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Study of the Structural, Morphological, Vibrational & Optical Properties of Synthesized Eu3+-Doped ZnS Nanocrystals

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Abstract- Here, we have reported that the structural, morphological, elemental composition, vibrational & Optical properties of the synthesized ZnS: Eu3+ nanocrystals. X-ray diffraction (XRD), Scanning electron microscope (SEM), Photoluminescence (PL) and Fourier transform infrared spectroscope (FTIR) studies have been done on all these samples. XRD patterns have clearly shown the cubic phase structure is present. The crystallite sizes of these nanoparticles were calculated using the Scherrer's equation and our estimated average crystallite size is 6.5 nm. The size of particle determined from the TEM image is close to the calculated value from XRD. In FESEM, Average particle size is found 5.5 nm. In EDS Spectra, the above figures confirm the presence of Zn, S, and Eu. No traces of other elements were noticed in the spectra indicating the purity of the samples. The role of dopant concentration of ZnS: Eu3+ nanocrystals and their photoluminescence properties are well investigated. It is found that photoluminescence properties are sensitive to the crystal structure which is controlled by dopant concentration. The emission intensity of the peak at 617 nm (5D0-7F2) of the Eu3+-ions is found to be sensitive to the doping of ZnS nanocrystals. In this present article, X-ray diffraction (XRD), Scanning electron microscope (SEM), HRTEM, EDS, Photoluminescence (PL) and Fourier transform infrared spectroscopy (FTIR) properties have been investigated in detail.

Keywords- ZnS: Eu3+ nanocrystals, Cubic, Hexagonal, X-ray diffraction (XRD), Scanning electron microscope (SEM), Photoluminescence (PL) and Fourier transform infrared spectroscope (FTIR).

I. INTRODUCTION

In past years, II–VI compound semiconductor phosphor have been paid great attention owing to their unique optical properties that by changing the particle size as well as by changing the compositions. A member of the most significant II–VI compound semiconductors is ZnS. Because of its ability to tune emission in the spectrum of visible light with shapes and sizes that vary, it is widely utilized in optoelectronic devices. ZnS phosphors have attracted considerable attention from the research community because of their wide band gap and tremendous potential applications in diverse areas such as solar cell, photo-catalysis, sensors, photonic, photonic devices, X- ray absorber, cathode-ray tube devices, optoelectronic devices and due to their unique physical properties having another potential application such as photo-electronics, optoelectronics, acousto-optic properties and quantum radio physics, are closely connected with its unique crystallographic properties because of its capability of undergoing polymorphic transformations, and this makes additional structural investigations of interest [1-4].

Recently, significant attention has been paid to rare earth ions doped semiconductor nanoparticles to find out the potential applications in photonic and bio photonic field [5]. A number of papers were published on the luminescence of nanocrystalline II–VI semiconductors doped with rare earth [RE] ions. Recently, Erwin et al. [6] have reported the important roles of crystal structure and shape of the nanocrystals in optimizing the efficiency of rare earth doped nanocrystals. In order to make these applications practically viable, it is important to find magnetic semiconductors which are ferromagnetic at or above room temperature. In this pursuit, considerable work has been carried out on transition metal doped Zn based chalcogenides namely ZnS, ZnSe and ZnTe [7, 8]. Among the most studied host materials for ZnS is one with great potential for device applications and it has been identified as an excellent host semiconductor for supporting RTFM when doped with a variety of 3d transition metal ions such as Eu, Mn [9], Co [10], Cu [11] Fe [12] and Cr [13]. Here, we present the influences of dopant concentration on the crystal structure and the structural, morphological, elemental composition, optical and vibrational properties of prepared ZnS: Eu3+ nanocrystals have been investigated in detail.

II. EXPERIMENTAL SECTION

1. Synthesis of Nano Crystals

The various sizes of ZnS nanocrystals were synthesized using Zinc acetate dehydrate (A.R, Glaxo, India) and thioacetamide (G.R. Loba Chemie, India) in glacial acetic acid and 2-methoxy ethanol (S.D. Fine Chem. India). A typical synthesis involves dissolving of cadmium acetate in 20 mL of glacial acetic acid with constant stirring. To this, the solution of thioacetamide in 20 mL of 2-methoxy ethanol was added while stirring. Then the reaction mixture was kept in an oil bath at 80 0C under stirring condition for 1:30 h. The precipitate was centrifuged and then washed twice with acetone and twice with methanol. All the samples were dried at 600C for 17 h in a vacuum oven. The required amount (2 mol%) of Eu (NO3)3.6H2O (Aldrich) was added to the aqueous solution of zinc acetate solution for Eu3+-ions doped ZnS nanoparticles, and then the same procedure was followed. The sonication was carried out for 2 h employing a direct immersion titanium horn in an open beaker kept in an ice bath. Five milliliters of 25% triethylamine were added dropwise during the sonication. The resulting product after sonication was washed extensively with water, centrifuged and dried under vacuum.

2. Characterization Study

The crystalline phases and size determination of the particles were identified by X-ray diffraction (XRD) using a D8 Advanced powder X-ray diffractometer using a Cu-Kα source (1.5418 Å radiation). Crystallite sizes (D, in Å) were estimated from the Scherrer equation: $D = K\lambda/\beta \cos\theta$, where λ is the wavelength of Cu-Kα radiation, β is the corrected half-width of the diffraction peak, θ is the diffraction angle and K is equal to 0.94. The size of the particles was also determined from TEM images obtained using a JEOL-TEM-2010 Scanning electron microscopy/transmission electron microscope with operating voltage of 200 kV. The excitation and emission spectra of all the nanocrystals were recorded at room temperature in a Shimadzu RF-5301 fluorescence spectrometer with both the excitation and the emission spectrum. All measurements were done at room temperature, using a solid sample holder. All samples were excited at 347 nm (bandwidth (Ex) = 10 nm, bandwidth (Em) = 10 nm), under same conditions. FT-IR spectra over the range 500–4000 cm−1 were performed on a Bruker Alpha FT-IR Spectroscopy. The ZnS: Eu nanocrystals mixed with solid KBr power was ground to a fine powder. Chemical analysis was carried out using scanning electron microscopy (SEM) with EDS attachment (CARL-ZEISS EVO MA15).

III. RESULTS & DISCUSSION

1. Structural Analysis

The XRD patterns of the nanocrystals are considerably broadened due to the very small size of the crystallites. To check the crystallinity and crystal structures of the synthesized nanoparticles, XRD studies were carried out and the results are shown in Fig. 1. The XRD scan was carried out for a

2-theta angle range of 15–750. The XRD patterns of the Eu doped nanoparticles show a single-phase with cubic zincblende structure with three diffraction peaks corresponding to (111), (220) and (311) diffraction planes of cubic zincblende structure as per the standard card (JCPDS No. 80-0020) [14]. No secondary phase was detected indicating that Eu are incorporated into the ZnS host lattice as substituent atoms. Broad XRD peaks indicate the nanocrystalline nature of the particles. The average crystallite size was obtained from the most prominent XRD peak (111) using Debye Scherrer formula. Because of the surface scattering of nanoparticles. Our estimated average crystallite size is 6.5 nm. However, in our case of 2 mol% Eu3+ doped ZnS nanocrystals, the mixture of single phase is obtained. In this case, the percentage of cubic phase is 59.86%. It reveals that the impurity states in doped semiconducting nanocrystals play a special role in affecting the crystal-field distortion, symmetry breaking. It is expected that Eu3+ ions are incorporated in ZnS because the ionic radius of the Zn ion is very close to Eu3+ ion (0.95 Å). Eu ion occupies a tetrahedral lattice site.

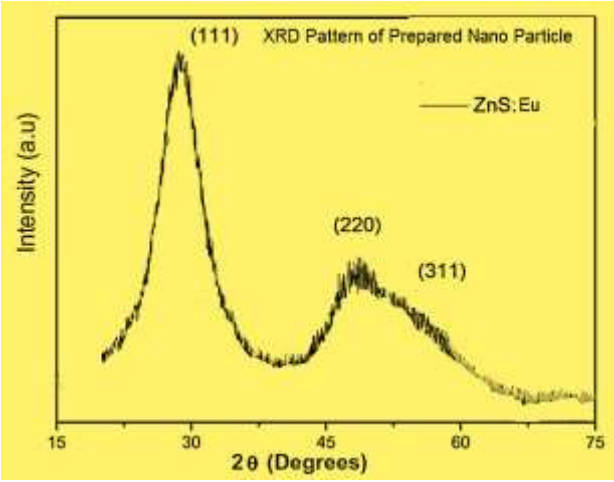

Fig. 1 XRD patterns of 2 mol % concentrations of Eu-doped ZnS nanocrystals.

2. Elemental Analysis

In order to analyze the amount of Eu doped ZnS nanoparticles were examined by EDS. Fig. 2 show typical EDS spectra of ZnS: Eu3+ (2 mol %) nanoparticles, respectively. The above figures confirm the presence of Zn, S, and Eu. No traces of other elements were noticed in the spectra indicating the purity of the samples. The estimated atomic percentages of Zn, S, and Eu were close to the nominal (target) values. The observed deviations in the estimated compositions were small.

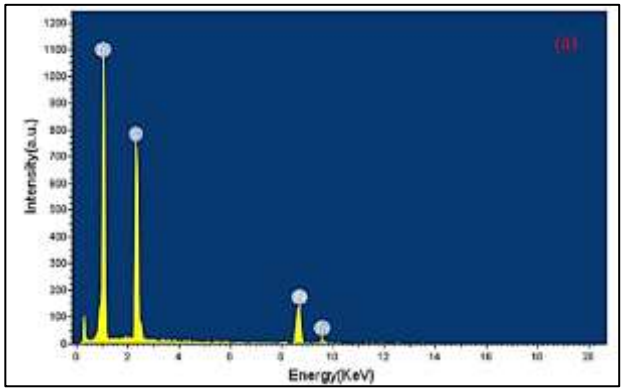

Fig. 2. EDS spectra of ZnS: Eu3+ nanoparticles

3. Scanning Electron Micrographs

Fig. 3 shows the SEM images of Eu3+ doped ZnS samples taken at the same magnification. These micrographs clearly indicate that the samples have nano crystalline nature and grain size varies from 6.5 to 13.5 nm. Average particle size is found 5.5 nm.

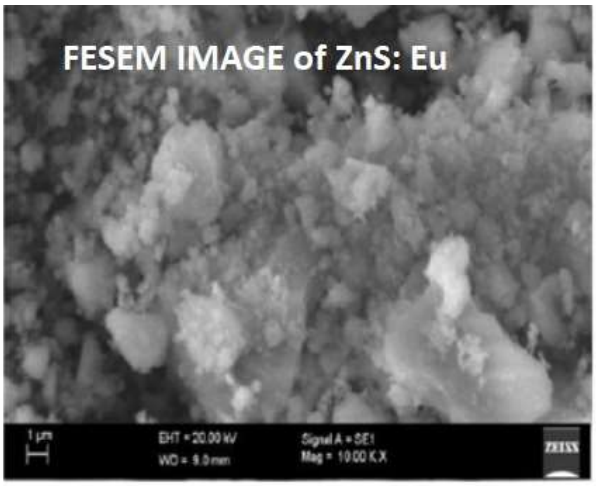

Fig. 3 FESEM Image of 2 mol % concentration of Eu-doped ZnS nanocrystals

4. HRTEM Analysis

Samples for HRTEM were prepared by making a clear dispersion of the nanocrystals in acetone and placing a drop of the solution on a carbon coated copper grid. The solution was allowed to evaporate

leaving behind the nanocrystals on the carbon grid. The size of particle determined from the TEM image is close to the calculated value from XRD. Fig. 4 shows the high-resolution TEM image of 2 mol% Eu-doped ZnS nanocrystals with the corresponding fast Fourier transformation (FFT) pattern and the measured lattice spacing in the HRTEM image is 4.94 Å, which corresponds to (111) plane of the monoclinic phase of Eu3+ ions. The small concentration (2 mol%) of Eu3+ ions would correspond to less than a monolayer on the surface of the ~ 6.5 nm ZnS nanoparticles. Therefore, the observed Europium lattice spacing and XRD peaks may be due to the appearance of isolated Europium nano crystallites.

Fig. 4 HRTEM image of 2 mol% Eu-doped ZnS nanocrystals

IV. PHOTOLUMINESCENCE ANALYSIS

1. Excitation & Emission Spectra

Fig. 5 shows the excitation and emission spectra of 2 mol% Eu-doped into ZnS nanocrystals. The sharp peak at 347 nm is assigned to the excitonic transition of ZnS nanocrystals. After excitation at 347 nm, the strong emission band have peaked at 617 nm (5D0-7F2) and 590 nm (5D0-7F1) are observed for Eu3+ doped ZnS nanocrystals. The emission spectra are attributed to the 5D0-7FJ (J = 0–2) transition of the Eu3+ ions, i.e. the bands of 570–603 and 603–640 nm is related to the transitions of 5D0-7F1 and 5D0-7F2, respectively. It is to be mentioned here that the Eu3+ ion has very negligible absorption excited at 347 nm because the excitation cross section at 347 nm of Eu3+ is very small relative to the ZnS excitation. It is reported that upon excitation of the ZnS host, the energy from non-radiative recombination of electron-hole pairs can be transferred to the high lying energy levels of the Eu ions [16]. Fig. 5 depicts the emission spectra of Eu activated ZnS nanocrystals. At the same experimental conditions, namely, same wavelength excitation with same bandwidth, we have investigated the luminescent intensity of Eu3+ doped nanocrystals. In the case of Eu activated ZnS nanocrystals (doped), the peaks at 617 nm (5D0-7F2) and 590 nm (5D0-7F1) are observed for doped samples after excitation at 347 nm. The most dramatic effect is that the intensities are significantly higher in doped nanoparticles.

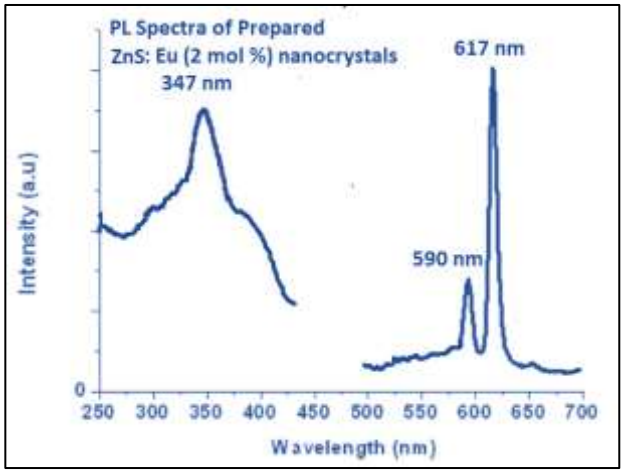

Fig. 5 Excitation and emission spectra of 2 mol% Eu doped ZnS nanocrystals

Effect of Dopant Concentration Ions

From these results, it is clear that Eu3+ ions occupy low symmetry sites in doped samples. Usually, the dopant ions are randomly distributed in the host lattice in doped samples, and as a whole, the local environments of the europium ions become anisotropic between europium ion and its surrounding crystal lattice. The europium ions distributed on the surface in the coated sample then the local environments of the europium ions become an isotropic coordination with higher symmetry and therefore the interaction between europium ion and its surrounding crystal lattice becomes weaker. As the electronic f–f transitions of the rare earth ions are localized in the atomic

orbital of the ions. The electronic structure of the RE ions is dominated by electron–electron and spin–orbit interaction within the 4f shell. The changes of atomic coordination number around Eu3+ and/or the Eu–O bond lengths reduce the Eu3+ local structure symmetries whose degradation enhances the effects of crystal field in the host matrix. As a result of the reduced symmetries, the interaction between the europium ion and its surrounding crystal lattice decreases the population of hypersensitive 5D0 energy level through a nonradiative relaxation process.

2. FTIR Spectral Analysis

FTIR analysis FTIR spectra of ZnS: Eu nanoparticles recorded at room temperature in the wavelength range of 4000–400 cm-1 are shown in Fig. 6. The templates like EDTA-type compounds belong to the class called complex ones, a group of poly aminocarboxylic acids or their salts, which are derivatives of iminodiacetic acid. A characteristic arrangement of these compounds is a nitrogen atom connected with two carboxymethyl groups N(CH2COOH)2. From the point of view of EDTA-type molecular structure, it may be treated as a tertiary amine or acetic acid derivative. The spectral band at 2352 cm-1 in Fig. 6 is associated with the N–H3+ stretching vibration of the amino acid zwitterions. The broad band around 3393 cm-1 is assigned to the O–H stretching vibration because all FTIR spectra are recorded by mixing samples with KBr. Hence there may be some adsorbed water vapor, as KBr is hygroscopic. The spectral transitions at 1583 and 1400 cm-1 are, respectively, related to the antisymmetric and symmetric C=O stretching vibrations of the carboxylate anion associated with EDTA [15]. On the other hand, EDTA shows no vibrational band around 2100 cm-1, suggesting that EDTA in a ZnS matrix does not form a double betaine structure. However, the carboxylate ion groups are still active in the entrapped EDTA in ZnS as evidenced by the observed spectral bands at 1637 and 1401 cm-1. The peaks appearing at 473 and 663 cm-1 are assigned to the Zn–S stretching vibration. The close similarity of the FTIR spectra of doped samples indicates that Eu have entered the ZnS lattice substitutionally.

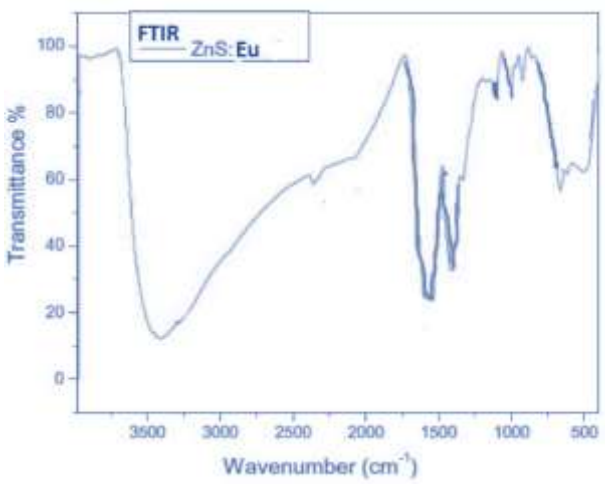

Fig. 6. FTIR spectra of traces on ZnS: Eu nanocrystals.

V. CONCLUSION

In conclusion, we have reported that the structural, morphological, elemental composition, vibrational & Optical properties of the synthesized ZnS: Eu3+ nanocrystals. In XRD patterns have revealed the cubic phase structure. our results highlight the role of doping of ZnS: Eu3+ nanocrystals and their effect on the photophysical properties. It is expected that Eu3+ ions are incorporated in ZnS because the ionic radius of the Zn ion is very close to Eu3+ ion (0.95 Å). Eu3+ ion occupies a tetrahedral lattice site. In FESEM analysis, the average particle size is found 5.5 nm. In HRTEM study, the small concentration (2 mol%) of Eu3+ ions would correspond to less than a monolayer on the surface about ~ 6.5 nm ZnS nanoparticles. In FESEM, Average particle size is found 5.5 nm. In EDS Spectra, the above figures confirm the presence of Zn, S, and Eu. No traces of other elements were noticed in the spectra indicating the purity of the samples. In FTIR spectra, all vibrational bond and various functional groups have obtained. In PL Spectra, after excitation at 347 nm, the strong emission band have peaked at 617 nm (5D0-7F2) and 590 nm (5D0-7F1) are observed for Eu3+ doped ZnS nanocrystals. The dopant ions play a special role in changing their crystal phase by changing the crystal-field distortion, and symmetry breaking. The luminescence intensity increases with increasing the concentration of dopant ions.

Maximum intensity has found at 2 mol % of dopant ions. Again, it can be seen that the emission intensity of the Eu3+-ions is sensitive to the doping of ZnS: Eu3+ nanocrystals.

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REFERENCES

1. G. Cao 2004 Nanostructures and Nanomaterials: Synthesis, Properties& Applications (London: Imperial College Press).
2. H. S. Nalwa (ed) 2000 Handbook of Nanostructured Materials and Nanotechnology (New York: Academic).
3. G. G. Roberts, E. L. Lind, E.A. Davis, J. Phys. Chem. Solids, 30, 833 (1969)
4. J. Sapriel, Appl. Phys. Lett., 19, 533 (1971)
5. T. Hayakawa, S. T. Selvan and M. Nogami, J. Sol-Gel Sci. Technol., 2000, 19, 779.
6. S. C. Erwin, L. Zu, M. I. Haftel, A. L. Efros, T. A. Kennedy and D. J. Norris, Nature, 2005, 43, 91.
7. Kunio Ichino, Yasuharu Morimoto, Hiroshi Kobayashi, Molecular beam epitaxy and structural properties of ZnCrS, Phys. Status Solidi C 3 (2006) 776–779.
8. Ming Luo, N.Y. Garces, N.C. Giles, Utpal N. Roy, Yunlong Cui, Arnold Burger, Optical and electron paramagnetic resonance spectroscopies of diffusion doped Co2+: ZnSe, J. Appl. Phys. 99 (2006) 073115–073709.
9. P. Vinotha Boorana Lakshmi, K. Sakthi Raj, K. Ramachandran, Synthesis and characterization of nano ZnS doped with Mn, Cryst. Res. Technol. 44 (2009) 153–158.
10. S. Sambasivam, D. Paul Joseph, J.G. Lin, C. Venkateswaran, Doping induced magnetism in Co–ZnS nanoparticles, J. Solid State Chem. 182 (2009) 2598–2601.
11. Huiyu Yan, Yuqi Li, Yanrui Guo, Qinggong Song, Yifei Chen, Ferromagnetic properties of Cu-doped ZnS: a density functional theory study, Physica B 406 (2011) 545–547.
12. S. Sambasivam, D. Paul Joseph, D. Raja Reddy, B.K. Reddy, C.K. Jayasankar, Synthesis and characterization of thiophenol passivated Fe-doped ZnS nanoparticles, Mater. Sci. Eng. B 150 (2008) 125–129.
13. JCPDS No. 80-0020
14. J. Ryczkowski, IR studies of EDTA alkaline salts interaction with the surface of inorganic oxides, Appl. Surf. Sci. 252 (2005) 813–822
15. R. Reisfeld, M. Gaft, T. Saridarov, G. Panczer and M. Zelner, Mater. Lett., 2000, 45, 154.