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Preparation of ZnS nanoparticles by hydrothermal method

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Abstract. ZnS nanoparticles were fabricated by hydrothermal method without using any capping agent. The hydrothermal temperature was 220°C. The product was received in powder form. The structure, composition and optical property of the resultant product were characterized by means of X-ray diffraction (XRD), transmission electron microscopy (TEM), UV-visible optical spectroscopy and photoluminescence (PL). The XRD pattern showed that the prepared ZnS nanoparticles have a zinc blende structure. The TEM image demonstrates clearly that the ZnS nanoparticles are in a spherical form with an average diameter of 25 nm. The UV-VIS spectra exhibited a blue-shift with respect to that of the bulk samples. The shift was attributed to the quantum size effect. The band gap of those samples have been calculated from absorption spectra and is found to be about 3.7 eV.

Keywords: ZnS nanoparticles, hydrothermal method, structural property.

1. Introduction
Zinc sulfide is an important II-IV semiconductor material with a wide band gap (3.72 eV for the cubic zinc blende phase and 3.77 eV for the hexagonal wurtzite phase at 300 K) and a large exciton binding energy (40 meV) [1]. It has a wide range of applications such as in optical sensor, solid state solar window layers, photoconductors, phosphors and catalysts. It has been extensively studied with the aim of controlling the size, morphology and crystallinity of ZnS nanocrystals in order to obtain desired physical properties.

In recent years, zero-dimensional (0D) ZnS nanostructures has attracted much attention because it can be used for biological detection and tagging [2]. Many methods have been used to synthesize ZnS nanoparticles such as sol - gel, electrochemical deposition, sonochemical, hydrothermal technique…

In this paper, we report the synthesis and characteristics of zinc sulphide nanoparticles obtained by using hydrothermal method with different reaction conditions. This is a simple method to fabricate nanocrystals from aqueous solutions at high temperatures and high vapour pressures. The advantage of this method over others includes the ability to create crystalline phases which are not stable at the melting point and create materials which have a high vapour pressure near their melting points. In the process, the decomposition of the precursors in a particular solvent depends on the temperature and pressure which was related to the filling fraction of the solvent within the reaction vessel and was kept constant for all the experiments. The important aim of studies is finding the effect of the synthesis conditions on the size, shape and crystal structure of the ZnS products.
2. Experimental

An autoclave, which is a thick-walled steel cylinder hermetically sealed in order to withstand high temperatures and pressures for prolonged periods of time, is used for hydrothermal method. In the internal cavity of the autoclave, a Teflon vessel used to prevent corrosion is inserted. The vessel has an inner diameter of 30 mm and a capacity of about 120 ml.

All the chemicals were of analytical grade and used without any further purification. We have performed experiments with different molar ratios of the compositions of Zn$^{2+}$ and S$^{2-}$ at the temperature of 220°C. Experiment details were as follows: ZnSO$_4$.5H$_2$O powder and Na$_2$S.7H$_2$O powder used as starting materials were dissolved separately in de-ionized water and stirred at room temperature for 30 min. Then they were mixed by dripping the Na$_2$S solution in drops into ZnSO$_4$ solution while stirring. Zinc and sulfur sources taken in 1:0.7, 1:1 and 1:1.3 molar ratios were used for synthesis of sample 1, sample 2 and sample 3, respectively. The chemical reaction may be described as follows [3]:

$$\text{ZnSO}_4 \leftrightarrow \text{Zn}^{2+} + \text{SO}_4^{2-} , \quad (1)$$

$$\text{Zn}^{2+} + \text{Na}_2\text{S} \leftrightarrow \text{ZnS} + 2\text{Na}^+ . \quad (2)$$

The white gels were charged into the Teflon-lined stainless steel autoclave, which was then filled with the mixed solution up to 50% of its volume. The closed chamber was placed inside a box furnace (Mermert - 500) at the temperature of 220°C for 12 h and then cooled down to room temperature naturally. The solution containing products were then centrifuged, had the supernatant layer poured off, washed with double distillated water. The wash procedure was repeated ten times to remove impurities in the sample. The final white products were dried at 60°C in air for 12 h.

The structure of the ZnS samples was analyzed by X-ray diffraction using a Brucker D5005 diffractometer. The microstructures and structures of the samples were characterized by transmission electron microscopy (JEOL JEM 1010) and high-resolution transmission electron microscopy (FEI Tecnai TF20 TEM/STEM). The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded by using a FL3-22 Jobin Yvon Spex spectrophotometer. The absorption spectra were obtained by a Shimadzu UV 2450 PC spectrometer. The diffuse reflectance was measured by a UV - VIS NIR Cary 5G spectroscopy.

3. Results and discussion

XRD patterns of ZnS products are given in figure 1. The spectra show various diffraction peaks at 2θ values of 28.6°, 33.1°, 47.6° and 56.4° corresponding to the diffraction planes (111), (200), (220) and (311), respectively. The peaks were perfectly indexed to the cubic zinc blende phase of ZnS.

![Figure 1. XRD patterns of ZnS nanostructures with 1:0.7, 1:1 and 1:1.3 molar ratios of Zn$^{2+}$:S$^{2-}$.](image)

The distances $d_{hkl}$ between successive lattice planes are calculated from Wulf - Bragg relation:

$$2d_{hkl} \sin \theta = n \lambda , \quad (3)$$

where $\lambda$ is the wavelength of X-ray, $\theta$ is the angle of incidence and the integer $n$ is known as the order of the corresponding reflection. The cell constant of the ZnS crystallites was determined from the XRD patterns using the following formula:
The results shown in table 1 are slightly larger than that of the standard ZnS phase ($a = 5.398 \, \text{Å}$).

The information on the crystalline size has been obtained from the following Debye - Scherrer relations [4]:

$$L = \frac{0.9 \lambda}{\beta \cos \theta},$$

(5)

where $\beta$ is the full width at half maximum (FWHM) of the diffraction peaks. The grain sizes are estimated to be 13.1, 14.6 and 28.1 nm for sample 1, sample 2 and sample 3, respectively.

The TEM and HRTEM analysis gives more detailed information on the microstructures of the ZnS nanoparticles. The TEM images (figure 2) show that the subspherical nanoparticles have an average diameter of about 15, 20 and 35 nm for samples 1, 2 and 3, respectively. It indicated that the higher Zn$^{2+}$:S$^{2-}$ molar ratios are, the smaller particle sizes become. Thus, by controlling the molar ratio the particle size can be varied.

HRTEM images (figures 3a, b) of sample 1 show that ZnS nanoparticles are of good crystallinity. Fast Fourier transform (FFT) pattern shown in figure 3c indicates the observed on figure 3b lattice plane is (111) plane. Lattice plane spacing was estimated to be around 0.31 nm. This value is in good accordance with the result of the other authors [1, 5, 6].

Table 1. Lattice constants and nanocrystal sizes calculated from XRD patterns for sample 1, sample 2 and sample 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Plane</th>
<th>$d_{hkl}$ (Å)</th>
<th>$a$ (Å)</th>
<th>$\bar{a}$ (Å)</th>
<th>$L$ (nm)</th>
<th>$\bar{L}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (111)</td>
<td>3.12</td>
<td>5.41</td>
<td>5.41</td>
<td>13.68</td>
<td>13.08</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(220)</td>
<td>1.91</td>
<td>5.40</td>
<td>12.50</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(311)</td>
<td>1.63</td>
<td>5.41</td>
<td>13.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 (111)</td>
<td>3.12</td>
<td>5.41</td>
<td>5.41</td>
<td>13.70</td>
<td>14.57</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(220)</td>
<td>1.91</td>
<td>5.40</td>
<td>14.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(311)</td>
<td>1.63</td>
<td>5.40</td>
<td>15.09</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 (111)</td>
<td>3.13</td>
<td>5.41</td>
<td>5.41</td>
<td>29.20</td>
<td>28.06</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(220)</td>
<td>1.91</td>
<td>5.41</td>
<td>27.84</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>(311)</td>
<td>1.63</td>
<td>5.41</td>
<td>27.14</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 2. TEM images of ZnS nanostructures with different molar ratios of Zn$^{2+}$:S$^{2-}$
a) 1:0.7           b) 1:1          c) 1:1.3

The Selected Area Electron Diffraction (SAED) pattern of ZnS nanoparticles is shown in figure 3d. As expected, the SAED pattern shows a set of rings instead of spots due to the random orientation of the crystallites, which relate to diffraction from different planes of the ZnS nanocrystallites [7, 8].
SAED pattern shows many rings, among them the strongest four rings correspond to the (111), (200), (220) and (311) planes of the cubic phase of ZnS.

In order to study optical absorption property of the samples, the ZnS powders were ultrasonically dispersed in double distilled water. The optical absorption spectra of the samples are shown in figure 4. From the curves, we can see the shoulder near 330 nm in each spectrum. In the case of the sample 3, the particle grain size is larger than that of other samples, so the shoulder becomes a weak peak at 340 nm. The shoulder or peak of the spectra corresponds to the fundamental absorption edges in the samples, which can be used to estimate the band gap of material. From the absorption measurements the band gap were obtained as 3.76 eV (330 nm), 3.74 eV (332 nm) and 3.65 eV (339 nm) for the samples synthesized with Zn\(^{2+}\):S\(^{2-}\) molar ratios of 1:0.7, 1:1 and 1:1.3, respectively. The band gap values were slightly decreased due to the increase of particle size. The band gap energy blue-shift with respect to that of the bulk samples was attributed to the quantum size effect.

Figure 3. a), b) HRTEM images, c) FFT pattern and d) SAED image of ZnS nanopowder prepared with Zn\(^{2+}\):S\(^{2-}\) molar ratio of 1:0.7

Figure 4. Absorption spectra of ZnS nanostructures with 1:0.7, 1:1 and 1:1.3 molar ratios of Zn\(^{2+}\):S\(^{2-}\)

Figure 5. Diffuse reflection spectra of ZnS nanostructure with Zn\(^{2+}\):S\(^{2-}\) molar ratio of 1:0.7

Figure 5 shows the diffuse reflection spectrum of sample 1 with Zn\(^{2+}\):S\(^{2-}\) molar ratio of 1:0.7. It shows a strong drop in reflection in the UV range approximately 4 eV, corresponding to the valence-to-conduction band transitions of the ZnS nanostructure. In order to verify absorption of the sample, the Kubelka - Munk function was used.

\[ F(R) = \left( 1 - R \right)^{2} / \bar{R} = K / S \]  

where \( R \), \( K \) and \( S \) are the reflection, absorption and scattering coefficient, respectively. The \( K/S \) spectrum of the nanostructured ZnS derived from the Kubelka - Munk function is shown in the inset of
The value of the optical band gap can be calculated by extrapolating the Kubelka-Munk function to $K/S = 0$ [9]. Its optical band gap is calculated to be about 3.78 eV (328 nm). The band gap is slightly larger than the value 3.76 eV which is calculated from the absorption spectra.

Photoluminescence property of the samples was investigated at room temperature. Emission spectra of the samples with the excitation wavelength of 320 nm (3.87 eV) are shown in figure 6a. The spectra of sample 1 and sample 2 showed a broad band peaked at 489 nm, 498 nm, respectively, and a shoulder nearby 454 nm, while that of sample 3 showed only a broad band peaking at 530 nm.

Broadening of the emission peak could be attributed to both the size distribution and the increase of the surface states owing to the increase in surface to volume ratio for smaller nanoparticles [1]. The origin of the emission band centered at 490 nm was attributed to the Zn-vacancy [1, 5, 6, 9, 10]. Thus, the blue-green emission could be assigned to some self-activated defect centers related to Zn-vacancies.

For investigation of the luminescence mechanism causing the blue-green emission, PLE spectra monitored at wavelength of 500 nm have been recorded. Figure 6b shows the PLE spectra of the samples. The blue-green emission band can be excited both at energies near the band edge of the ZnS (the UV region) and at energies below the band edge (the visible region). In the visible region, for sample 1 two peaks at 359 nm (3.45 eV) and 390 nm (3.18 eV) were observed; but for sample 2 or sample 3 only one peak at 369 nm (3.36 eV) or 378 nm (3.28 eV), respectively, was obtained. These peaks are related to the defect states and the surface states located within the band gap. In the UV region, only for sample 3 shoulder at 332 nm (3.73 eV) related to the near-band-edge absorption was observed. For samples 1 and 2, absorption related to the near band edge was not exhibited. The reason of this fact is that the nanoparticles of samples 1 and 2 have smaller sizes than those of nanoparticles of sample 3; therefore, number of the surface states is increased due to the increase of the surface to volume ratio. In this case, excitation via the surface states is dominated.

### 4. Conclusions

Nanocrystalline ZnS have been successfully synthesized by a hydrothermal method. X-ray diffraction studies revealed that the synthesized particles have cubic zinc blende structure. The nanoparticle size increases from 13.1 nm to 28.1 nm with decreasing the Zn$^{2+}$:S$^{2-}$ molar ratio from 1:0.7 to 1:1.3. The band gap values increases from 3.65 eV to 3.76 eV with decreasing the nanoparticle size. The blue-green emission band in photoluminescence spectra is related to the zinc vacancy in the lattice.

### References

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