUCTION

Nanoscience is an emerging area of science which concerns itself with the study of materials that have very small dimensions, in the range of nano scale. Nanotechnology has the capacity to improve our ability to prevent, detect and remove environmental contaminants in air, water and soil in a cost effective and environmentally friendly manner. Nanoscience and nanotechnologies are revolutionizing our understanding of matter and are likely to have profound implications for all sectors of the economy, including agriculture and food, energy production and efficiency, automotive industry, cosmetics, medical appliances and drugs, household appliances, computers and weapons[1].

Semiconductor nanoparticles have been attracting widespread scientific and technological interest due to their unique size-tunable optical and electronic properties as well as their potential applications in solar cells, light-emitting diodes and bio-labels[2-4]. The synthesis and characterization of these particles are quite important for betterment of optical devices. Zinc selenide (ZnSe) of II–VI group semiconductor is one of the most typical and important crystalline material for both application and research of quantum dots[5]. ZnSe is a wide band gap (2.69 eV) semiconductor with large binding energy and a small exciton with Bohr radius of 3.8 nm at room temperature[6,7]. Figure 1 shows the crystal structure of ZnSe. Doped semiconductor nanoparticles have been regarded as a new class of materials which have wide range of applications in sensors, displays, electronic devices, laser devices and nonlinear optical devices, etc.[8]. The properties of semiconductor nanoparticles depend mainly on their shape and size due to high surface-to-volume ratio.

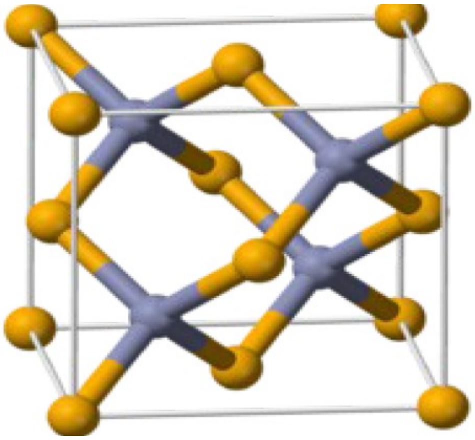

Figure 1 : Crystal structure of ZnSe

Polymers are a large class of materials consisting of many small molecules called monomers, that can be linked together to form long chains, thus they are known 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. A typical polymer may include tens of thousands of monomers. Because of their large size, polymers are classified as macromolecules. Humans have taken advantage of the versatility of polymers for centuries in the form of oils, tars, resins and gums[9]. Poly vinyl alcohol (PVA) was first prepared by Hermann and Haehnel in 1924 by hydrolyzing polyvinyl acetate in ethanol with Potassium hydroxide[10]. PVA is produced commercially from polyvinyl acetate, usually by a continuous process. PVA has an excellent film forming, emulsifying and adhesive properties. It is odorless and nontoxic. It has high tensile strength and flexibility. PVA is the raw material to make other polymers like polyvinyl nitrate (PVN). PVA is completely water soluble and thus is used as a thickener in some suspensions and emulsions. Although usually amorphous, it can be drawn into a semi crystalline fiber. However, the melting point of the crystallites is above the thermal degradation temperature[11].

Nickel occurs as Ni^{2+} in octahedral, square-planar and tetrahedral symmetries depending on the host material. The nickel ion (d^8) gives rise to the free ion terms ^3F, ^3P, ^1D, ^1G and ^1S of which ^3F is the lowest. In octahedral symmetry, these terms split or transform as $^3F \rightarrow {}^3A_{2g}(F) + {}^3T_{2g}(F) + {}^3T_{1g}(F)$, $^3P \rightarrow {}^3T_{1g}(P)$, $^1D \rightarrow {}^1E_g(D) + {}^1T_{2g}(D)$, $^1G \rightarrow {}^1A_{1g}(G) + {}^1T_{1g}(G) + {}^1T_{2g}(G)$ and $^1S \rightarrow {}^1A_{1g}(S)$. Of these various transitions, the spin allowed transitions $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ will be intense. The other transitions are spin-forbidden and will be weak. The terms $^3A_{2g}(F)$, $^1E_g(D)$ and $^1A_{1g}(D)$ correspond to the lowest strong field configuration $t_{2g}^6\, e_g^2$, whereas $^3T_{2g}(F)$, $^3T_{1g}(F)$, $^1T_{2g}(G)$ terms correspond to $t_{2g}^5\, e_g^3$ and $^3T_{1g}(P)$, $^1T_{2g}(G)$, $^1E_g(G)$ and $^1A_{1g}(S)$ to $t_{2g}^4\, e_g^4$. The ground state is $^3A_{2g}(F)$ for all the strengths of the crystal field as depicted in Figure 2.

Polymers are used as stabilizers during the prepara-

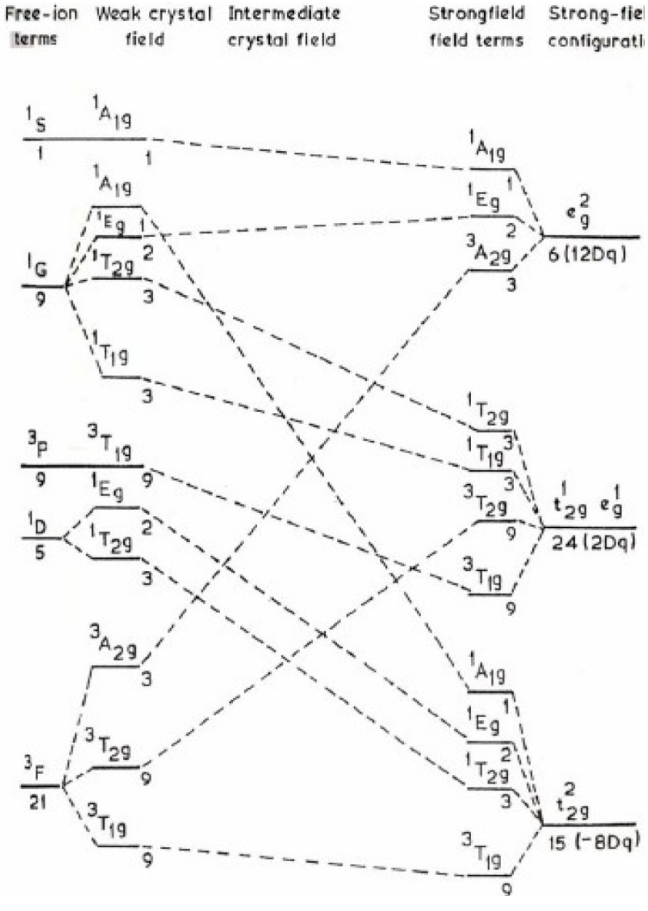

Figure 2 : Correlation diagram for d^8 configuration

tion of semi conductor nanoparticles[12]. PVA is a semi crystalline, water soluble and low electrical conductivity polymer. ZnSe has been prepared by various growth techniques, such as molecular beam epitaxy (MBE)[13], atomic layer epitaxy (ALE)[14] and chemical bath deposition[15]. In the present investigation, ZnSe nanoparticles using PVA as assisting agent is prepared from the technique reported in the literature[16]. To the best of our knowledge, there is no previous literature reported on the Ni^{2+} doped PVA assisted ZnSe nanoparticles. Thus in the present work, we have performed some systematic analyses of the samples using X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) techniques. Different physical parameters have been evaluated for the prepared samples and the results are discussed.

EXPERIMENTAL

Zinc chloride ($ZnCl_2$, 99 mM, 4 mL), PVA (2.2 g), NaHSe (50 mM), $NiCl_2$ (1 mM) are used as starting materials. $ZnCl_2$ 99 mM of 4 mL volume was added to 2.2 g PVA (13,000 g/mol) and the volume of solution was made up to 50 mL by double distilled water. Solution was left for 24 h at room temperature to swell. The solution was warmed up to 60^{o} C and stirred for 4 h until viscous transparent solution was obtained. One milliliter of Sodium Hydrogen Selenide (NaHSe) (50 mM) was dropped into the solution with gentle stirring and 1 mM of 4 mL volume of $NiCl_2$ was added to get transparent solution. Solution was casted on flat glass plate dishes. After the solvent evaporation, a thin film containing Ni^{2+} doped PVA assisted ZnSe nanoparticle was obtained. The film was washed with de-ionized water to remove other soluble salts before measurements[17]. The XRD pattern of the prepared sample is recorded on PANalytical X Pert Pro X-ray powder diffractometer with copper K_{α} radiation. Bruker FT-IR Spectrophotometer is used for recording the FT-IR spectrum of the prepared sample in the region 500-4000 cm^{-1}. The refractive index of the prepared sample is measured using an Abbe's refractometer. Density of the prepared sample is measured by using density meter.

RESULTS AND DISCUSSION

Ni^{+2} doped ZnSe nanoparticles were prepared using Poly vinyl alcohol as assisting agent. The spectroscopic techniques such as XRD and FT-IR studies have been carried out and the physical parameters are measured for the prepared samples.

XRD studies

Figure 3 represents the XRD pattern of PVA assisted Ni^{2+} doped ZnSe nanoparticles. The reaction between Zn and Se ions in the PVA medium doped with Ni ions has a great effect on crystallization as well as the size of the formed ZnSe nanoparticles. The PVA sample has diffraction peak angles at $2\theta = 19.25^{o}$, 25.61^{o}, 28.58^{o} and 29.55^{o} corresponding to (111), (100), (002) and (101) plane reflections. The crystalline nature of PVA results from the strong intermolecular interaction between PVA through intermolecular hydrogen bonding. The crystallite size (D) was calculated according to the Scherrer's formula[18]. $D = (K\lambda / \beta \cos\theta)$, where K is a constant (shape factor, about 0.9), λ is the wavelength of X-ray radiation ($\lambda = 1.5405A^{0}$), β is the full width at half maximum (FWHM) of the diffraction line and θ is the diffraction angle. Based on the FWHM, the average crystallite size was estimated to be 12.8 nm, which indicates the particle is in nanosized.

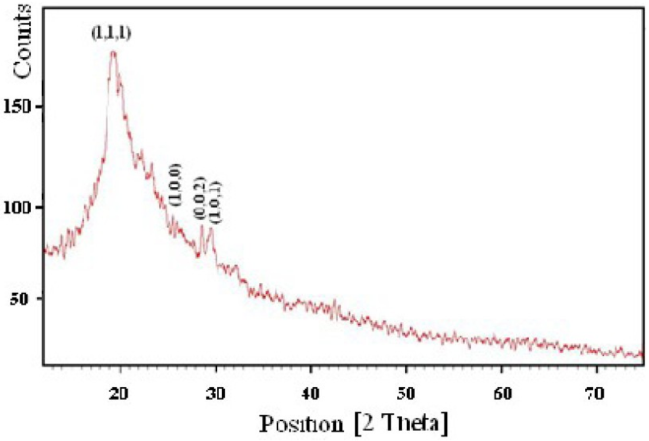

Figure 3 : XRD pattern of Ni^{+2} doped PVA assisted ZnSe nanoparticles

FT-IR studies

Figure 4 shows the FT-IR spectrum of Ni^{2+} doped PVA assisted ZnSe nanoparticles at room temperature in the region 500-4000 cm^{-1}. The spectrum exhibited bands which are the characteristic of stretching and bending vibrations of O–H, C–H, C=C and C=O groups. The band observed at 583 cm^{-1} corresponds to the O-H stretching frequency[19] which indicated the presence of hydroxyl groups. The band at 839 cm^{-1} is assigned to stretching mode of CH_2 group. The band at 1086 cm^{-1} and the band at 945 cm^{-1} are assigned to the stretching mode of CO and CC groups[20]. The band at 1246 cm^{-1} is assigned to stretching mode of CH group. The band at 1373 cm^{-1} is assigned to stretching vibration of CH_2 group. The band at 1428 cm^{-1} is assigned to bending vibration of CH_2 group[21]. The bands observed at 1540, 1655 cm^{-1} are assigned to C = C stretching. The band observed at 1715 is assigned to C = O group. The band observed at 2375 cm^{-1} is assigned to combinational frequency of (CH + CC) group. The band observed at 2922 cm^{-1} indicates an asymmetry in stretching mode of CH_2 group. The IR band positions and their assignments are presented in TABLE 1.

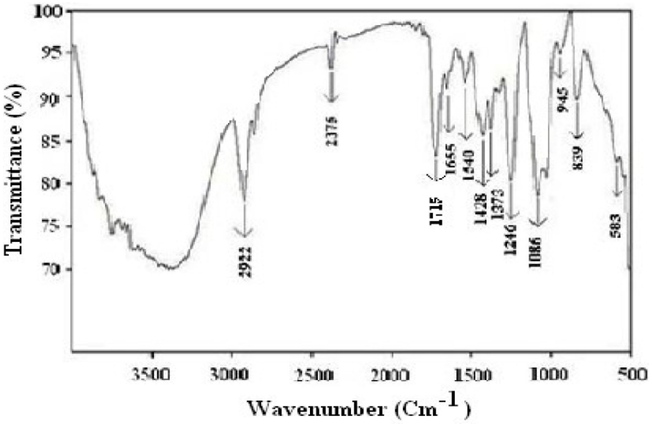

Figure 4 : FT-IR spectrum of Ni^{+2} doped PVA assisted ZnSe nanoparticles

TABLE 1 : Assignment of peak positions and their corresponding frequencies in IR spectrum of Ni^{2+} doped PVA assisted ZnSe nanoparticles

S. No.	Vibrational frequency (cm^{-1})	Band assignment
1	583	OH (st)
2	839	CH_2 (st)
3	945	CC (st)
4	1086	CO (st)
5	1246	CH(st)
6	1373	CH_2 (st)
7	1428	CH_2 (b)
8	1540	C = C (st)
9	1655	C = C (st)
10	1715	C = O (residual cetate)
11	2375	(CH + CC)
12	2922	CH_2 (st)

st: stretching b: bending

Physical parameters

Refractive Index and density of the prepared sample was measured by using Abbe's refractometer and density meter. By using refractive index, density and other physical parameters are calculated and are given in TABLE 2.

TABLE 2 : Physical parameters of Ni^{2+} doped PVA assisted ZnSe nanoparticles

S. No.	Physical Parameter (units)	Evaluated Value
1	Average molecular weight (g/mol)	2.262
2	Mass of the Co (II) ions doped CdSe (g)	0.023
3	Volume of the film (cm^3)	0.021
4	Density (ρ) (g/cm^3)	1.124
5	Refractive index (μ)	1.654
6	Optical dielectric Constant (ε) (± 0.005)	2.737
7	Reflection loss (R)	0.060
8	Molar Refractivity (R_m) (cm^{-3}) (± 0.005)	0.737
9	Ion concentration (N) (10^{22}ions/cm^3)	0.028
10	Electronic polarizability (α_e) (10^{-23}ions/cm^3)	30.78
11	Inter-ionic distance (r_i) (A^o) (± 0.005)	15.19
12	Polaron Radius (r_p) (A^o) (± 0.005)	6.113
13	Urbach Energy (ΔE) (eV)	0.043

The Dielectric constant (ε) was calculated from the refractive index by using the relation[22]

$$\varepsilon = n_d^2$$

The reflection loss from the refractive index can be calculated by using the formula[23]

$$R = [(n_d-1)/(n_d+1)]^2$$

The molar refractivity (R_M) for the prepared sample was evaluated using the relation[24]

$$R_M = [(n_d^2-1)/(n_d^2+2)]M/D$$

Where M is the average molecular weight and D is the density in g /cc.

Electronic polarizability α_e is calculated using the formula[25]

$$\alpha_e = 3\,(n_d^2 - 1)/\,4\pi N\,(n_d^2 + 2)$$

Where N is the number of ions per unit volume

The Polaron radius and Inter-ionic separation are calculated using the Formulae[26]

$\mathbf{r_p = (1/2)\ [II / 6N]^{1\backslash 3}}$ **and** $\mathbf{r_i = (1/N)^{1\backslash 3}}$

CONCLUSIONS

The discipline of nano science and nanotechnology has recently become one of the most important areas of knowledge encompassing various scientific disciplines including physics, chemistry, biology and engineering. In recent years, polymer-nanoparticle composite materials have attracted the interest of a number of researchers, due to their synergistic and hybrid properties derived from several components. Whether in solution or in bulk, these materials offer unique mechanical, electrical, optical and thermal properties. Such enhancements are induced by the physical presence of the nanoparticle and by the interaction of the polymer with the particle and the state of dispersion. One advantage of nanoparticles, as polymer additives appear to have is that compared to traditional additives, loading requirements are quite low. Nanostructured materials can be utilized in fabricating novel active devices with improved functionalities. From the physical and spectral investigations of Ni^{2+} doped PVA assisted ZnSe nano- particles, the following conclusions were drawn: Powder XRD pattern confirms the prepared sample is nanosized. The observed bands in the FT-IR spectrum indicate the presence of stretching and bending vibrational modes of O–H, C–H, C=C and C=O groups. The physical parameters like density, refractive index, molar refractivity, ionic concentration, electronic polarizability, polaron radius, inter ionic distances and Urbach energy are evaluated.

ACKNOWLEDGEMENTS

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))

REFERENCES

[1] M.Kidwai, P.Sapra; Org.Prep.Proc.Int., **33**, 381 **(2001)**.

[2] Q.A.Zhang, J.Ding, Y.L.Shen, D.P.Chen, Q.L.Zhou, Q.X.Chen, Z.W.He, J.R.Qiu; J.Alloys Compd., **508**, L13 **(2010)**.

[3] S.Wang, P.Li, H.Liu, J.B.A.Li, Y.Wei; J.Alloys Compd., **505**, 362 **(2010)**.

[4] M.S.Niasari, A.Sobhani, F.Davar; J.Alloys Compd., **507**, 77 **(2010)**.

[5] H.Yang, C.Guang, X.Su, A.Tang; J.Alloys Compd., **402**, 274 **(2005)**.

[6] X.D.Liu, J.M.Ma, P.Peng, W.J.Meng; Langmuir, **26**, 9968 **(2010)**.

[7] P.T.K.Chin, J.W.Stouwdam, R.A.J.Janssen; Nano Lett., **9**, 745 **(2009)**.

[8] J.F.Suyver, S.F.Wuister, J.J.Kelly, A.Meijerink; Nano Lett., **1**, 429 **(2000)**.

[9] L.Qi, H.Colfen, M.Antonietti; Nano Lett., **1**, 61 **(2000)**.

[10] J.Fromageau, E.Brusseau, D.Vray, G.Gimenez, P.Delachartre; Trans.Ultras.Ferroelect.Freq.cont., **50**, 1318 **(2003)**.

[11] Sk.Muntaz Begum, G.Nirmala, K.Ravindranadh, T.Aswani, M.C.Rao, P.Sambasiva Rao, R.V.S.S.N.Ravikumar; J.Mol.Stru., **1006**, 344 **(2011)**.

[12] I.Sondi, O.Siiman, S.Koster, E.Matijevic; Langmuir, **16**, 3107 **(2000)**.

[13] J.S.Song, J.H.Chang, D.C.Oh, J.J.Kim, M.W.Cho, H.Makino; J.Cryst.Growth, **249**, 128 **(2003)**.

[14] C.D.Lee, S.L.Min, S.K.Chang; J.Cryst.Growth, **159**, 108 **(1996)**.

[15] A.M.Chaparro, M.A.Martinez, C.Guillen, R.Bayon, M.T.Gutierrez, J.Herrero; Thin Solid Films, **361**, 177 **(2000)**.

[16] Y.Badr, M.A.Mahmoud; Spectrochim.Acta Part A, **65**, 584 **(2006)**.

[17] S.K.Muntaz Begum, M.C.Rao, Y.Aparna, P.S.Rao, R.V.S.S.N.Ravikumar; Spectrochim.Acta, **A98**, 100 **(2012)**.

[18] M.M.Ahmed, C.A.Hogarth, M.N.Khan; J.Mater.Sci.Lett., **19**, 4040 **(1984)**.

[19] C.H.Linga Raju, J.L.Rao, B.C.V.Reddy, K.Veera Brahmam; Bull.Mater.Sci., **30**, 215 **(2007)**.

[20] G.N.Hemantha Kumar, J.Lakshmana Rao, N.O.Gopal, K.V.Narasimhulu, R.P.S.Chakradhar, A.Varada Rajulu; J.Poly., **45**, 5407 **(2004)**.

[21] A.Tawansi, A.H.Oraby, H.M.Zidan, M.E.Dorgham; J.Physica B, **254**, 126 **(1998)**.

[22] P.V.Kamat; Prog.React.Kinet., **19**, 277 **(1994)**.

[23] R.N.Bhargava, D.Gallagher, X.Hong, A.Nurmikko; Phys.Rev.Lett., **72**, 416 **(1994)**.

[24] L.M.Gan, B.Liu, C.H.Chew, S.J.Xu, S.J.Chua, G.L.Loy, G.Q.Xu; Langmuir, **13**, 6427 **(1997)**.

[25] J.Huang, Y.Yang, S.Xue, B.Yang, S.Liu, Shen; J.Appl.Phys.Lett., **70**, 2335 (**1997**).

[26] A.Klinokowski; J.Non-Cryst.Solids, **72**, 117 **(1985)**.