

Synthesis and Characterisation of ZnS Nanoparticles

Parvathy P¹, Shabna S²

^{1,2}Department of Physics, Sree Narayana College Chengannur

Abstract: ZnS nanoparticles are prepared by Coprecipitation method using EDTA (Ethylenediaminetetraacetic acid) as capping agent. It is characterised by UV-Visible spectra, X-ray diffraction studies. UV – Visible absorption spectra are used to find the optical band gap and the value obtained has been found to be 4.5eV. The particle size of nanoparticles calculated from XRD pattern has been approximately 4 nm.

Keywords: Coprecipitation method, ZnS nanoparticle, UV – Visible, XRD

1. Introduction

Nanostructure science and technology is a broad and interdisciplinary area of research and development activity that has been growing explosively worldwide in the past few years. Nanomaterials are cornerstones of nanotechnology. Nanomaterials can be metals, ceramics, polymeric materials, or composite materials. Their defining characteristic is a very small feature size in the range of 1 to 100 nanometers (nm). By comparison, the diameter of a human hair is about 5 orders of magnitude larger than a nanoscale particle.

Nanotechnology is the understanding and control of matter at dimensions between approximately 1 and 100 nm, where unique phenomena enable novel applications. Encompassing nanoscale science, engineering and technologies nanotechnology involves imaging, measuring, modelling and manipulating matter at this length scale.

A nanometer is one-billionth of a meter. A sheet of paper is about 100,000 nanometers thick; a single Au atom is about a third of a nanometer in diameter. Unusual physical, chemical, and biological properties can emerge in materials at the nanoscale. These properties may differ in important ways from the properties of bulk materials and single atoms or molecules.

Although widespread interest in nanomaterials is recent, the concept was raised over 40 years ago. Physicist Richard Feynman delivered a talk in 1959 entitled “There is a Plenty of Room at the Bottom”, in which he commented that there were no fundamental physical reasons that materials could not be fabricated by manoeuvring individual atoms. Nanomaterials have actually been produced and used by humans for hundreds of years – the beautiful ruby red colour of some glass is due to gold nanoparticles trapped in the glass matrix. The decorative glaze known as luster, found on some medieval pottery, contains metallic spherical nanoparticles dispersed in a complex way in the glaze, which gives rise to its special optical properties.

Development of nanotechnology has been spurred by refinement of tools to see the nanoworld, such as more sophisticated electron microscopy and scanning tunnelling microscopy.

Surfaces and interfaces are also important in explaining nanomaterial behaviour. In bulk materials, only a relatively small percentage of atoms will be at or near a surface or interface (like a crystal grain boundary). In nanomaterials, the small feature size ensures that many atoms, perhaps half or more in some cases, will be near interfaces. Surface properties such as energy levels, electronic structure, and reactivity can be quite different from interior states, and gives rise to quite different material properties.

2. Importance of ZnS nanoparticles

ZnS is proved to be versatile material because of their applications in optoelectronic devices due to large variation of band gap as a function of particle size. ZnS has attracted much attention owing to its wide applications including UV light emitting diodes, efficient phosphors in flat panel displays, and photo catalysis. ZnS nanoparticles have the capabilities for applications in areas such as nonlinear optical devices and fast optical switches and they have been studied extensively.

Nanostructured ZnS such as nano crystals, nano wires and nano belts exhibit excellent optical and electronic performances, which differ much from the bulk ZnS material due to the three dimensional electrons and holes confinement in a small volume. The surface of a nano particle is more important than the bulk because nano particle have larger surface to volume ratios, surface atoms are bound by weaker forces because of missing neighbours, which leads to high surface reactivity.

ZnS has a direct wide band gap. Semiconductor has also been widely used as a phosphor in luminescent devices due to its emission in the visible range. Their optical property, due to quantum confinement effect, dramatically changes and in most cases improves as compared with their bulk counter parts.

ZnS crystals usually exhibit a polymorphism of two phases with different stacking sequences of closely packed planes to each structure. Since the inherent crystal structures of ZnS play an important role in its physical and chemical properties, the preparation of ZnS nano crystals with controllable phase is vital to develop them as building

blocks in constructing the future nano scale upto electronic devices.

3. Present Work

In the present work, nanoparticles of ZnS were synthesized by chemical precipitation technique. The formation of nanoparticles by the chemical method is confirmed with UV-Visible and X-ray Diffraction method. Z-scan technique was employed for the nonlinear characterization of the nanocomposites. A Q-switched Nd: YAG laser at 532 nm was used as the source of light in the Z scan experiments. The structural charecterisation of the sample was done using X-ray diffraction method.

4. Synthesis of MnS Nanoparticles

Uniform particles are usually prepared via homogeneous precipitation reaction. Chemical precipitation method deals with growing nanoparticles of inorganic materials through chemical reaction of their precursors. By slowing the reaction temperature or using suitable stabilizing agents, the growth rate of the particle and its particle size can be controlled. Often suitable capping agents are used to achieve the desired grain size.

ZnS nanoparticles of present study are prepared through simple chemical precipitation method using Zinc sulphate as precursor. The principle involved in this technique is the precipitation of metal ions with sulphate ions in the solution. 0.1 M aqueous solution of Zinc Sulphate and 0.1 M aqueous solution of Sodium Sulphide were mixed in the presence of EDTA as capping agent. First solutions of 50ml ZnSO₄ and 50ml Na₂S were prepared in double distilled water. 10ml of ZnSO₄ and 5ml of EDTA were mixed together and stirred for 30 minutes on a magnetic stirrer to get a homogeneous solution. This was followed by drop wise addition of 10ml of Na₂S under vigorous stirring for 1 hour. A white colour precipitate was obtained which was separated by centrifugation and washed up to 6 times with double distilled water and finally with acetone. The precipitate was then dried and powdered.

5. Analysis of UV – Visible absorption spectrum of nanoparticles of ZnS

5.1. Introduction

The optical properties of semiconductors span a wide range of phenomena and aid greatly in understanding the basic physical properties of semiconductors. These phenomena are also used in the development of optical devices widely used in research and industry. The optical properties are divided into electronic and lattice properties. Electronic properties concern processes involving the electronic state of a solid, while lattice properties involve the vibration of the lattice (creation and absorption of phonons). In the case of semiconductors electronic properties receive much attention, particularly so far as practical applications are concerned. The electronic excitations in a semiconductor crystal consists of a loosely bounded electron- hole pair (the Mott-Wannier exciton), usually delocalized over a length much

longer than the lattice constant. As the diameter of the semiconductor crystallite approaches exciton Bohr diameter, its electronic properties start to change. This is the so-called quantum size effect which can be observed as a blue shift of the optical band gap from that of the bulk crystal.

Nanocrystals or quantum dots of II-VI semiconductors such as CdS, CdSe, ZnS, ZnO etc provide unique opportunities for investigating the effects of strong confinement of electrons and phonons on optical properties. Ultraviolet-visible spectroscopy is widely used for establishing the quantum confinement effect in nanostructured materials. UV-VIS absorption spectra can also be used for calculating the optical band gap of semiconductor nano materials

5.2. UV – Visible absorption spectrum of nanoparticles of ZnS.

Figure 5.1 shows the UV-Visible absorption spectrum of as-prepared ZnS nanoparticles. The spectrum shows an absorption peak at ~258 nm. The sharp optical absorption peak observed in the present study indicated the high mono dispersivity of the sample. The bulk exciton binding energy of ZnS is 29 meV, which is less compared to the thermal energy available at room temperature (30 meV) to destroy the exciton. Therefore, in bulk ZnS exciton is not detectable at room temperature. However, for nanocrystals of grain size comparable to that of bulk Bohr exciton radius, the overlap of the electron and the hole wave functions in the spatially confined structure is enhanced increasing the excitonic binding energy. Thus even at the room temperature, the excitonic peak can be observed in the optical absorption spectra of nanocrystals. The Bohr exciton radius of ZnS is 2.5 nm. Rossetti et al. observed an exciton peak at 290 nm for the ZnS nanoparticles of size 3 nm dispersed in methanol and attributed it to the transitions between 1Se – 1Sh levels. Wageh et al. synthesized nanoparticles of size ~ 4 nm using mercaptoacetic acid as a capping agent. The authors observed an absorption peak at 295 nm and attributed it as an excitonic peak. An exciton peak at 240 nm was observed by Mahamuni et al. for nanoparticles of ZnS of size ~ 0.7 nm. Thus the peak observed at 258 nm in the absorption spectrum of the as- prepared nanostructured ZnS samples of the present study can be attributed to the excitonic transition between 1Se – 1Sh levels.

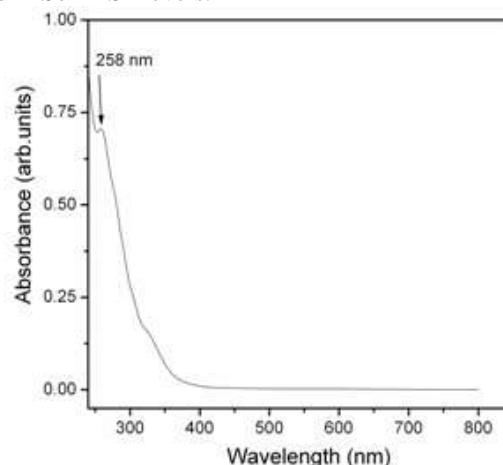


Figure 5.1: UV-Visible absorption spectrum of nanoparticles of ZnS.

If a sharp excitonic peak is observed in the absorption spectra of semiconductor nanoparticles, then the average band gap value can be directly calculated by subtracting the exciton binding energy from the energy value corresponding to excitonic peak. The exciton binding energy of nanoparticles of diameter d can be calculated from the

$$\text{expression, } \frac{3.572e^2}{4\pi\epsilon_0\epsilon_\infty d}$$

In the present study, the exciton binding energy of ZnS nanoparticles was calculated to be 0.245 eV and the band gap value was calculated to be approximately 4.5 eV. X-ray Diffraction Studies of Nanoparticles of ZnS

A detailed knowledge of the structure and composition of nanomaterials is a key to understand their properties. Among the various methods used for the structural characterization of nanophase materials, X – ray diffraction (XRD) is a powerful tool, since it is non destructive and highly quantitative. The wavelength of X-rays is on the atomic scale making X-ray diffraction a primary tool for probing structure of nano-materials. X-ray diffractograms of nanomaterials provide a wealth of information on phase, composition, crystallite size, lattice strain etc. X ray diffraction pattern of nanoparticles are conspicuously different from that of their bulk counterparts. The small grain size of the clusters in nanophase materials gives their diffraction pattern the appearance of an amorphous material even though they are not completely amorphous. The maxima of the peaks do not align with expected bulk peak positions and peak shapes, peak intensities and peak widths may differ from extrapolated bulk estimates.

In the present work, X-ray diffraction patterns of the as prepared ZnS samples are recorded using a Philips Xpertpro diffractometer and using $\text{CuK}\alpha$ radiation over the diffraction angles (2θ) from 20 to 600. Figure 4.1 shows the XRD pattern of as prepared ZnS nanoparticles of the present study. The figure shows three diffraction peaks at 2θ values of 29.2, 47.5, and 57.50 corresponding to d values of 3.030, 1.909, and 1.601 Å respectively. The peaks are identified to originate from (111), (220) and (311) planes of the cubic (zinc blend) phase of ZnS (JCPDS Card No. 80-0020). None of the three most intense peaks of hexagonal phase corresponding to (100), (101) and (002) reflections is found in the diffraction pattern of the as-prepared ZnS sample excluding any possibility for the presence of wurtzite phase of ZnS in the sample.

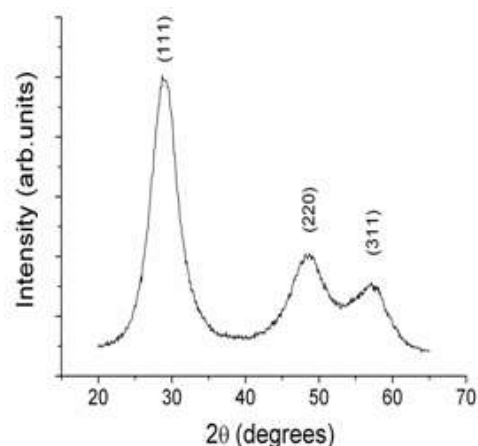


Figure 4.1: XRD pattern of nanoparticles of ZnS

Table 4.1: Comparison of JCPDS values of ZnS with the observed values

d values (Å) observed from XRD pattern	d values (Å) from JCPDS data for cubic ZnS	d values (Å) from JCPDS data for hexagonal ZnS
3.03	3.09 (111)	3.27 (100)
1.91	2.67 (200)	3.09 (002)
1.60	1.89 (220)	2.89 (101)
	1.62 (311)	2.25 (102)
		1.89 (110)

The broadening of the diffraction peaks in figure 4.1 indicates the nanocrystalline nature of the sample. Line broadening in the XRD pattern of nanoparticles is a good criterion to use in nanostructure analysis. In Bragg's law, a crystal is viewed as a plane containing several lattice points. The reflection of X – rays will take from these angles with the angle of reflection being equal to the angle of incidence. The reflected beams are in phase when the path length between the beams is an integral multiple of the wavelength. The planes of light traveling after reflection will be in phase only when Bragg's condition, i.e. $n\lambda = 2d\sin\theta$ is satisfied. For all angles other than θ , destructive interference will take place leading to the cancellation of intensity. For crystals containing thousands of planes, Bragg's law imposes severe restrictions on θ and the cancellation of intensities is usually complete. Thus the width of the diffraction peak is determined by the number of planes in the crystallite and the dynamical diffraction theory of perfect crystals predicts the existence of very sharp diffraction lines, in which there may be only a small inherent broadening due to the uncertainty principle. Scherrer used this principle to obtain a relationship between line broadening and the particles size. The derivation of Scherrer equation is given below:

Bragg's law is given by,

$$2d \sin \theta = n\lambda \quad \dots\dots\dots (4.1)$$

For first order diffraction,

$$2d \sin \theta = n\lambda$$

Multiplying both sides by an integer 'm' such that $md = D$, the thickness of the crystal

$$2md \sin \theta = m\lambda$$

$$2 D \sin \theta = m\lambda \quad \dots\dots\dots (4.2.)$$

Eqn (3.2) can also be interpreted as the 'n'th order reflection from a set of planes with interplanar distance 'D'

Differentiating both sides of eq (3.2) remembering $m\lambda$ is a constant

$$2D \cos \theta \Delta\theta + 2 \sin \theta \Delta D = 0 \quad \dots\dots\dots (4.3.)$$

$\Delta\theta$ can be positive or negative. Considering magnitude only eq (4) leads to

$$D = \Delta D \sin \theta / \Delta \theta \cos \theta \quad \dots\dots\dots (4.4.)$$

Since the smallest increment in 'D' is d, using $\Delta D = d$ and substituting $\lambda/2$ for $d \sin \theta$ [from eq (3.2)], we get

$$D = \lambda/2 \Delta \theta \cos \theta \quad \dots\dots\dots (4.5)$$

Let $\theta_1 = \Delta + \Delta \theta$, be the highest possible angle that can be got before complete destructive interference and let $\theta_2 = \Delta - \Delta \theta$ be the lowest angle that can be got before complete destructive interference. Now we can interpret 2Δ as the angular width of the X-ray diffraction line. In the X-ray diffraction meters what is recorded is the variation in intensity of the diffraction lines with $2\theta_1$, so in the X-ray diffractogram we can see diffracted X-ray overall scattering angles between $2\theta_1$ and $2\theta_2$.

If we assume a triangular shape for the peak, the full width at half minimum (FWHM) will be

$$\beta = (2\theta_1 - 2\theta_2)/2 = \theta_1 - \theta_2$$

$$\text{or } \beta = (\Delta + \Delta\theta) - (\Delta - \Delta\theta) = 2\Delta\theta$$

$$\dots\dots\dots (4.6.)$$

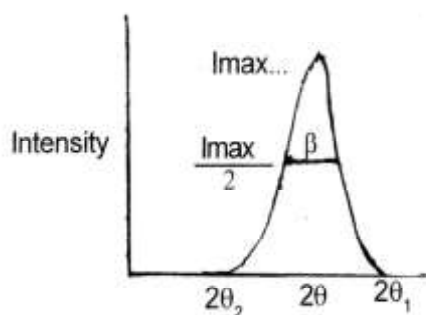


Figure 4.2: Schematic diagram showing to calculate Full Width at Half Maximum

Substituting β for $2\Delta\theta$ in eq (3.5); we get,

$$D = \lambda/\beta \cos \theta \quad \dots\dots\dots (4.7.)$$

This is essentially the Scherrer equation. A more rigorous treatment (using a Gaussian function, rather than a triangular function) gives

$$D = 0.9\lambda/\beta \cos \theta \quad \dots\dots\dots (4.8.)$$

For spherical crystals of diameter 'D', knowing the wave length λ of the X-ray and analyzing the spectrum, the thickness 'D' of the crystalline sample can be determined. The grain size of the as prepared ZnS nanoparticles of the present study is calculated using equation 4.8 and is approximately 4 nm.

6. Conclusion

Zinc Sulphide nanoparticles have interesting chemical and physical properties suitable for technological applications. The direct and wide band gap and the polymorphism

behavior of the ZnS crystals make them as appropriate for different kinds of semiconductor optical devising. In the present work, nanoparticles of ZnS are prepared by co-precipitation method. X-ray Diffraction Pattern of the samples was recorded and the grain sizes calculated from Debye-Scherrer equation was found to be approximately 4nm. The band gap of the nanoparticles of ZnS was calculated from the UV-Visible absorption spectrum and was found to be 4.5eV. The result suggests that ZnS nanoparticles are applicable in optical detector laser, sensor, imaging, photo electrochemistry, photocatalysis and biomedicine.

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