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Zinc Sulphide nanomaterials doped with rare earth Neodymium -An Optical study

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Abstract: ***Neodymium doped Zinc Sulphide nanoparticles were prepared by chemical precipitation route. The samples were heated at 150 250, and 350 ^{o}C. The average crystal size of the prepared ZnS nanopowder is determined by XRD. ZnS is effectively used for detecting cancer cells in human body. It is a first-rate light transmission material with high refractive index 2.27 also makes ZnS useful in photonic crystal devices that drive in the region from visible to near infrared. XRD, SEM, FTIR UV-Vis and EDS characterize the samples. The percentage of doping material in the crystal is confirmed from the EDAX spectra. The size of the particles increased as the annealing temperature was increased. The crystallite size varied from 20nm to 25 nm as the calcinations temperature increased. The emission peak of the sample is observed at 300 nm resulting in blue emission. The solid state theory based on the delocalized electron and hole within the confined volume can explain the blue-shifted optical absorption spectra. Band gap of doped ZnS decreases to 3.27 eV and remains constant at higher temperatures which are due to the quantum confinement of the value. The UV Absorption spectra show a shift towards 202nm. The Nd doped ZnS is highly effective and can significantly enhance the photo catalytic degradation.***

Key words: **Nanocrystals, Zinc Sulphide, doping, Neodimium.**

I. INTRODUCTION

Semiconductor nanoparticles, which have changed properties resulting from quantum confinement, have drawn considerable interest and are currently being, investigated Semiconductor nanoparticles exhibit size-dependent electronic band gap energies [1]. In addition to these, doped semiconductor nanoparticles have tremendous potential for use in light emitting applications. Zinc sulphide is an extensively studied group II-VI semiconductor with wide direct band gap 3, 65 eV [1]. ZnS finds application in field of photoluminescence (PL), Electro luminescence (EL) and cathodo luminescence (CL) due to better stability [2]. Properties of nanocrystals make them an interesting category of material for opto-electronic applications It finds application as Light Emitting Diode, reflector, dielectric filter material, indicator, analysis of water pollution, environmental studies, pathological investigations, etc.blue shift in the optical absorption spectrum, size dependent luminescent, enhance oscillator strength, non linear optical effects, geometrical structure ,chemical bonds, Ionization potential, mechanical strength, melting point etc. are all affected by particle size[3-4]. The optical properties of nanocrystalline semicon-ductors have been studied extensively in recent years. The change in the properties of nanoparticle is driven mainly by two factors, namely, the increase in surface to volume ratio and change in the electronic structure of the material due to quantum confinement effects [5]. The band structure of the semiconductor changes with decreasing particle size [6]. This study aims to investigate variation of Band gap energy of ZnS: Nd with temperature and grain size.

II. MATERIALS AND METHODS

Nanoparticles of Nd-doped ZnS were prepared by chemical co precipitation method. All the chemicals were of AR grade and were used without further purification. Freshly prepared aqueous solutions of the chemicals were used for the synthesis of nanoparticles. These particles were prepared at room temperature by dropping simultaneously 50 ml of 0.4 M solution of zinc scetate 50 ml of 0.1 M solution of Neodymium oxide and sufficient amount of Hydrogen sulfide is passed into the solution. Which was vigorously stirred using a magnetic stirrer. The role of EDTA was to stabilize the particles against aggregation which may lead to an increase in the size of the particles. The precipitate was separated from the reaction mixture, washed several times with distilled water and then with alcohol to remove the impurities, including traces of EDTA Then it has been heated up to 150^{o}C so that the water content in the sample should be removed. After annealation, sample is

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taken and made into fine powder form. This powdered sample is doped with Neodymium and again annealed. The sample was then characterized by X-ray Diffraction (XRD) and Fourier Transform Infrared (FTIR) studies.

A. Characterization methods

The surface topography and microstructure were studied using Field Emission Scanning Electron Microscopy (FESEM). Perker Elmer Lamda 25 UV-Vis spectrometer was used to study the optical properties of nanopowder. Infrared spectra were recorded using a Nicolet (Impact 410) FTIR spectrometer, using transparent pellets of the compounds in KBr matrices.KBr was used as the background file. All spectra were measured from approximately 4000 to 400 $cm^{-1.}$ Energy Dispersive X-ray Spectrum Analysis (EDX) was used to determine percentage composition of La in ZnS.

III. RESULTS AND DISCUSSION

A. Determination of particle Size from XRD Pattern

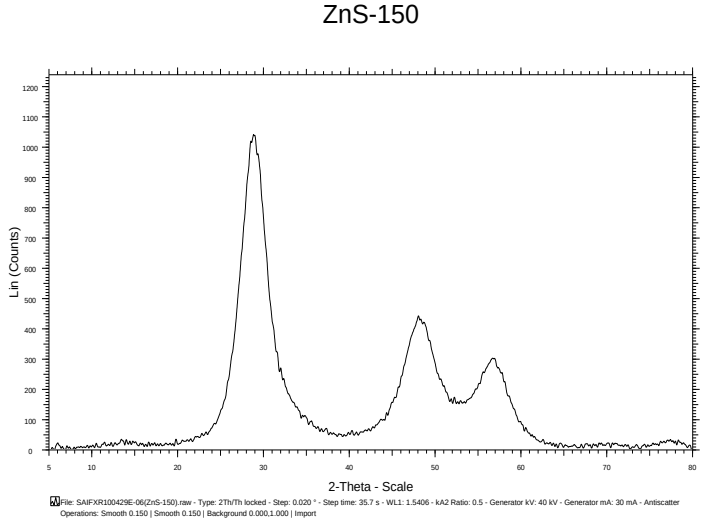
The XRD pattern consists of sharp intense peaks of ZnS which confirms the good crystalline nature of ZnO and peaks originated from(111),(220), (311),(422), (200), (331), (400), (222), and (420) reflections of hexagonal ZnO [4]. The XRD patterns, Fig 1, of nanometer sized particles are quite striking because of the size dependent and structure specific features observed. Therefore XRD techniques are widely used for the particle size determination and structure determination of nanoparticles. The patterns are compared with JCPDS card No: 77-2100. XRD is a genuine tool to test the phase of a material, ie, whether it is crystalline or amorphous. The degree of crystallinity of nanoparticles increases with annealing temperature. The percentage of lattice contraction with annealing temperature can also be studied using X-ray diffraction pattern. Particle Size, can be calculated by the formula [4,7], Debye- Scherrer's formula

$$L = K \lambda / \beta \cos \theta. \qquad (1)$$

K=0.89, λ the X-ray wavelength = 0.154095 nm, β the full wavelength at half maximum and θ the half diffraction angle.

B. XRD pattern ZnS: Nd at various temperatures

Particles annealed at temperatures, 150˚C, 250˚C, 350 ˚C, have grain sizes 21.7 nm, 22 nm and 25 nm. The Values are tabulated in Table 1. From the above study, it is observed that there is a continuous increase in the particle size with temperature. According to Ostwald ripening [8] the increase in the particle size is due to the merging of the smaller particles into larger and is a result of potential energy difference between small and large particles and can occur through solid state diffusion



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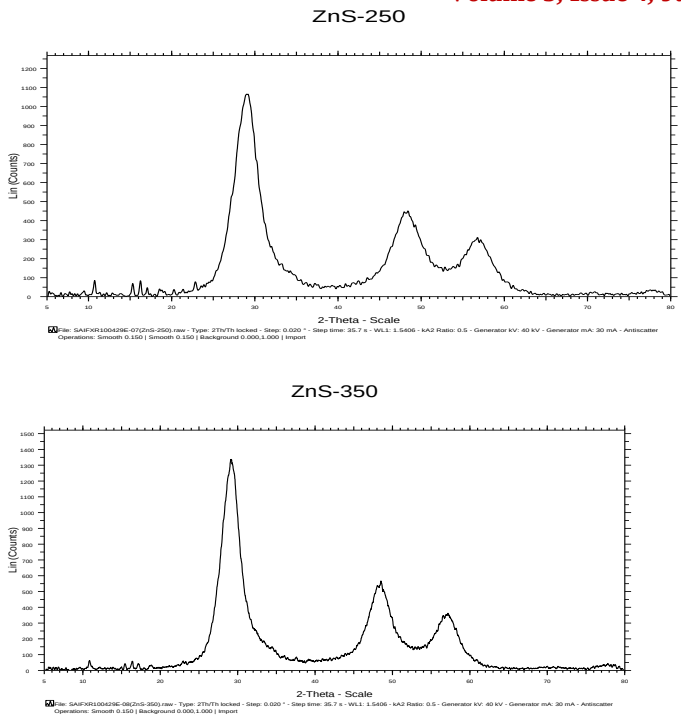

Fig.1 XRD pattern of ZnS:Nd at 150,250 and 350°C

Table 1. Particle size of nanomaterial ZnS: Nd at various temperatures

Temperature ^{o}C	FWHM	$\beta \times 10^{3}$	2θ	θ	Particle size(L) Nm
150	0.364	6.34	12.875	6.4375	21.7
250	0.343	5.98	13.051	6.5255	22
350	0.312	5.44	13.352	6.676	25

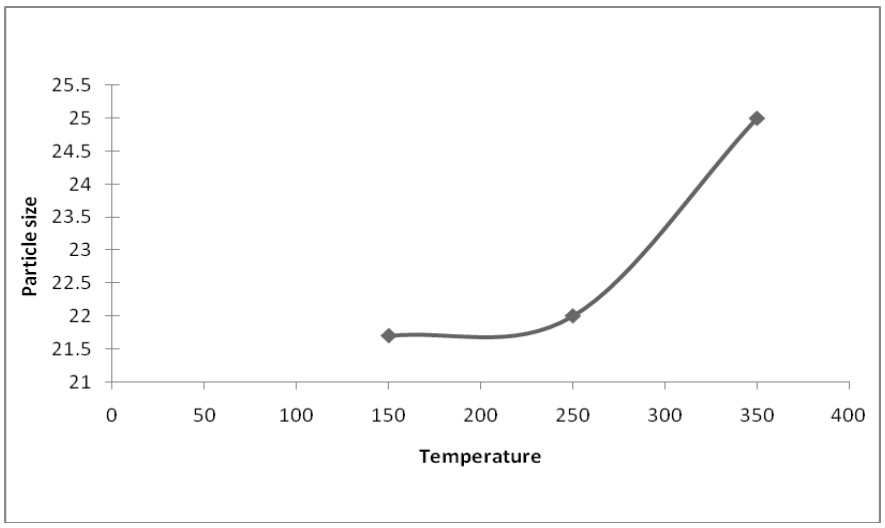

Fig.2.Variation of particle size with temperature

C. FTIR spectra of nanocrystalline ZnS: Nd

Infrared bands depicted in Fig 3, at 418.56cm^{-1} is assigned to the stretching vibrations of ZnS. The stretching

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frequency of bulk ZnS is 483.72cm^{-1}.Three intense bands are centered at 1384.08cm^{-1},1023.37cm^{-1}and 1550.06cm^{-1} and are attributed to the stretching vibrations of C=O, C=C and C-H groups in acetate species, which suggest it presents as absorbed species in the surface of nanoparticles.

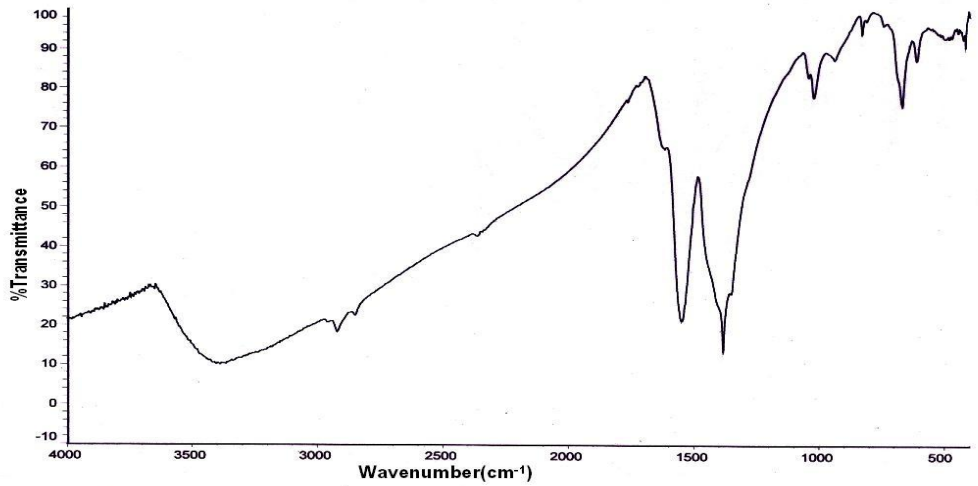

Fig.3. FTIR spectrum of ZnS: Nd nanoparticle

The broad absorption peak centered at 3389.47cm^{-1} and 2922.47cm^{-1} corresponds to O-H stretching and bending frequencies of water indicating the existence of water in the surface of nanoparticles. Weak additional bands were observed at 992, 984 and 865 cm at lower temperature. These modes indicate the presence of resonance interaction between vibrational modes of sulphide ions in the crystal [9] Our measurement of the spectrum of powdered sample yields the bands, which are in good agreement with the reported values

D. Scanning Electron Microscopy (SEM)

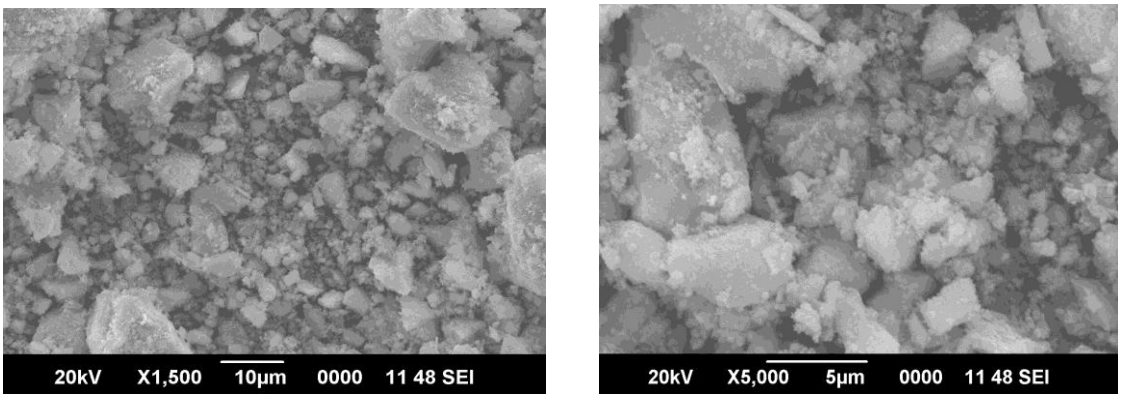

Fig.4 SEM Image of ZnS: Nd nanoparticle under high magnification

The Fig.4 depicts the Scanning electron micrographs of ZnS: Nd nanomaterials synthesized under aqueous medium. The orientation growth of ZnS crystal in water is higher [6] Spherical shaped morphology is observed in the micrograph of ZnS:Nd The SEM pictures show distinguished spherical morphology .the SEM pictures exhibit spherical morphology with self aligned prismatic nanoparticles. The morphology of ZnS nanopowder as revealed by FESEM showed nanoparticle of size 15-100 nm

E. Energy Dispersive Spectrum Analysis (EDS)

An EDS or EDAX spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well. The EDS spectrum shown in the Fig 5 EDS spectrum corresponds to a single element. The higher a peak in a spectrum, the more concentrated the element is in the spectrum. An EDS spectrum plot not only identifies the element corresponding to each of its peaks, but the type of X-ray to which it corresponds as well. EDAX of ZnS:Nd nanoparticle is plotted using the recorder and the EDAX data is measured as Zinc Sulphide ≈ 95.88 % and Neodymium≈ 4.12%

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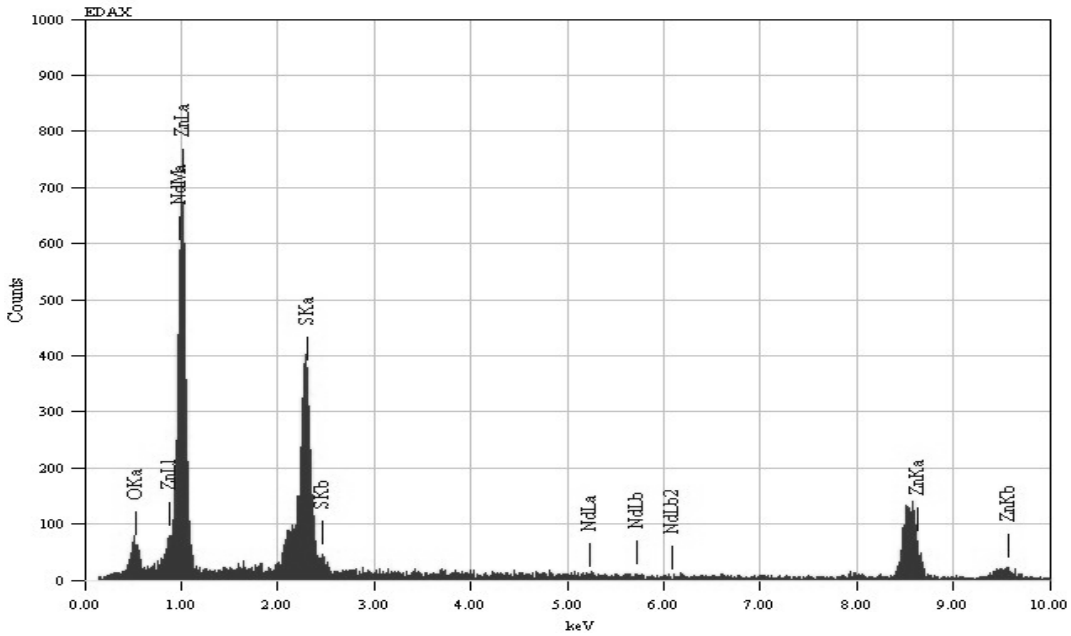

Fig 5. EDAX of Nano ZnS: Nd

F. UV Absorption spectra of ZnS: Nd

Materials with nanoscale microstructure are increasingly becoming important for their technological importance due to their unique electrical, magnetic, and optical properties. They can be distinguished from the nano crystalline and nanophase materials on the basis that in case of nanocrystalline materials only one phase exists. While in the case of nanomaterials more than one Gibbson solid phase are present and out of which at least one of the phases is in nm size range.

From Fig. 5, it can be seen that the strongest absorption peak of the as-prepared sample appears at around 200 nm, which is fairly blue-shifted from the absorption edge of the bulk ZnS (345nm). ZnS has good absorption for light in the wave-length of 220-350 nm [10]. Semiconductor crystallites in the diameter range of a few nanometers show a three dimensional quantum size effect in their electronic structure.

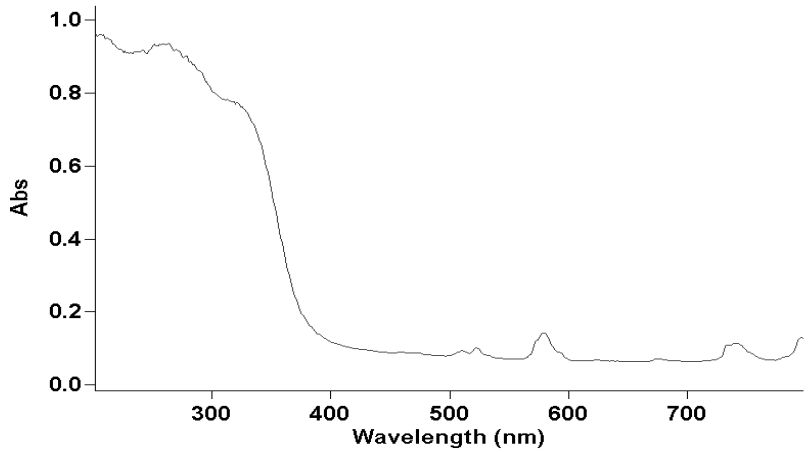

Fig.6. UV Absorption spectra of ZnS: Nd nanomaterial

These quantum size effects on the band gap absorption energy can be measured by UV-VIS absorption spectroscopy. From the UV study we can calculate the energy band gap. The fundamental absorption, which corresponds to the transmission from valence band to the conduction band, is employed to determine the band gap of the material.

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The exact value of the band gap is determined by extrapolating the straight line to the x-axis of the UV absorption graph plotted between E_g Vs αhω . The material is reported as direct band gap material. For higher values of absorption coefficient, optical absorption showed a power load dependence on photon energy [9, 10].

$$h\omega = \alpha(\omega) = B(h\omega - E_g)^{\gamma} \qquad (2)$$

Where exponent γ can take values 2,3,1/2 and 3/2 for indirect allowed ,indirect forbidden, direct allowed and direct forbidden transition respectively. E_g is the optical band gap.

It was noticed that the optical band gap value of nano ZnS, 3.88eV, which is higher than the bulk value of ZnS, 3.68 eV [12]. From the figure it is found that band gap of doped ZnS decreases to 3. 27 eV and remains constant at higher temperatures which is due to the quantum confinement of the value. The decreasing particle size is due to a strong hybridization of the s-p states of the ZnS host and the d states of the impurity atoms [13]. This hybridization results in a faster energy transfer between the ZnS host and impurity atoms yielding a higher quantum efficiency and it was argued that through this hybridization, the spin-forbidden transition of the impurity becomes less spin-forbidden, resulting in a shorter decay time [11].

G. UV Reflection spectra of ZnS: Nd

The reflection spectra of ZnS: Nd depicted in Fig 6 shows a strong drop in reflection in the UV range 350nm corresponding valence to conduction band transition of the ZnS: Nd nanostructure

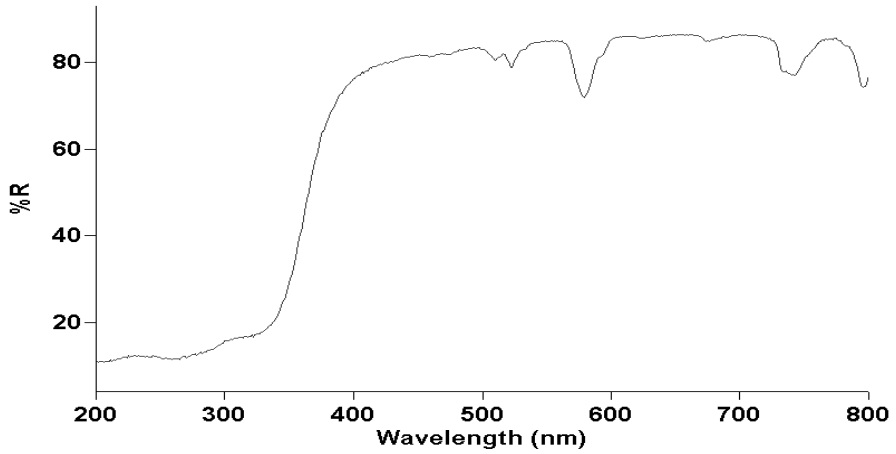

Fig.7 UV Emission spectra of ZnS: Nd Nanomaterial

IV. CONCLUSION

Nd doped ZnS nanoparticles have been prepared by chemical co-precipitation method. The strongest absorption peak appears at around 202 nm, which is fairly blue-shifted from the absorption edge of the bulk (345 nm). The XRD results indicated that the particle size of nano ZnS: Nd is much small as compared to that of pure nano ZnS and decreases with the Lanthanum loading. From the XRD results, it is clear that as temperature increases, particle size also increases. The change in particle size cause large variation in the physical properties since 1 nm size change may introduce a considerable change in the number of surface atoms with lower coordination and broken exchange bonds [13]. Absorption peaks in the FTIR spectrum of ZnS with different particle size were explained. The shifting of the bands observed in the FTIR spectra is due to quantum size effects. The solid-state theory based on the delocalized electron and hole within the confined volume can explain the blue-shifted optical absorption spectra. Band gap values were determined from the optical transmission studies of the as-prepared samples. Band gap of doped ZnS decreases to 3.27 eV and remains constant at higher a temperature which is due to the quantum confinement of the value. The composition of the prepared sample is established from the EDAX on the sample. With decreasing particle size, a strong hybridization of the s-p states of the ZnS host and the d states of the Nd impurity is likely to occur. The UV Absorption spectra show a shift towards

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202nm. The Nd doped ZnS is highly effective and can significantly enhance the photo catalytic degradation.

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REFERENCES

[1] Efros A.L., and Rosen M., "The electronic structure of semiconductor nanocrystals" Annu.Rev.Mater.Sel, 36, 475-521, 2003.

[2] Havanseak, K. "Nanotechnology at present and its promises in the future", Materials Science Forum, 414-415, 85-94,2003.

[3] Dutta J. and Sugunan A., "colloidal self organization for nanoelectronics" in B.Y.Majlis, and S.Shaari (Ed) IEEE international conference on semiconductor electronics, KualaLampur, A6-A11. 2004.

[4] Gates, B.D. Xu Q., Love L.C., Wolfe D.B.and Whitesides, G.M. "Unconventional nanofabrication", Annu.Rev.Mater.Res,34,339-372. 2004.

[5] Cullity B.D., Elements of X-ray Diffraction, Second Edition, Addison Wiley. Publishing Co 1978.

[6] Zhong Lin Wang (ED.), Characterization of Nanophase Materials, Wiley-Vch, Verlag 2000.

[7] Noor Shahima Begum, Farweez Ahmed H.M, Bull.Mat.Sci. 31,1,73-82. 2008

[8] Nanda K.K.,.Kruis F.E and Hassan H., Phys.Rev.Lett. 89, 256103-110, 2002.

[9] Pratima Ctauhao, S Annapoorni and S.K Trikha.Bull.Mater.Sci., 21, 5.pp 381-385, 1998.

[10] Lappen and P.E..Lannoo. M, Calculation of band gap for small CdS and ZnS. Physical Review B, 39, 15, 1989.

[11] Nobert Adolph lange and Gordon M.Forker B.S "Hand book of Chemistry" 1980.

[12] Sibi Kurian, Shajo Sebastian, Jose Mathew and George, K C, Indian J. Pure Appl.Phys, 42, 926. 2004.

[13] Bhargava R N and Gallagher D,Phys. Rev. Lett, 72, 416.1994.