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Crystallographic, Morphological and Optical Properties of $Zn_{1-x}Co_xS$ Nanocrystals

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Cobalt doped zinc sulphide nanocrystals were prepared by co-precipitation route at room temperature. The structural, morphological and optical properties of prepared samples were characterized by X-ray diffraction, scanning electron microscopy, transmission electron microscopy and UV-visible spectroscopy. From XRD patterns, $Zn_{1-x}Co_xS$ samples have cubic crystal structure with single in phase. The lattice constant and volume of unit cell were increased with increasing cobalt doping. The crystallite size of prepared samples was in the range of 4-7 nm. The surface morphology of prepared samples was characterized by using transmission electron microscopy. The pure and cobalt doped ZnS samples have spherical like structure. The dislocation density and strain was decreased with increasing cobalt doping. The energy band gap of pure ZnS sample was higher as compared to the cobalt doping, indicated cobalt substitution in ZnS host matrix. Based on this study, the prepared samples have useful in opto-electronics devices and solar cell.

Keywords: Nanocrystals, ZnS, Dislocation density, Strain, Optical study.

INTRODUCTION

Nanomaterials are in wide expansion worldwide due to its unique functional properties. A great effect has been made to the design and controls the development of nanocrystals such as ZnS [1,2].

Zinc sulphide is an efficient luminescent material that belongs to the II-IV semi-conducting material with wide band gap energy of 3.7 eV and a large exciton binding energy (40 meV) [3,4]. Zinc sulphide has versatile potential applications electro luminescent device, optical coatings, photoconductor, field effect transistor, optical sensors, photovoltaic cells and LEDs due to its excellent properties [5-9]. This is also a most promising material in biological application [10]. Interesting, the properties of ZnS has been change due to the doping of transition metals such as Ni, Fe, Mn, Cr, Co and Cu [11-17]. Among them, the doping of Co into ZnS matrix become wide versatile owing their solubility in the ZnS lattice.

Here, we are reporting the role of cobalt doping to study structural, morphological and optical properties of ZnS particles doped with Co^{2+}. Transition metal ions doped ZnS nanocrystals can be obtained in many ways such as spray-based method, γ-irradiation method, chemical precipitation method, polymerization and sol-gel method [18-22]. The co-precipitation method for the synthesis of ZnS as this method is simple, low-cost and availability of the equipments. Crystal phase and average crystallite size were measured using XRD. Scanning electron microscopy is used to study the particle size and morphology. Optical energy band gap of Co doped ZnS nanocrystals were study using UV-visible absorption spectroscopy.

EXPERIMENTAL

$Zn_{1-x}Co_xS$ samples for concentration x = 0.00, 0.05 and 0.10 are prepared by co-precipitation route. Appropriate amount of analytical grade of zinc acetate dihydrate and sodium sulfide dissolved in separate beaker of distilled water and under vigorous stirring for 2 h to obtain homogeneous and clear solution. Sodium sulphide was added drop by drop to obtain precipitate (pH 13.5). A white precipitate was obtained which was separated by centrifugation. The precipitate which is separated is washed several times with distilled water and ethanol then dried under vacuum at 60 ºC to get the powder samples of ZnS nanocrystals. For the synthesis of Co doped ZnS nanocrystals were prepared at room temperature by mixing calculated amounts of zinc acetate solution and cobalt acetate solution followed by drop wise addition of saturated solution of sodium sulfide up to pH 13.5. The mixture was vigorously stirred for 2 h. The precipitate was filtered from the reaction mixture and washed several times with ethanol to remove all sodium particles. The wet precipitate was then dried. Similarly prepared for samples of 5 %, 10 % Co doped ZnS samples.

Structural characterization of prepared samples was measurement using X-ray diffraction (Model: PW-3710). The structural analysis of the synthesized samples was carried out

using a powder X-ray diffractometer (XPERT-PRO) with a Cu-K_α radiation source of wavelength 1.5406 Å. The surface morphology and particle size of prepared samples were characterized using by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The optical properties of pure and Co doped ZnS samples were study using by ultra-visible spectroscopy.

RESULTS AND DISCUSSION

Powder diffraction study: X-ray diffraction patterns of pure and Co doped ZnS nanocrystals were shown in Fig. 1. From figure, it was confirmed that all the prepared samples have cubic crystal structure without any extra impurities. In addition, broad peaks of pure and co doped ZnS nanocrystals in X-ray diffraction indicates that all samples have nanocyralline structure. The lattice constant of samples was calculated using XRD patterns.

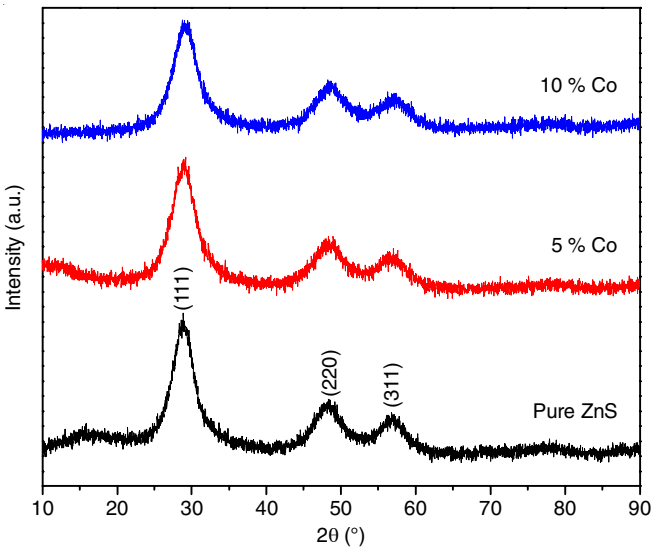

Fig. 1. X-ray diffraction patterns pure Co doped ZnS nanocrystals

The lattice constant of pure ZnS nanocrystals is 5.3387 Å. The lattice constant of of the samples decreased with increasing Co doping. It may attribute due to the small ionic radius of Co^{2+} as compared to the Zn^{2+}. Similar result obtained by reported literature [23]. Further, volume of unit cell was also increased with increasing Co doping in ZnS host matrix. The lattice constant and volume of unit cell are tabulated in Table-1. Based on this study, the Co substituting in ZnS host crystal structure.

The crystallite size was calculated using Scherer's formula and found to be in the range of 4-7 nm. Although, increasing the cobalt doping average crystallite size increased. The strain of pure ZnS nanocrystals small as compared to the Co doped ZnS nanocrystals. The crystallite size was increased but strain decreased with increasing Co doping as depicted in Table-1. The dislocation density was decreased with increasing Co doping. It may be due to the decreasing crystallite size. The crystallite size, dislocation density and strain of prepared samples are depicted in Table-1. From Table-1, it is clear that micro-strain changing with increasing cobalt doping.

Morphological study: The particle size and surface morphology of cobalt doped ZnS nanocrystals was also studied using transmission electron microscopy. TEM images of ZnS samples show the nanocrystalline nature (Fig. 2a). TEM image shows that particles are nearly in spherical shape with average particle size of 3-6 nm for the pure ZnS sample. This value is consistent with the XRD result of pure ZnS sample. TEM image of 5 % Co doped ZnS (Fig. 2b) and TEM image of 10 % Co doped ZnS as shown in Fig. 2c.

Optical study: Fig. 3a shows the absorption spectra of pure as well as that the Co doped ZnS nanocrystals. The absorption edge of the Co doped ZnS nanocrystals is observed at about 330-340 nm. From absorption spectra, the absorption edge of the spectra clearly increased with increasing cobalt doping. It means that the absorption edge is associated with decreasing in the band gap.

TABLE-1
LATTICE CONSTANT, VOLUME, CRYSTALLITE SIZE, DISLOCATION DENSITY AND STRAIN OF PURE AND Co DOPED ZnS NANOCRYSTALS

Samples	Lattice constant (Å)	Volume $(Å)^3$	Crystallite size (nm)	Dislocation density × 10^{16} line/m	Strain
Pure ZnS	5.3387	152.161	4.5058	4.93	0.0449
5 % Co	5.3176	150.366	6.3078	2.51	0.0325
10 % Co	5.3092	149.658	6.4547	2.71	0.0373

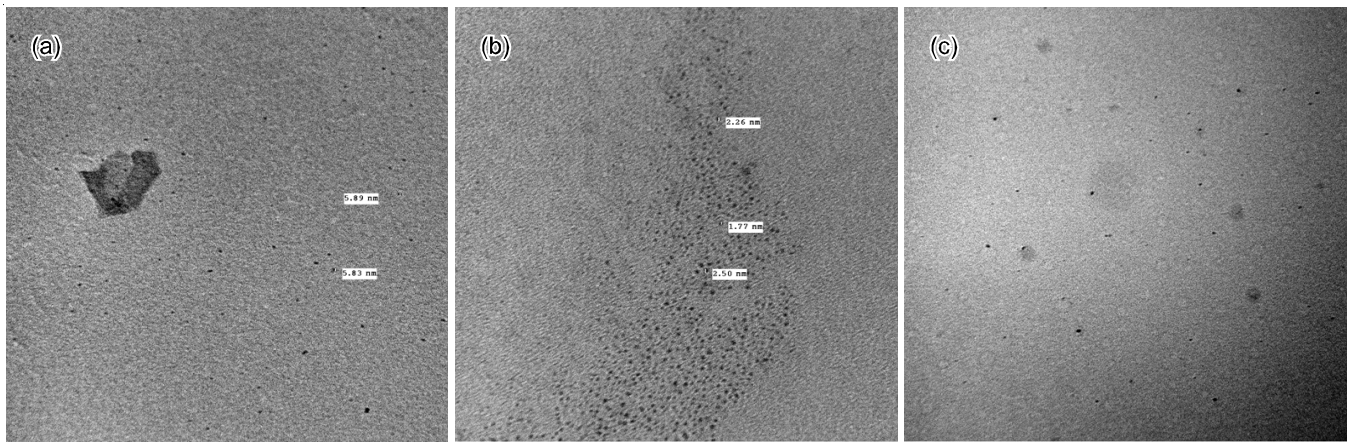

Fig. 2a. TEM images of pure ZnS nanocrystals (a), (b) 5 % Co doped ZnS nanocrystals, (c) 10 % Co doped ZnS nanocrystals

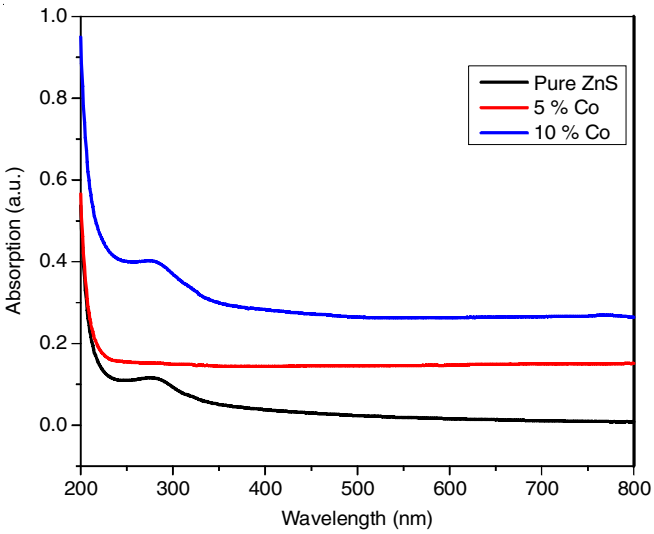

Fig. 3a. Absorption spectra of pure and Co doped ZnS nanocrystals

In the Fig. 3(b), the value of energy band gap E_g were determined by extrapolating straight line portion of $(\alpha h\nu)^2$ against hν graph. The calculated value of direct band gap for pure, 5 % and 10 % Co doped ZnS nanocrystals were 5.771, 5.994 and 6.029 eV respectively. Similar result was obtained by Patel *et al*. [24].

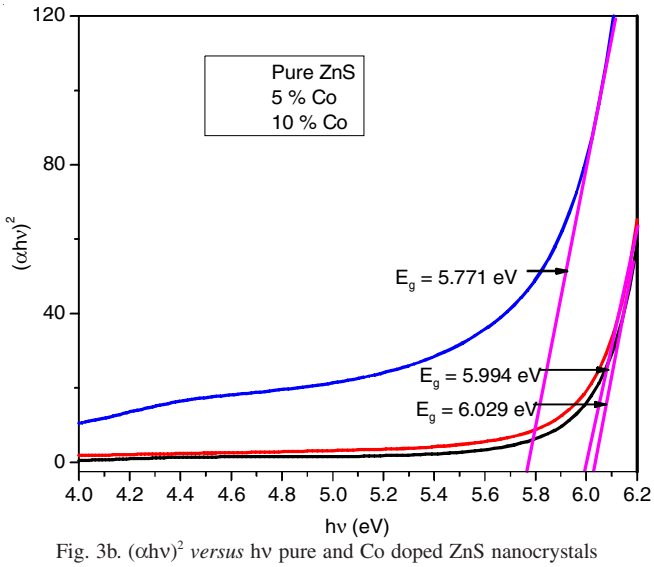

Fig. 3b. $(\alpha h\nu)^2$ *versus* hν pure and Co doped ZnS nanocrystals

Conclusion

Various concentrations (0, 5 and 10) of Co doped ZnS nanocrystals were successfully synthesized using by co-precipitation technique. Synthesized samples possess cubic structure which is revealed by XRD analysis. XRD patterns showed that the samples were $Zn_{1-x}Co_xS$ and there are no other impurities present in it. TEM images showed nanocrystalline nature of all samples. Blue shift was observed when Co is doped into the ZnS nanocrystals.

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