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Room Temperature Ferromagnetism in ZnS: Y Nanoparticles

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ABSTRACT: *Nanoparticles of ZnS: Y (0, 3 and 5%) is synthesized by a chemical co-precipitation method at 300 K using PEG as capping agent. The effect of Y (yttrium) doping on the structural, optical and magnetic properties of ZnS nanoparticles is investigated. The structural study is analyzed by X-ray Diffraction pattern. The calculated crystallite size of pure ZnS is 9.49 nm and Y (3 and 5 %) doped ZnS nanoparticles are 7.77, 9.17 nm. Morphology and size of the nanoparticles are probed by field emission scanning electron microscope, which shows that the shape of the nanoparticles is spherical. An Energy Dispersive X-ray Analysis spectrum confirms that the doped samples consist of ZnS: Y stoichiometric composition. The transmittance spectrum of ZnS and Y doped nanoparticles is performed by UV-diffuse reflectance spectrometer. It shows that whenever increase in doping content, the transmittance of the visible to near infrared increases and short wavelength (UV) decreases. Transmittance spectra validates that the absorption increase at UV region when augments in the Y content. The thermal analysis of Y doped nanoparticles is analyzed by using thermo gravimetric (TG) and differential scanning calorimetry (DSC) method. Magnetization hysteresis measurements are performed at 300 K using vibrating sample magnetrometry (VSM). It reveals that the doped samples are ferromagnetic at room temperature. Thus the present studies illustrate that ZnS: Y nanoparticles might find applications in spintronics devices. This is the first ever magnetic report on ZnS: Y nanoparticles.*
Keywords: *EDAX, FESEM, TG-DSC, Transmittance, VSM*

I. INTRODUCTION

During past few decades nanomaterials have wide variety of applications due to their extremely fascinating and peculiar properties.The size of the material is reduced to reach the nanoscale regime, its conductivity, melting point, boiling point, magnetic and optical properties are drastically different from their bulk counter parts. This drastic change is as a result of the fact that at the nanoscale dimension it obeys quantum mechanics. The significant properties of nanometer dimensions are such as large fraction of surface atoms, high surface energy spatial confinement and reduced imperfections, unlike in the case of bulk materials. Nowadays the preparation and characterization of the II-IV semiconductor is revealed in reduced dimensions and provide the possibilities of fabricating novel materials. Owing to wide range of optical and electrical as well as semiconducting properties, ZnS is a pervasive semiconductor that has been studied widely as an important phosphor for optoelectronic and energy applications.It has better chemical stability compared to other Chalcogenide [1]. The doped semiconductor crystal not only improves the optical properties, it may also lead to desirable material properties for spintronic applications [2]. Spintronic device is a new class of research has stimulated by the room temperature ferromagnetism. Ferromagnetism is very important in industry and modern technology, and is the basis for many electrical and electromechanical devices such as electromagnets, electricmotors, generators, transformers, and magnetic storage devices.Doping of ZnS nanoparticles by transition metal or rare-earth ions may result in diluted magnetic semiconductors (DMS). Most of the reported ferromagnetism in ZnS nanoparticles is doped by transition metal [3-7]. Nowadays ferromagnetic property of rare earth doped ZnS wide band gap semiconductor has been attracted enormously.Howevera very few studies on Nd, Eu^{3+} and Gd -doped ZnS nanoparticles [2, 8-9] have been studied. The synthesis of the rare-earth doped ZnS has been usually hindered by their trivalency with larger radii. The origin of the ferromagnetic order in doped ZnS may due to local magnetic moment of dopant, which are distributed randomly and couple with one another by exchange interaction [2]. Doped ZnS nanoparticles can be successfully synthesized by techniques such as sol-gel processing, micro-emulsion, pulse laser ablation in liquids and co-precipitation method. Consequently, it is significant to find a simple preparation method as the chemical coprecipitation; it does not demand any costly apparatus building, process simplicity, effectiveness of doping, low impurity and higher yield. These are used for air pollution control, illuminated screens on electronic devices, and the polishing of optical-quality glass. The Y ion is a paramagnetic material. The addition of a small amount of these ions influences the magnetic parameters and this is due tochanges of magneto-crystalline anisotropy through rare earth- ZnS interaction.Hence magnetic Y^{3+} ions are introduced into nanoparticles of non-magnetic gives rise to ferromagnetism.ZnS semiconductor, then interesting magnetic properties is imminent.Inspite of this, there are no reports on systematic studies on Y-doped ZnS nanoparticles. This has inspired to synthesize Y doped ZnS nanoparticles and investigate their structural, optical, magnetic and thermal properties.

II. EXPERIMENTAL DETAILS

All synthesized nanoparticles were carried out in distilled water for its inherent advantages of being simple and environment -friendly. The main advantage of rare-earth doped nanoparticles synthesized in water is their easy functionalization compared to quantum dots [10].$Zn_{1-x}Y_xS$ (x = 0, 0.03, and 0.05) nanoparticles were prepared by coprecipitation method at ambient temperature. Zinc sulphide reaction mechanism has been already reported in our previous paper [11] .Yttrium doped ZnS nanoparticles were synthesized by using Yttrium (III) acetate, hydrates an additional precursor to the above stock solution. The powder was sintered at 400°C for 2 hours under air atmosphere.

The thermal analysis was executed by Thermogravimetry-Differential Scanning Calorimetry (NETZSCH STA 449F3). The structural analysis of the synthesizedsamples was studiedby recording the XRD spectrum using Diffractometer system = XPERT-PRO in the range of 10^0 to 80^0 with step size of 0.02^0 using Cu-Kα radiation. The transmittance spectra of prepared samples were carried out at room temperature by using (Perkin Elmer-Lambda 35)diffuse reflectance Spectro photometer in the wavelength range of 200 nm-1100 nm. The morphology andelemental composition of the nanoparticles were probed using FESEM; JSM.6701*F, Japan. The magnetic hysteresis (M-H) loops were measured using vibrating sample magnetometer (Lakeshore-7400).

III. Results and discussion

3.1Thermal studies

Fig.1 represents the combined plots of TG and DSC at a heating rate of $10^{\circ}C\ min^{-1}$ under nitrogen atmosphere from 30 to 1200°C.The thermogravimetry (TG) and differential scanning calorimetry (DSC) are used to study the thermal decomposition and crystallization behavior of the 5% Y-doped ZnS nanoparticles. From the TG data, it is noticed that the weight loss of the nanoparticles are found to take place up to 1200°C. Curve (a) demonstrates TG curves of ZnS: Y nanoparticles. There are two obvious weight loss regions up to 1200°C. The first stage of weight loss 2.8%can be seen up to 459°C, which represents the evaporation and degradation of sulphuric acid group [12]. Further mass loss has been observed up to 1200°C, which inferred that ZnS is oxidized to ZnO [13]. It can be concluded that Y-doped ZnS nanoparticles possess good thermal stability.Curve (b) shows that the DSC analysis of 5% Y -doped ZnS nanoparticle.Two peaks are noted in the DSC curve. The endothermic peak around 204°C probably corresponds to the dehydration, evaporation of organic and lattice deformation of ZnS: Y.The composition does not vary in the annealing range from 100°C to 200°C, whereas, beyond 204° C, the doped ions are released from the ZnS matrix [14]. Secondly, exothermic peak is observed at 615° C is believed to be the beginning of phase transition. Additionally, above 700 to 884°C, thereis a smooth downward trend in DSC curve with significant weight loss. This may be due to release of residual sulfur ions from the sample [15]. Endothermic peak is usually harmless, whereas exothermic decomposition might damage or destroy the texture and structure of a sample. As the temperature further increases from 900 to 1200°C the sample eventually suffer from oxidation. The reported Y-doped ZnS nanoparticles [14] has the first endothermic peak around 60°C but in our report both endothermic and exothermic peak is high which confirms that the prepared sample has high thermal stability and decomposition temperature.

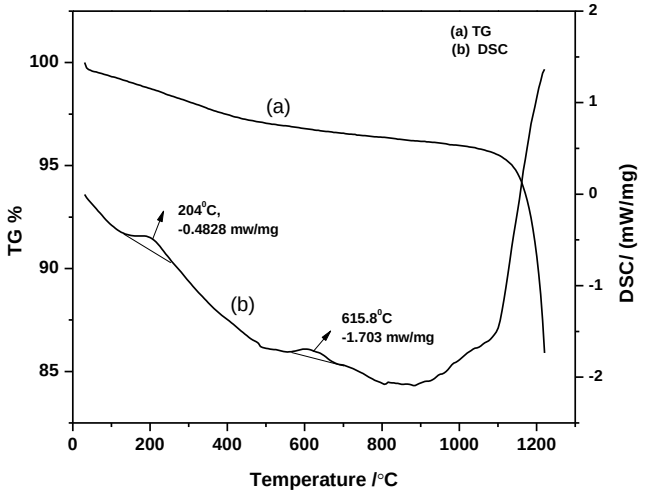

Fig.1.TG and DSC curves of ZnS: Y (5 %) nanoparticles

3.2 Structural Analysis

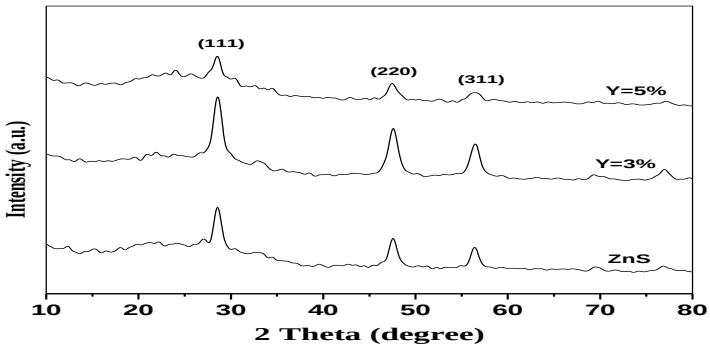

Fig. 2 XRD pattern of ZnS and ZnYS

Fig. 2 illustrates the XRD pattern of ZnS and Yttrium doped ZnS nanocrystals from which the crystalline forms of the same were determined. All the samples exhibit three distinct peaks $2\theta = 28.5^0$, 47.8^0 and 56.5^0 which represent the indices of (111), (220) and (311) planes of cubic structure as per PCPDS file no (JCPDS No.65-5476). Furthermore, it is noted that the doped nanoparticles exhibit typical structure of ZnS crystal which indicates the high purity of the synthesized sample. The reason could be due to the fact that the Y^{3+} ions moved into either the interstitial positions or the substitutional sites of the ZnS crystal structure. The obvious decrease of (111) diffraction peak intensity for 5% Y-doped sample shows the restrain of the crystallization compared to lower doping concentration. The crystallite size can be calculated by Scherrer's equation. The crystallite size for ZnS is 9.49 nm and doped ZnS are found to vary in the range of 7.77 and 9.17 nm with increasing trend as the amount of Y^{3+} value increases.

3.3 Morphology and compositional analysis

The typical FESEM image of 5% Y-doped ZnS nanoparticles is shown in Fig.3 (a). It can be seen that the surface of the sample is found to be spherical in shape and some of the particles have agglomerated. The average diameter of sample is found to be 31 nm. The diameter of nanoparticles is given by the histogrampresented in Fig.3 (b). Fig. 4 represents an Energy Dispersive X-ray Analysis spectrum acquired from the 5% Y-doped ZnS which confirms that the particles consist of Zn, S and Y. The substitution of Y into ZnS cubic structure is successfully synthesized. Furthermore, there are some other small peaks which display that the synthesized sample contains small amount of impurities. The result of composition analysis is indexed in the Fig.4which reveals theweight percentage of 5% doped ZnS nanoparticles.

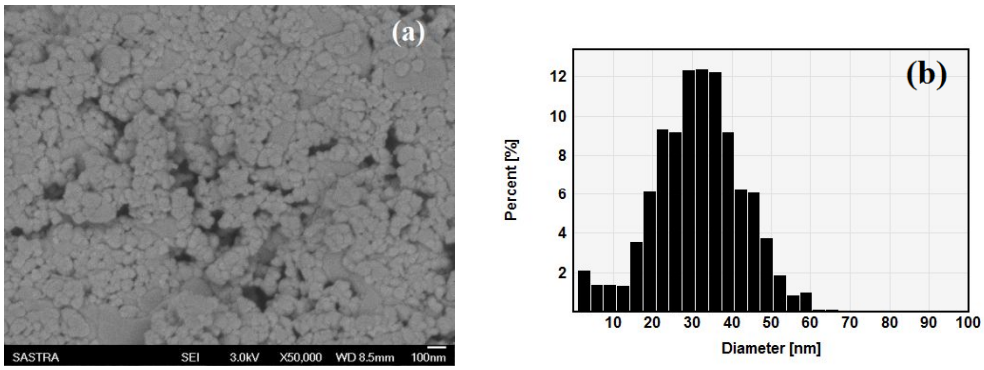

Fig. 3 (a) FESEM image (b) histogram of 5 % Y doped ZnS

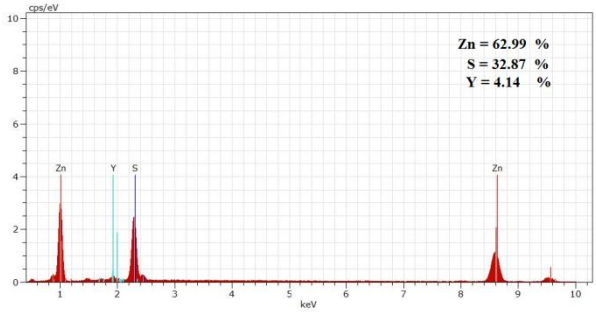

Fig.4 EDAX spectrumof ZnS: Y (5%)

3.4 Optical properties

The transmittance and absorption spectra of nanoparticles in the near-infrared (IR) and near-ultraviolet (UV) regions is the most important optical characteristics of nanoparticles. Fig. 4 shows that the transmittance spectra in the UV-Visible region of the undoped and Y -doped ZnS nanoparticles. Transmittance in the visible region is higher for 5% Y dopant. Rayleigh scattering is strongly pronounced when particle size is much smaller than one-tenth of the incident light wavelength, and the scattering intensity is inversely proportional to the fourth power of the wavelength. The crystallite size of nanoparticles was 7-9 nm, which was much smaller than one-tenth of the wavelength of the shorter UV region (200-250 nm).Therefore, the transmittance in this region rapidly decreased with decreasing wavelength due to the Rayleigh scattering effect [16]. It can be seen that the wavelength at the range of 300–850 nm under consideration, the maximum transmittance for Y= 0, 3 and 5% is 78, 85 and 91% and corresponds to λ = 835,829 and 833 nm. From Fig. 5 the transmittance spectrum of ZnS involves a relatively deep dip corresponding to the absorption band in the range 278-407 nm, with the minimum transmittances T = 13 % (λ =330 nm). 3 and 5% Y-doped ZnS involves the absorption band in the range 302-395 nm, with the minimum transmittances T = 12.7% (λ=332) and 10.5 % (λ=335) respectively. The long wavelength part of the transmittance band is flatter and smoother than the short-wavelength part [17]. Thus, the yttrium doped ZnS nanoparticles more suitable for the transparent coating material of a UV shield [16].

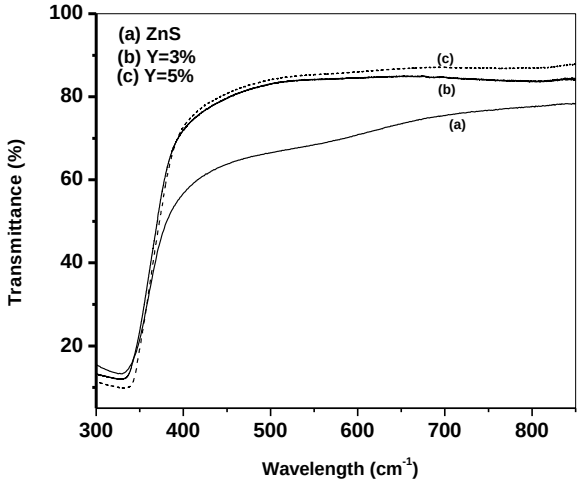

Fig. 5 Transmittance spectra of ZnS: Y

3.5Magnetic studies

The room temperature (300 K) M–H curves for the Y -doped ZnS nanoparticles are shown in Fig. 6 (a) and (b).The magnetization as a function of the external field is described by a hysteresis curve. As shown in Figure 6(a)and (b), results of magnetic characterization show obvious ferromagnetic behavior for both compositions. Besides, the increase of saturation magnetization is observed from 275.93 to 295.6x10^{-6} emu/g for 3 and 5% ZnS: Y nanoparticles. 3% Y-doped ZnS nanoparticles exhibits the soft ferromagnetic nature.

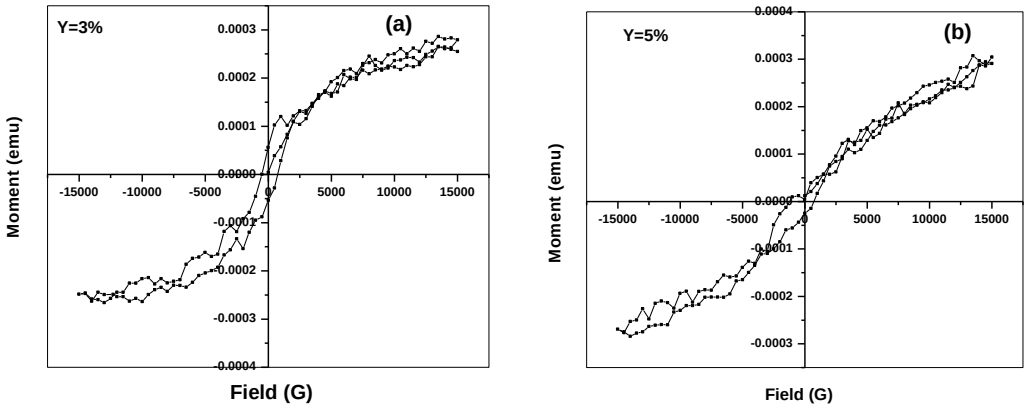

Fig.6 M-H curves of Y-doped ZnS nanoparticles

It is speculated that the ferromagnetism in the Y-doped ZnS samples may be a result of the intrinsic coupling between intermediate '4d' spins on the Y ions and the free delocalized (valence s and p electrons) carries. The incorporation of Y^{3+} ion in the ZnS host lattice as a substituent is prompting to the ferromagnetism, since it is confirmed by the presence of Y atoms in the EDAX spectra. Fig.6 (b) reveals that when doping concentration is augments, ferromagnetic nature of Y-doped sample is also increases. Moreover; M-H curve of 5% Y-doped ZnS depicts the hard ferromagnetic nature due to the antiferromagnetic property of yttrium. It validates that the yttrium substitution for zinc in the ZnS lattice is in Y^{3+} state. Here the observed ferromagnetism is mainly due to the Y ions substituted into the ZnS host lattice, which is not due to the Y related metal clusters are not noticed in XRD studies.Theweakening of ferromagnetism with increasing the rare dopant for instance (Nd and Gd) with ZnS nanoparticle has been observed [8, 9]. However in our studies increase in dopant, ferromagnetism is increased which may due to the Y^{3+} surface enrichment hinders crystallite growth and it enhances the vacancy creation [18].The enhancement of ferromagnetism for the ZnO: Y nanoparticles originate from the increase of defects including oxygen vacancies and interstitials have been reported [19].It is concluded that the Y-doped ZnS nanoparticles exhibit some unusual properties related to its unique structure and ferromagnetic behavior at room temperature. The results show that sintered Y-doped ZnS nanoparticles are ferromagnetic, while as-synthesized ZnS NPs are diamagneticwhich has been reported our previous paper [11]. There is no magnetic report on Y doped ZnS of any form for comparison. This is the first ever report on magnetic studies of Y doped ZnS nanoparticles.

IV. CONCLUSION

Y-doped ZnS nanoparticles are synthesized successfully through chemical co-precipitation method. Structural analysis indicates that the Y -doped ZnS nanoparticles crystallize in a cubic structure without forming other secondary phases. The average diameter of the particle size and spherical shape of the nanoparticles were probed by FE-SEM image. The transmittance spectra reveal the incorporation of Y^{3+}into the ZnS nanoparticles. Transmittance spectra validates that the absorption increase at UV region when augments in the Y content which issuitable for the transparent coating material of a UV shield. The thermal analysis of Y doped nanoparticles confirms the prepared sample has high thermal stability and decomposition temperature. Magnetization hysteresis measurements reveal that the doped samples are ferromagnetic at room temperature. Thus the present studies illustrate that ZnS: Y nanoparticles might find applications in spintronics devices.

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