Effect of Indium Incorporation on The Physical Behavior of ZnS Nanoparticles

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Abstract: In–doped ZnS nanoparticles are synthesized via chemical co-precipitation method using different precursor solutions of zinc acetate (source of Zn\textsuperscript{2+} ions), sodium sulphide (source of S\textsuperscript{2−} ions), indium sulphate (source of dopant In\textsuperscript{3+} ions), ammonium hydroxide (works as a complexing agent) and EDTA (as a capping agent). The effect of different concentrations of Indium (0%, 1%, 3%, and 5%) on the structure, morphology, and elemental composition properties of nanoparticles have been studied using different characterization techniques. XRD study shows the formation of cubic structure in the synthesized nanoparticles. The average size of nanoparticles calculated using Debye - Scherrer’s equation is in the range of 5.7–2.4 nm. It has been observed that the size of ZnS nanoparticles decrease with an increase in Indium concentration. SEM micrographs have explored the surface feature of the nanoparticles. It clearly shown that the morphology of spherical nanoparticles is changing with In concentration. The elemental identification and mapping has indicated the homogeneous distribution of Zinc, Sulfur and Indium content in synthesized nanoparticles. FT–IR spectra have recognized the existence of characteristics absorption peaks for In-doped ZnS.

Keywords: In–doped ZnS, co-precipitation method, structural analysis, FT–IR analysis,

I. INTRODUCTION

Inorganic semiconducting nanoparticles have attracted much interest of the research community worldwide because of their emerging properties and application in different technological fields. Primarily nanoparticles formed by solution based chemical processes have enticed great attention due to proficiency of controlling their size and shape which leads to dynamic changes in their properties [1]. The unique properties of these nanoparticles differ considerably from their bulk forms due to their large surface-to-volume effect [2]. Surface atoms play a dominant role when the size of these particles approaches nano-regime. Hence, creating additional electronic states in the band gap and enhancing the physical and chemical properties of nanoparticles [3]. Due to these characteristics, semiconductor nanoparticles have wide range of applications in electroluminescent devices, solar energy conversion, projection television, fluorescence microscopy, IR detectors, photovoltaic devices, gas sensors, surface acoustic devices, medical and biological labeling and diagnostics [4–6]. Therefore, to study new materials in nano-scale range for the development of futuristic devices is required.

Semiconductors belongs to II–VI group of periodic table like ZnS, ZnSe, CdS, CdSe, ZnO etc., have been very popular due to their wide-ranging opto-electronic properties [7–10]. Among II–VI inorganic semiconductors, Zinc Sulphide (ZnS) is found to be a versatile, nontoxic and chemically stable semiconductor. ZnS crystallizes in two different crystal forms: zinc blende (lattice constant, a = 5.409 Å) and wurtzite (lattice constant, a = b = 3.812 Å & c = 6.26 Å) structure[11]. As a wide band gap material, it is suitable for optoelectronic devices, light emitting laser diodes, optical windows for visible and ultra violet light, flat panel displays, etc., [12-14]. Moreover, ZnS is the most prominent host material for various dopants which modify its properties appreciably. Addition of dopant impurities changes the electronic structure and hence enhances the physical, chemical, optical, and magnetic behavior of the host material [15–17]. Furthermore, it is important to investigate the effect of Group IIIA elements such as Boron (B), Aluminium (Al), Indium (In) and Gallium (Ga) as dopants on the properties of ZnS because these elements have +3 valance states and hence can provide an extra electron. Although many studies on the synthesis of Al doped ZnS, Ga doped ZnO, In doped ZnO and In doped ZnS films, but works on In-doped ZnS nanoparticles is limited [18-20]. Even the available reports mainly focused on either bulk materials or thin films of In-doped ZnS [21,22].

Hence, this article presents the work on the synthesis and characterization of In-doped ZnS (0%, 1%, 3%, and 5%) nanoparticles prepared by co-precipitation method. Further, the effect of Indium incorporation on the structure, morphology, and elemental composition is investigated.

II. EXPERIMENTAL AND CHARACTERIZATION DETAILS

A. Experimental Details

In the present work, chemicals used were of analytical grade purchased from Merck, India. Sodium sulphide (Na\textsubscript{2}S) and zinc acetate (Zn(CH\textsubscript{3}COO)\textsubscript{2}) have been taken as precursors for sulphur and zinc sources respectively while Indium sulphate (In\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}) is used as the source of In dopant. Ammonium hydroxide
(NH₄OH) has been used as complexing agent as well as pH controller. Agglomeration of particles is controlled by using ethylene-diamine-tetraacetic acid (EDTA) which acts as a capping agent.

In a typical experiment to synthesize pure ZnS nanoparticles, 0.5 M solution of Zn(CH₃COO)₂ and 1 M solution of Na₂S were prepared separately in distilled water and stirred magnetically until a clear solution was obtained. The pH of the solution containing zinc source was optimized at 11 ± 0.5 using NH₄OH (30%). Then, Na₂S solution was added dropwise using a burette to the above mixture and simultaneously 10 ml of 0.5% EDTA solution was added under continuous stirring. The complete mixture was stirred swiftly for 3 h at 40 ± 5 °C using a magnetic stirrer till a fine precipitate was formed. Similar procedure also followed to prepare In-doped ZnS nanoparticles with changing concentrations of Indium. The white precipitates as a final product were obtained by filtering final solution, then washed with distilled water and acetone multiple times successively to eliminate unwanted impurities and lastly dried in hot air oven at 60 °C for 5 h.

B. Characterization Details

The X-ray diffraction (XRD) spectra have been obtained to investigate the structural properties of the synthesized nanoparticles using PANalytical X’pert PRO, x-ray diffractometer having wavelength (1.5406 Å) in the 2θ scanning range from 20° to 70°. The morphology and compositional study of the nanoparticles have been done using scanning electron microscope (SEM) JEOL-JSM-IT500, with energy dispersive X-ray (EDX) attachment. Fourier transmission infra-red (FT–IR: PERKIN ELMER) spectra have been recorded in the spectral range of 500–4000 cm⁻¹.

III. RESULTS AND DISCUSSION

A. Structural Analysis

XRD spectra of the chemically synthesized of the In-doped ZnS nanoparticles with different concentrations (0%, 1%, 3%, and 5%) are presented in Fig. 1. In all the results, the three prominent diffraction peaks positioned at 2θ = 28.7°, 48.1° and 56.7° could be indexed to the (111), (220) and (311) lattice planes of the zincblende ZnS structure respectively, that are match well with JCPDS file no. 05-0566 [23]. The broad diffraction peaks is an indication for the existence of nano-size particles in the synthesized samples. Moreover, this zincblende structure of the ZnS nanoparticles is not affected by the Indium substitution in the lattice as indicated by the same pattern for all the concentrations of individual doped nanoparticles. Also no additional peaks indicating the impurity phases such as Indium metal clusters were observed in the XRD patterns.

In the recorded XRD spectra, a slight shift in the diffraction peaks towards the lower diffraction angles side and the substantial decrease in the intensity of peaks have been observed with an increase in the Indium doping concentration. These changes directly indicate the inclusion of Indium into the host lattice with the replacement of Zinc ions having ionic radius of 0.74 Å by Indium ions of ionic radius 0.80 Å. Furthermore, the full width at half maximum (FWHM) is also slightly increased with increasing Indium doping concentration, hence reducing crystallite size which could be attributed to the lattice defects created by the dopant into ZnS lattice.

Fig. 1. XRD patterns of ZnS nanoparticles doped with different Indium concentrations (0%, 1%, 3% and 5%).

The average particle size (D_{app}) is estimated from FWHM of the prominent XRD peaks by Debye–Scherrer’s equation [24] as

\[ D = \frac{k\lambda}{\beta \cos \theta} \]

where \( k \) is 0.91 for spherical symmetry, \( \beta \) is the FWHM of the prominent diffraction peak, \( \theta \) is diffraction angle, and \( \lambda \) is the wavelength of \( \lambda \)-rays. The estimated particle sizes are listed in Table 1, along with other structural parameters, lattice constant (\( a \)), microstrain (\( \varepsilon \)) and dislocation density (\( \delta \)).

The lattice constant is calculated using following equation [24] as

\[ a = d \sqrt{h^2 + k^2 + l^2} \]

where \( d \) is interplanar spacing corresponding to miller indices \( h, k \) and \( l \) for the dominant peaks.

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The results indicate a steady decrease of crystallite size and lattice constant while increase of lattice imperfections with increasing Indium concentration. This could be due to many factors which include the number of free Zn$^{2+}$ cations and S$^{2-}$ anions released from precursors, the presence of capping agent EDTA, which inhibits the growth and the aggregation of ZnS and most importantly, the systematic increase of Indium doping which gradually reduces the concentration of Zn$^{2+}$ in the system. These factors together influence the growth rate of ZnS nanoparticles which results in an inhibited grain growth of Indium doped ZnS nanoparticles. Hence, it becomes evident that with the increase in Indium concentration, the lattice constant and particle size decreases steadily because of incorporation of Indium ions of larger ionic radius.

### B. Compositional Analysis

EDX analysis has been performed to identify the composition of desired elements in synthesized nanoparticles. EDX spectra of ZnS-In (0%) and ZnS-In (5%) nanoparticles are shown in Fig. 2. The spectra clearly disclose the presence of probable elements sulfur and Zinc in the sample ZnS-In (0%) and in addition to that, Indium in the ZnS-In (5%) doped samples. The presence of Carbon peak which belongs to Carbon coating of samples for EDX analysis is also shown in the result.

**Table- I: Physical properties of ZnS nanoparticles for different concentrations of Indium (0%, 1%, 3% and 5%)**

| Indium concentration in ZnS | Particle size (D_{avg}) nm | Lattice constant (a) Å | Microstrain \((ε=1/4tanθ)\) | Dislocation density \((δ/D_{avg}^2)\) line/m² |
|-----------------------------|-----------------------------|------------------------|------------------|-------------------------------|
| 0%                          | 5.7                         | 5.388                  | 1.98 x 10⁻²      | 3.08 x 10⁻⁶                   |
| 1%                          | 4.9                         | 5.374                  | 2.04 x 10⁻²      | 4.14 x 10⁻⁶                   |
| 3%                          | 3.0                         | 5.362                  | 3.59 x 10⁻²      | 11.49 x 10⁻⁶                  |
| 5%                          | 2.4                         | 5.345                  | 4.15 x 10⁻²      | 17.50 x 10⁻⁶                  |

**Table- II: Compositional analysis of ZnS nanoparticles doped with Indium (0%, 1%, 3% and 5%).**

| Indium concentration in ZnS | Zinc     | Sulfur | Indium |
|-----------------------------|----------|--------|--------|
| 0%                          | 46.73    | 53.27  | --     |
| 1%                          | 45.52    | 53.52  | 0.96   |
| 3%                          | 44.28    | 52.75  | 2.97   |
| 5%                          | 42.43    | 52.64  | 4.93   |

It has been observed that synthesized nanoparticles contained S metal slightly more than the zinc metal. However, the incorporation of Indium in ZnS structure has been clearly identified as the atomic percent (at.%) of Zinc reduces from 42.43% to 46.73% with the simultaneous increase in at.% of Indium from 0% to 4.93% while the at.% of Sulfur remains nearly consistent. The observed variations in the composition for In-doped ZnS nanoparticles are clear indications for the substitution of Indium into lattice sites of ZnS structure by replacing the Zinc atoms.

### C. Structural Morphological and Elemental Mapping

Fig. 3(a) and Fig. 3(b) illustrate the morphology of ZnS-In (0%) and ZnS-In (5%) nanoparticles respectively. It is clear that all particles have spherical morphology which is changes with the introduction of Indium in ZnS structure. The effect of capping agent EDTA that interacts and controls the grain growth during the synthesis process can also be observed from the formation of nano-size particles without agglomeration. Elemental mapping images (Fig. 3c-e) for ZnS-In (5%) shown homogeneous distribution of elements (Zn, S and In) in the ZnS nanoparticles. The doping of

![Fig. 2. EDX spectra ZnS nanoparticles doped with different Indium concentrations (0%, and 5%).](image_url)

![Fig. 3. SEM micrographs for patterns of (a) ZnS:In (0%) (b) ZnS:In (5%) nanoparticles and elemental mapping (c), (d, and (e) for elements Zn, S and In respectively in ZnS-In (5%) sample.](image_url)
Indium has been realized with its uniform dispersal over the entire area.

D. FT–IR Analysis

FT–IR spectroscopy is used to recognize different functional groups or adsorbing species present in materials which are represented by IR absorption band and peaks in the spectra due to several vibrational modes. FT–IR spectra of as-synthesized In–doped ZnS nanoparticles are shown in Fig. 4. In all the spectra, single broad and strong band at ~3340 cm\(^{-1}\) and a medium peak at 1630 cm\(^{-1}\) may be allocated to usual polymeric stretching of hydroxyl (–OH) group which indicates the occurrence of moisture in the In–doped ZnS samples [24]. The absorption band at 2110 cm\(^{-1}\) which is prominent in ZnS-In (0%) and ZnS-In (1%) nanoparticles can be credited to vibration of C−H stretching mode [24]. The sharp and medium peaks between 1650 to 1400 cm\(^{-1}\) in all the spectra belongs to stretching of double C=O and single C−O mode respectively that are associated to carboxyl –COOH group of zinc acetate [2,14]. The peaks at 1510 cm\(^{-1}\) can be attributed to N−O asymmetrical stretching mode indicating the traces of EDTA capping on nanoparticles. The absorption peak near 1251 cm\(^{-1}\) belongs to N−H stretch mode of NH\(_2\)OH [14].

IV. CONCLUSION

In–doped ZnS nanoparticles (0%, 1%, 3%, and 5%) have been synthesized via chemical co-precipitation method in the presence of EDTA capping agent. The XRD analysis shows that undoped and In–doped ZnS nanoparticles synthesized with zincblende structure and have particles size lying in the range of 5.7−2.4 nm. The inclusion of Indium doping into ZnS structure results to the decrease in particles size due to increase in microstrain and dislocation density. The compositional result analysis shows that Zn, S and In are present in the samples in proportional amount while Indium dopants substitute into the lattice sites of ZnS structure. The morphological analysis revealed that synthesized nano-size particles are spherical in shape, uniformly distributed and free from agglomeration due to the capping effect of EDTA. FT–IR spectra advocate the interaction of different reagents in the In–doped ZnS nanoparticles and successful incorporation of Indium ions in ZnS lattice. The characteristic absorption peaks for In–doped ZnS nanoparticles are also confirmed from FT–IR analysis.

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