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A Review on Synthesis and Characterization of ZNS:CR

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Abstract**—***This paper reports, synthesis, characterization and practical application of nanocrystalline chromium (Cr) doped Zinc sulphide (ZnS) nanoparticle, synthesized by co-precipitation method. The structural properties of ZnS:Cr nanoparticles have characterized by X-ray diffraction (XRD) analysis. The XRD patterns show hexagonal structure in nanoparticles. It is found that, the increase in molar concentration of chromium as doping agent increases the particle size. Absorption spectra, electrical properties and functional group have obtained by using UV-Vis spectrophotometer and FTIR by which band gap is obtained. The obtained values have been founded to in the semiconductor range i.e. 3.1 to 4.5 eV. It was also found that on increasing molar concentration of doping agent optical band gap (Eg) increases due to quantization effect. Using EDS, percentage of chemical compositions of material can be obtained.*

Keywords:—*ZnS:Cr, XRD X-ray diffraction, FTIR, Chemical co-precipitation, optical band gap.*

1. INTRODUCTION

During the past two decades, the "small-particle" research has become quite popular in various fields of science and technology. The ‘‘small-particles’’ now we call nanostructured materials are very interesting materials both for scientific reason and practical application. Semiconductor nanocrystals represent a class of materials that have interesting optical and electrical properties by controlling their band gap. They have attracted much attention over the past few years because of their novel

properties originating from quantum confinement effect [8]. In the case of semiconductor nanoparticles, radiative or nonradiative recombination of an exciton at the surface states becomes dominant in its optical properties with a decrease of particle size [12]. Therefore, the decay of an exciton at the surface states will influence the qualities of the material for an optoelectronic device. These size dependent optical properties have many potential applications in the areas of solar energy conversion, light emitting devices, chemical/biological sensors and photocatalysis [15] Wide band gap II–VI semiconductors are expected to be the novel materials for the optoelectronic devices [9]. In optoelectronics, it finds use as light emitting diode, reflector, dielectric filter and window material [9]. Cr-doped ZnS in order to get experimental evidence on the magnetic behavior of doped system. Nevertheless the theoretical and experimental researches on Cr doped ZnS are still limited. Keeping in view the above discussion, In the present paper an effort has been made to study the structural and optical properties of ZnS:Cr nanoparticles of different molar $Cr(NO_3)_2$ as doping agent and thioacetamide (CH_3CSH_2) as capping agent. The main purpose of the present research is to study the effect of Cr doping on structural and optical properties of ZnS:Cr nanoparticles synthesized by co precipitation method and its practical application.

2. EXPERIMENTAL PROCEDURE

Zinc chloride (ZnCl2), sodium sulfide (Na2S) and chromium (III) nitrate $Cr(NO_3)_2$ as starting materials poly(vinyl alcohol) [CH2CH (OH)]nas a capping agent for control particles size and double-distilled water as dispersing solvent were used to prepare ZnS:Cr nanoparticles. Preparation of ZnS:Cr nanoparticles by co-precipitation method The ZnS:Cr nanoparticles were prepared by the chemical co-precipitation method as follows. First, ZnCl2 was dissolved in double-distilled water with 0.1 molar concentrations and then obtained molar solution was stirred for 20 min at room temperature to achieve complete dissolution. Sodium sulfide and chromium chloride was also dissolved in double-distilled water separately as per molar concentration. Afterwards, first sodium sulfide solution was added drop by drop to the zinc chloride solution. Next the chromium chloride solution with desired molar concentration was added to this solution. Then, an appropriate amount poly (vinyl alcohol) [CH2CH(OH)]n (0.1 M) was added to the reaction medium to control the particle size of ZnS:Cr. The resulting solution was stirred continuously for 4 h. In the final step, the white obtained precipitate was filtered and dried at 60 ^oC temperature to remove both water and organic capping and other by products formed during synthesis [11]. After sufficient drying, the precipitate was crushed to fine powder with the help of mortar and pestle. It is necessary to mention that different sample of nanoparticles has been obtained by changing the molar concentration of doping agent.

3. CHARACTERIZATION

XRD- Analysis:

The X-ray diffraction (XRD) patterns of ZnS:Cr nanoparticles were recorded by Bruker system using Cu Kα radiation (λ=0.154056 nm) with 2θ ranging 20–70°.

UV- Analysis:

The optical absorption spectra of nanoparticles were measured using a USB-2000 UV–visible spectrophotometer. Therefore, obtained nanopowders have been suspended in glycerol using magnetic stirrer and their optical absorption spectra has been recorded at room temperature over the range 200 to 800 nm for determining the energy band gap values.

4. RESULTS AND DISCUSSION

Structural Characterization The XRD patterns of prepared ZnS:Cr nanoparticles with different amounts of doping agent (CrCl2). All of the crystalline Bragg peaks in the XRD pattern ((111), (220) and (311) planes) are in a good agreement with the diffraction data of

hexagonal structure with cell parameters a=3.600 Å and c=6.130 Å. Furthermore, The peak broadening in the XRD patterns clearly indicates the formation of ZnS:Cr nanocrystals with very small size. The peak broadening at lower angle is more meaningful for the calculation of particle size, the mean crystallite size of nanoparticles was also estimated using the Scherrer formula, reflection from the XRD pattern as follows: Where λ, B, and θ are the X -ray wavelength of the radiation used (Kα(Cu) = 0.154056 nm), the full width at half maximum (FWHM) of the diffraction peak and the Bragg diffraction angle, respectively.

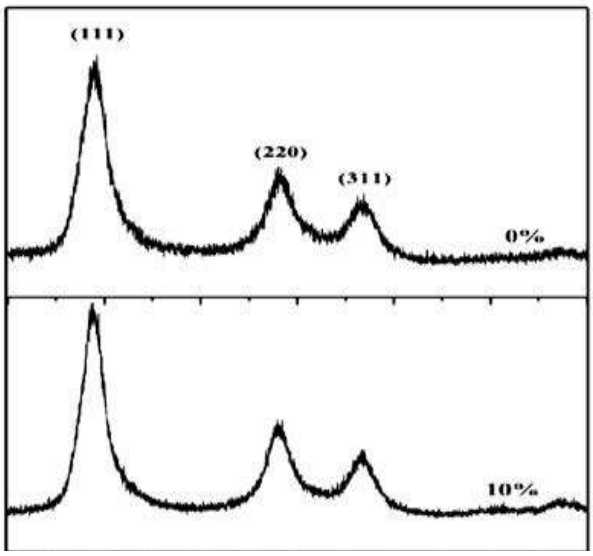

Figure 1. Values of mean Crystallite Size Obtained from XRD for Different Molar Doping Agent

Optical Characterization

The absorption spectra of the different samples are shown in Figure 2. The absorption edge is observed in the range of 325–280 nm, which is blue shifted compared to bulk ZnS. As the Cr concentration increases, the absorption edge shifts to lower wavelength side and intensity also increases with increasing Cr concentration compared to undoped ZnS. This blue shift of the absorption edges for different sized nanocrystals is related to the size decrease of particles and is attributed to the quantum confinement limit reaching of nanoparticles. The quantum confinement effect is expected for semiconducting nanoparticles, and the absorption edge will be shifted to a higher energy when the particle size decreases [4]. It is necessary to mention that the optical band gap values of the ZnS:Cr nanoparticles were determined by Tauc's relation (Tauc, Where hν, αo and Eg are photon energy, a constant and optical band gap of the nanoparticles, respectively[3].

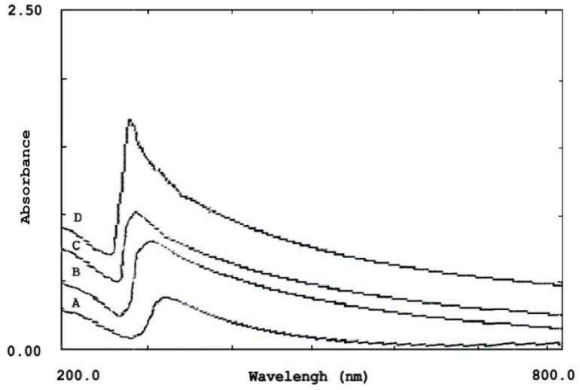

Figure 2. Absorption Spectra of the Different Samples

Absorption coefficient (α) of the powders at different wavelengths can be calculated from the absorption spectra. The values of optical band gap 'Eg' increases with the increase in molar concentration doping agent and therefore decrease particles size that as mentioned earlier is due to quantum confinement effect. The optical band gap values of nanoparticles have changed from 3.82 to 4.42 eV by decreasing the particle sizes. The increase in band gap with increase in Cr concentration is attributed to size quantization effect due to the small size of the particles [1]Chemical reaction rate directly affects the time evolution of the number of nuclei, which determines both nucleation and growth process. First, the influence on nucleation is obvious: nucleation is faster when the chemical reaction is faster. Second, growth will be strongly influenced by the nuclei number already formed at a given time. A great number of nucleation favours a fast autocatalytic growth, giving rise to a large number of small particles. Rate of reaction controls this kind of growth, being the autocatalytic growth faster as chemical reaction is faster. But in nanoparticle formation, there is another contribution to the growth molecules on the surface of small

particle will tend to diffuse through solution and add to the surface of larger particle (growth by ripening).[4] A slow chemical reaction favours continuous nuclei, keeping always a certain number of nuclei in the system. As a result, growth by ripening can take place during the whole process. This fact explains the bigger particle size obtained from a slow reaction. One can conclude that a slow chemical reaction rate is associated with a more important ripening contribution to the growth. A high number of nuclei are still forming at this stage when the reaction is slow at the same time; some particles have already grown to the final value of size. This means that in this case (slow reaction rate), nucleation and growth takes place simultaneously.[11] This overlapping of nucleation and growth processes, which is more pronounced as the chemical reaction is slower, leads to larger nanoparticle sizes (Dios et al., 2005).[12]Rate of reaction depends on the molar concentration of reactants solution and increases with the increase in molar concentration of reactants solution. Mean crystallite size and study, the molar concentration of reactants solution varies from 0 M to 1.5 M, the reaction rate is highest for 1.5 M solution and hence the particle size obtained is smallest for 1.5 M solution as compared to other materials in the series, which is in consistent with the above made argument.

5. CONCLUSIONS

It is possible to produce different size ZnS:Cr nanoparticles using a simple chemical co precipitation method by using different molar concentration of doping agent. XRD and Optical band gap data have been obtained to confirm nano size of the particle. It is also observed that the particle size depends on molar concentration of doping agent. A decrease in formation rate of nanoparticles gives rise to a larger final particle size for all the studied synthesis conditions. Chemical reaction rate affects both nucleation and growth process. Nucleation and growth take place simultaneously when the chemical reaction is slow. Besides, a slow chemical reaction rate is associated with a more important ripening contribution to the growth. As the particle size depends upon the molar concentration of doping agent, a decrease in the size of particle is observed with the increase of molar concentration of doping agent. The mean crystallite size range of particles was between 1.5 and 2.45 nm, depending on molar concentration of doping agent. The optical band gap values of ZnS:Cr nanoparticles have changed from 3.1 to 4.5 eV by increasing the molar concentration of doping agent. These values exhibit a blue shift in Eg which is related to the size decrease of the particles and to the quantum confinement limit reaching of nanoparticles. Considering these results, the chemical co-precipitation method using thioacetamide (CH_3CSH_2) as a capping agent is efficient for the preparation of ZnS:Cr nanoparticles suitable for modern optoelectronic technology and other electronics industries.

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