International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN: 0974-4290
Vol.7, No.3, pp 1284-1289, 2014-2015

ICONN 2015 [4th -6th Feb 2015]
International Conference on Nanoscience and Nanotechnology-2015
SRM University, Chennai, India

Synthesis and characterization of cupric chloride doped zinc sulphide nanoparticles

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Abstract : In recent years, the research on semiconductor nanoparticles has stimulated much interest because of their unique optical and electrical properties. The nanosized semiconductor crystallites could produce optical properties which are different from bulk materials. Among the semiconductor nanoparticles, Zinc Sulphide is an important II–VI semiconductor material researched extensively because of its wide range of applications in electroluminescence devices, phosphors, light emitting displays and optical sensors. Semiconductor nanoparticles doped with transition metal ions have attracted much attention because of their luminescent properties. Hence an attempt is made to synthesize cupric chloride doped zinc sulphide nanoparticles. The synthesized nanoparticles are subjected to X-ray diffraction to calculate the average nano-crystalline size using Debye – Scherrer formula and are found to be 2nm. The morphological analysis of the sample is studied using Scanning Electron Microscope. The UV-Visible spectrophotometer shows the absorption edge of the nanoparticles in range 292 to 261 nm. A FT-IR spectrum confirms the characteristic ZnS vibration peaks. Keywords: Nanoparticles, Debye – Scherrer, XRD, UV-Vis, SEM.

Introduction

In recent years, research on semiconductor nanoparticles stimulated great interest because of their unique optical and electrical properties. Cubic ZnS with a bulk bandgap of 3.7 eV is a common and attractive choice as a host semiconductor for doping to produce nanophosphors in EL applications due to its stability, low cost, and low toxicity[1-4]. An important subset of semiconductor NCs are those doped with a small percentage of dopants to alter their electronic, magnetic, and optical properties for various desired applications[5-17]. It can also be used for electroluminescent devices and photodiodes[18-19]. In recent years, much effort has been devoted to the research of doped metal chalcogenide nanostructured materials. This kind of nanomaterials exhibits unusual physical and chemical properties in comparison with their bulk materials, such as size-dependent variation of the band gap energy. Furthermore, impurity ions doped into these nanostructures can influence the electronic structure and transition probabilities[20]. One of the promising applications of doped semiconductor NCs is solid state lighting based on AC electroluminescent (EL) devices that are expected to have high electrical-to-light conversion efficiency.

As an important II–VI semiconductor material, ZnS is chemically more stable and technologically better than other chalcogenides (such as ZnSe), so it is considered to be a promising host material. Doping

transition elements receive much attention in research because many functions can be added by transporting and controlling numerous types of spin state. In addition, it can be indicated that the properties are closely related to the concentration of metal-doped because it can change the energy band and form luminescence of different energy level. Many approaches have been used for the preparation of metal-doped ZnS and controlling their morphology. The development of novel and simple synthetic route has to be considered in order to obtain high yield of product. Hence, in the present investigation an attempt is made to synthesize cupric chloride doped zinc sulphide nanoparticles by wet chemical co-precipitation method and characterize the synthesized samples using x-ray diffraction, UV-Vis absorption, SEM and FT-IR studies.

Materials and methods

Cupric chloride doped ZnS nanoparticles have been synthesized using wet chemical co-precipitation method at room temperature. Zinc chloride ($ZnCl_2$), cupric chloride ($CuCl_2$), and sodium sulfide ($Na_2S.H_2O$) are used without further purification. Solution of 0.1 M zinc chloride, 0.1M sodium sulfide and 0.01M of cupric chloride is prepared in separated flask.

In the synthesis, cupric chloride in the burette is added drop wise into zinc chloride solution. Then sodium sulfide solution added drop wise into the above solution and stirred for 2 hours. Kept it without disturbing for 24 hours, then centrifuged using acetone, ethanol and finally with distilled water and heated for 1 hour at 160 degree Celsius at hot air oven. Then grained to powder and stored in a sample vial.

The crystalline structure, phase purity and size of the nanoparticles are determined by X-ray powder diffraction technique. The X-ray powder diffractometer (Shimadzu 6000) with monochromated CuKα radiation (λ=1.5406Aº) is used. The samples are scanned over the required range for 2θ values (20-60˚). The morphology and the microstructure of the samples are tested by scanning electron microscopy (SEM) using a Hitachi S-3000H microscope. The optical absorption measurements obtained from the colloidal solution are performed in UV-Vis spectrophotometer and FT-IR analysis is performed using Shimadzu IR affinity-1.

Results and discussion

XRD analysis

The XRD pattern of cupric chloride doped ZnS nanoparticles is shown in Figure 1. The well defined diffraction peaks corresponding to the lattice planes of (111), (220) and (311) are observed. These peaks matches very well with the cubic zinc blended structure (JCPDS No. 05-0566), confirming the purity of the synthesized samples. However it is further observed an additional peak at 32º may be due to the incomplete substitution occurred during experimental reaction step. A partial amount of copper may not be well substituted due to non-sufficient energy[21].

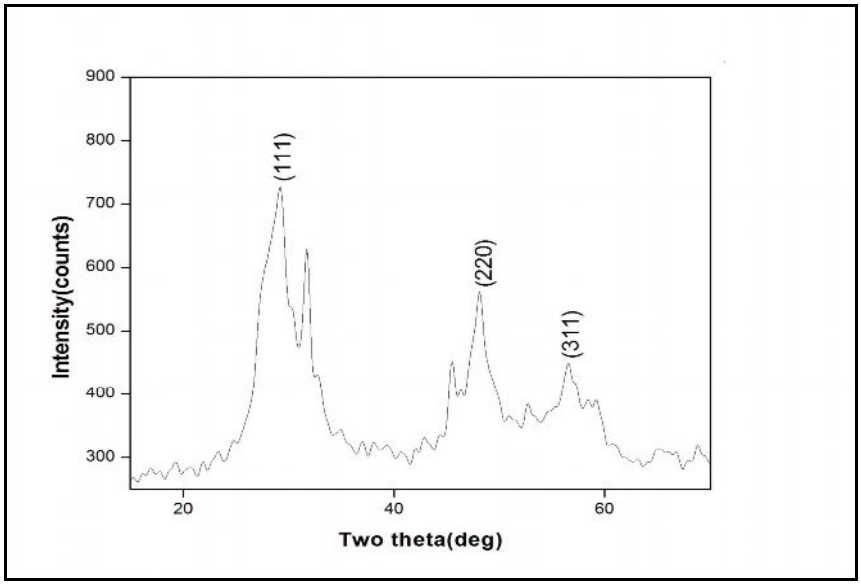

Figure 1. XRD Pattern of 0.01 M $CuCl_2$ doped ZnS

As ZnS is doped with cupric chloride, the peak broadening is observed[22]. This broadening of peaks indicates the nanocrystalline nature of the sample. The XRD Data of 0.01M cupric chloride doped ZnS nanoparticles is given in Table 1. According to Debye-Scherrer formula[23], crystallite size can be calculated using the equation

$D=0.9\lambda/\beta\cos\theta$

where λ is X-ray wavelength, β is the angular line width at half maximum intensity and θ is the Bragg's angle. The average crystallite size from X-ray technique is found to be 2nm.

Table 1. XRD Data of 0.01M cupric chloride doped ZnS

2θ (deg)	FWHM β	Particle Size D (nm)	d-spacing (Å)	hkl value	Lattice Constant a (Å)
29.6357	5.55720	1.47	3.01196	111	5.2168
47.6000	4.15000	2.09	1.90883	220	5.3989
56.9000	5.65000	1.59	1.61695	311	5.3628

SEM Analysis

SEM images of cupric chloride doped ZnS nanoparticles of different magnifications are shown in Figure.2. SEM images show that the synthesized nanoparticles are found to be in cluster form and agglomerated in some places.

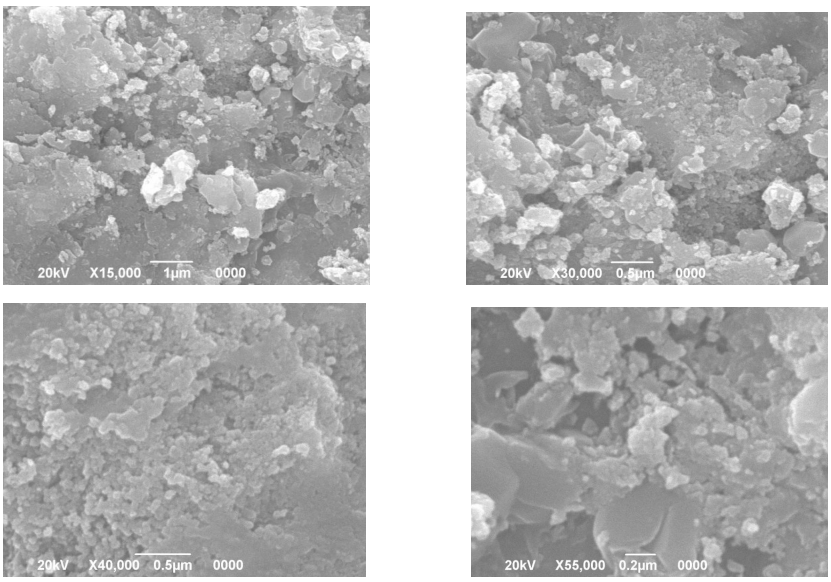

Figure 2. SEM images of 0.01M $CuCl_2$ doped ZnS nanoparticles

UV-Vis measurement

The UV-Visible absorption spectroscopy of the prepared samples is recorded from the SHIMADZU UV-Visible absorption Spectrometer. Figure 3 shows the UV-Visible absorption spectrum of $CuCl_2$ doped ZnS. The absorbance versus wavelength traces for the sample is recorded in the range 200-800 nm. The spectrum shows absorption edge of the nanoparticles in the range - 292 to 261 nm, showing these nanoparticles being blue-shifted as compared to bulk ZnS for which the peak is at 340 nm. The blue shift in the absorption edge is due to the quantum confinement of the excitons present in the sample, resulting in a more discrete energy spectrum of the individual nanoparticles. The effect of the quantum confinement on impurity depends upon the size of the host crystal. As the size of the host crystal decreases, the degree of confinement and its effect increases[24].

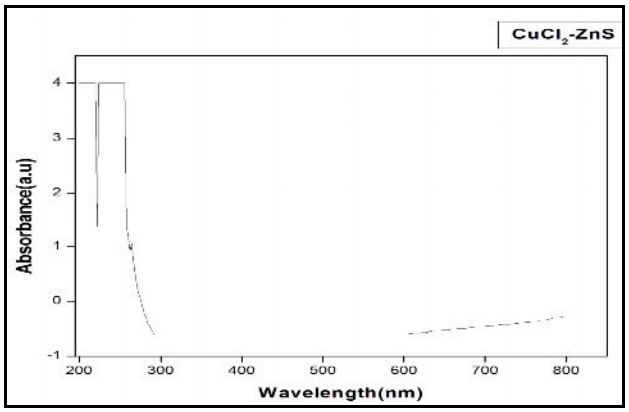

Figure 3. UV-Vis spectrum of 0.01 M $CuCl_2$ doped ZnS

The absorption edge shifts towards the lower value of wavelength due to the Cu doping. It is observed that the rate of nucleation is increased with $CuCl_2$ doping, which produces relatively small particle leading to quantum confinement effect.

FT-IR spectral Analysis

FT-IR spectral analysis is performed using Shimadzu IR affinity-1 and FT-IR absorption spectra are recorded in the range of 4500-500 cm^{-1} wave numbers. A straight line between two lowest points in the respective spectra region is chosen as a baseline. Potassium bromide (KBr) acting as a non-absorbing medium is mixed with a solid sample (0.3-0.5 wt%) by an agate mortar and pestle to prepare a pellet specimen.

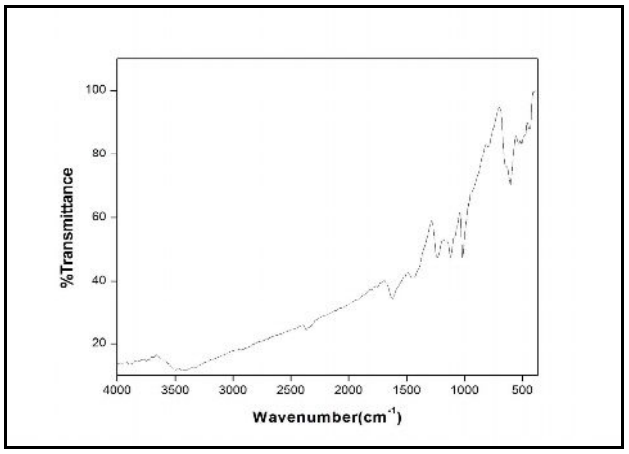

Figure 4. FT-IR spectra of 0.01M $CuCl_2$-doped ZnS

Figure. 4 show the FT-IR spectrum of cupric chloride doped ZnS nanoparticles. The characteristic ZnS vibration peaks are observed at 1118, 601 and 439.77 cm^{-1}. The peaks at 2931, 2816, 1620cm^{-1} are due to microstructure formation of the samples. The observed peak values are in good agreement with the literature[25-26]. The broad absorption band around 3500 cm^{-1} corresponding to -OH group indicates the existence of water absorbed in the surface of the samples. The bands around 1650 $cm^{-1}$and 1500 cm^{-1} are due to the C=O stretching modes arising from the absorption of atmospheric CO_2 on the surface of the samples[27-28]. It may be due to the fact that the Cu atom may be partially substituted into Zn position in ZnS nanoparticles. The partial metal substitution result is consistent with XRD experiment.

Conclusion

Nanoparticles of cupric chloride doped ZnS have been synthesized successfully by simple chemical precipitation method. The XRD of the samples confirm the formation of Nanoparticles of $CuCl_2$ doped ZnS and their cubic structure. Particle size and lattice parameter have been calculated from XRD analyses which confirm the nano structure of the samples. SEM images show that the synthesized nanoparticles are found to be in cluster form with agglomeration in some places. The absorption spectrum obtained using UV-Visible

spectrophotometer shows the absorption edge of the nanoparticles in the range 292 to 261 nm. A FT-IR spectrum confirms the characteristic ZnS vibration peaks. These nanoparticles can be tested for various applications such as light emitting displays and optical sensors.

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