



Achieving room temperature ferromagnetism in ZnS nanoparticles via Eu^{3+} doping



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ABSTRACT

This paper reports the structural as well as the magnetic properties of ZnS:Eu³⁺ (0, 1, 2, 3, and 4 at%) nanoparticles prepared by a hydrothermal method. The compositional, structural and magnetic properties of ZnS:Eu³⁺ nanoparticles were investigated by energy dispersive X-ray spectroscopy, X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and vibrating sample magnetometry (VSM) measurements. XRD studies confirmed that all the samples had a cubic structure with good crystallinity. TEM showed that the particles were polycrystalline with a mean size of 5–8 nm. XPS revealed the oxidation state of the Eu in the ZnS lattice to be +3. All the Eu³⁺-doped ZnS nanoparticles exhibited room temperature ferromagnetic behavior as a function of doping concentration. The observed RTFM may be interpreted by the contribution of the magnetic moments from the unpaired 4f electrons of Eu³⁺ in the ZnS:Eu³⁺ nanoparticles. The interesting magnetic properties of ZnS:Eu³⁺ nanoparticles may be further explored for new generation spintronic devices.

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1. Introduction

Diluted magnetic semiconductor nanostructures (DMSs) have been the topic of recent years due to their feasibility of accommodating both charge and the spin degree of freedom and are obtained by doping magnetic impurities such as transition metals or rare earth ions into the non-magnetic semiconductor host. The notion of simultaneously employing both spin and charge in a solitary semiconductor medium leads to the exciting field of spin based electronic devices, i.e., spintronics [1,2]. Recently, ZnS based diluted magnetic semiconductor nanostructures have been the focus of myriad research investigations owing their promising applications in spintronic as well as photonic devices. Basically, the 3d electrons in 3d transition metals (TM) are exterior and delocalized, resulting in strong direct exchange interactions but possess less total magnetic moment per atom. Although, rare earth metals, the 4f electrons, are localized and the exchange interactions are indirect through 5d or 6s conduction electrons, which lead in high total magnetic moment per atom due to its high orbital momentum. A huge number of transition metal (TM) doped ZnS nanostructures exhibiting room temperature ferromagnetism have been reported by various research groups [3–6]. However, only two room temperature ferromagnetic reports are available on

rare earth ions (Nd and Dy) doped ZnS nanoparticles [7,8]. Among the various rare earth ions, Eu³⁺ is one of the best magnetic ion owing to its high magnetic momentum per atom. Recently, many researchers reported the room temperature ferromagnetism in Eu doped ZnO by various synthesized techniques [9–11]. Surprisingly, there are no experimental results on magnetic studies of ZnS:Eu nanostructures, nevertheless the above cited result denotes the prospect of room temperature ferromagnetism in zinc sulfide, which is alike to zinc oxide. It is well known that a relatively affordable and simple preparation route is essential in engineering applications of nanoparticles. In the present study, ZnS:Eu³⁺ (0, 1, 2, 3, and 4 at%) NPs were synthesized by a hydrothermal method and their chemical, structural magnetic properties were studied. This technique is beneficial for producing good quality nanoparticles due to its simplicity and low cost.

2. Experimental

ZnS:Eu³⁺ (0, 1, 2, 3, and 4 at%) nanoparticles were synthesized by a hydrothermal method. All starting chemicals, including zinc acetate dehydrate $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, europium nitrate pentahydrate $\text{Eu}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, and sodium sulfide (Na_2S), were analytical research (AR) grade purity. The synthesized process was as follows, 0.2 M of zinc acetate as well as pertinent amount of europium nitrate was dissolved in 40 ml of deionized water and stirred for 30 min. After that, 0.1 M of sodium sulfide solution was

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added to the above solution. The eventual mixture was transferred into a teflon autoclave of 100 ml volume and was maintained at 100 °C for 20 h. The as-formed nanoparticles were filtered and washed many times with deionized water and then dried at 100 °C for 12 h.

Chemical analysis was carried out using an EDAX attached to Scanning electron microscope (CARL ZEISS EVO MA15). Crystal structure of the prepared nanoparticles was determined by X-ray diffraction equipped with Cu-K α radiation ($\lambda=1.540$ Å) and the system was operated at 40 KV and 30 mA. An X-ray Photo electron Spectroscopic measurements were performed using Thermo (UK) Fisher Scientific Theta probe AR-XPS system. The particle size confirmation was done by Transmission Electron Microscope (Tecnai-12, FEI). Magnetic properties (M-H) of the nanoparticles were studied through vibrating sample magnetometer (Lakeshore 7410).

3. Results and discussion

Fig. 1(a) shows the energy dispersive X-ray analysis spectrum of ZnS:Eu (3 at%) nanoparticles. The EDAX spectrum of this sample exhibits the Zn, S and Eu signals and the atomic ratio is found to be 47.46, 49.42 and 3.12, respectively, which is close to the targeted stoichiometry. Moreover, no traces of other elements were

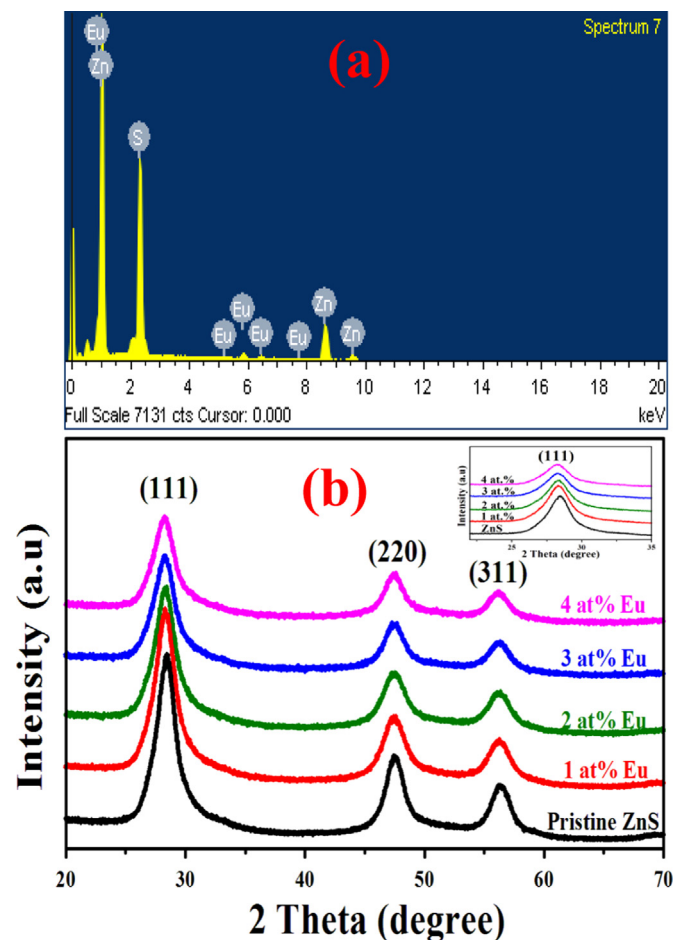


Fig. 1. (a) EDAX spectrum of ZnS:Eu³⁺ (3 at%) and (b) XRD patterns of ZnS:Eu³⁺ (0, 1, 2, 3, and 4 at%) nanoparticles and (inset) the magnified regeion of (111) peak of all the samples.

observed, indicating that the purity of the prepared nanoparticles. The X-ray diffraction patterns of ZnS:Eu³⁺ (0, 1, 2, 3, and 4 at%) nanoparticles are shown in Fig. 1(b). The main diffraction peaks are readily indexed to cubic type ZnS (JCPDS: 50-0005) for all the nanoparticles. No diffraction peaks from some other chemical species such as europium sulfides or sulfide oxides are noticed within the detection limit of the XRD. It is obvious that the prominent peak position of all the Eu doped nanoparticles slightly shifts to lower angles when compared to those of pristine ZnS with increasing dopant concentration (Fig. 1(b) inset shows that the magnified regeion of (111) peak) and which is due to the ionic radius of Eu³⁺ (0.094 nm) was much bigger than that of Zn²⁺ (0.074 nm). The above results indicating that the successful incorporation of Eu³⁺ ions in the ZnS matrix and occupy the Zn²⁺ sites. In addition, it is observed that the replacement of Zn²⁺ ions by Eu³⁺ ions decreases the intensity of the XRD peaks, which insinuate that the degree of crystallinity of the nanoparticles decreases. The average size of the nanoparticles is calculated to be around 4–8 nm, using Debye-Scherrer's formula.

The morphologies and particle sizes of as prepared nanoparticles were investigated by transmission electron microscopy (TEM). Fig. 2(a)–(c) shows the TEM micrographs of ZnS:Eu³⁺ (0, 2 and 4 at%) nanoparticles. From TEM, it is observed that all the nanoparticles are slightly agglomerated and the agglomeration increases with increasing Eu³⁺ concentration. This is the most routine hurdle in nanoparticles. Nanoparticles have a higher relative surface area and higher relative number of surface atoms and these atoms have unsaturated coordinations and each atom have vacant coordinate sites. They strive to make bonds and such bonds tend to form between adjacent particles, this causes the agglomeration in nanoparticles. The estimated average size of the synthesized nanoparticles lies in the range of 5–8 nm. No other diffraction rings were observed in the SAED (Fig. 2(d)) patterns confirming that cubic ZnS is the main phase, which is in good agreement with the XRD results.

To further investigate the chemical composition and the bonding state, we performed the X-ray photo electron spectroscopy. Fig. 3 (a) depicts the XPS survey scan of the ZnS:Eu (4 at%) nanoparticles. The peaks due to zinc are located at 1022.28 and 1045.66 eV corresponds to the binding energies of the core levels 2p_{3/2} and 2p_{1/2}, respectively. The binding energy difference was found to be 23.38 eV, confirming that the valence state of the Zn is +2 [4,5]. The binding energy of the sulfur 2p peak was 162.05 eV. The two characteristic peaks at 1135.20 and 1165.44 eV are attributed to the core levels of Eu 3d_{3/2} and 3d_{5/2}, respectively, which indicates that the Eu ions are trivalent [12]. Hence, it is strongly demonstrated that we have incorporated the Eu³⁺ ions and dispersed them in the ZnS host lattice. In addition, no other impurity phases were observed in the ZnS:Eu³⁺ nanoparticles. Fig. 3(b) shows the RT M–H curves of ZnS:Eu³⁺ (0, 1, 2, 3, and 4 at%) nanoparticles. The pristine ZnS shows the expected diamagnetic feature, which is an intrinsic nature of ZnS (not shown in figure). All the Eu³⁺-doped ZnS nanoparticles displayed the weak ferromagnetism. Although, the ferromagnetic behavior of the doped samples increases with increasing Eu³⁺ doping concentration. The 4 at% Eu³⁺-doped ZnS showed the clear hysteresis loop as well as highest magnetization (Ms) value of all the samples prepared.

The observed ferromagnetism in these samples could be attributed to three possibilities, such as EuS, Eu metal cluster and intrinsic nature of the Eu³⁺-doped ZnS nanoparticles. The existence of a secondary phase could be ruled out, since EuS is paramagnetic at 300 K, metallic Eu is helimagnetic Θ_N with a about 92 K. Moreover, no impurity phases were founded in

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