Luminescence and Structural Properties of ZnS:Cu Nanocrystals Prepared Using a Wet Chemical Technique

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Cu doped Zinc sulfide (ZnS:Cu) nanoparticles were prepared with a wet chemical synthesis by mixing the reactants in a double distilled water solvent. Mercaptopropionic acid was used as a capping agent. Properties of the particles were investigated using UV absorption, photoluminescence spectroscopy (PL), and X-ray diffraction analysis (XRD). The average particle size of the sample’s nanoparticles from the TEM image is 15.5 nm. The XRD pattern of the ZnS:Cu nanoparticles reveals a zinc-blende crystal structure at room temperature. The PL spectra includes four bands, due to the emission of traps and the surface state.

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I. INTRODUCTION

ZnS is an important II-VI, direct band gap semiconductor and is commercially important, having a wide optical band gap (3.7 eV [1]), rendering it a very attractive material for optical applications, especially in nanocrystalline form. Nanodimensional ZnS is found to exhibit excellent optical and optoelectronic properties which differ greatly from the bulk ZdS [2–4]. ZnS and ZnS:Cu are commercially used as catalysts [5–8] and phosphors, in thin film electroluminescence devices [9, 10], solar cells [11], flat panel displays [12, 13], light emitting and laser diodes [14, 15], optical sensors [16], and also biological labeling [17]. The study of the optical properties of ZnS:Cu nanocrystals is important for the development of nanocrystal phosphors with efficient luminescence and the understanding of the impurity-related optical transitions in semiconductor nanocrystals [18]. A variety of methods have been deployed in order to synthesize and control the size of nanoparticles [19–22].

The aim of the present work is to improve the synthesis method of Cu doped ZnS nanoparticles and study the effect of doping on the physical properties. The effects of the Cu concentration on the luminescence intensity and XRD are discussed.

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II. EXPERIMENT

II-1. Chemicals
Zinc chloride (Anhydrous, Merck), Copper(II) chloride dihydrate and sodium sulfide.9H2O (Merck), mercaptopropionic acid (Fluka).

II-2. Synthesis
In a dry nitrogen atmosphere, 50 ml of CuCl2 was added to 50 ml of an aqueous solution of ZnCl2, whilst being stirred. Mercaptopropionic acid (MPA) was added dropwise into the mixture, and an aqueous solution was also added as a surfactant in order to prevent nanoparticle agglomeration in the solution. Then 50 ml of Na2S solution was injected drop by drop into the above solution whilst being stirred. The final mixture was stirred for 60 min. The ZnS:Cu nanoparticles were then separated by centrifugation (3500 rpm for 10 min) and washed with acetone to get rid of any unreacted solvent. For drying, the particles are kept in a petri dish for about 12 h.

II-3. Characterization
Absorption spectra were measured using a Scan Cary 100 UV-vis spectrometer. X-ray diffraction (XRD) measurements were performed on a Philips PW 1840 diffractometer with Cu-Kα radiation (40 kV, 40 mA), scan rate 0.02 2θ/s within a range of 2θ of 20° – 70°. XRD patterns were recorded using an automatic divergence slit system. The photoluminescence (PL) measurement was carried out at room temperature using a Shimadzu RF-5000. Transmission electron microscopy (TEM) images were taken using a Philips CM10 system.

III. RESULTS AND DISCUSSION
The XRD patterns of the Cu doped ZnS in different Cu concentrations are depicted in Figure 1. The three diffraction peaks corresponded to the (111), (220), (311) planes, indicating a zinc-blende crystal structure (JCPDS 05-0566, a = 0.5406 nm). Also there are two weak peaks at 39.9° and 42.2° corresponding to the (411) and (422) planes, respectively [23]. In addition, in CdS:Cu (9%) all the peaks are shifted to higher diffraction angles due to the strain of a high concentration of Cu. The size of ZnS:Cu nanocrystals was approximately estimated by Hall’s method [24]:

\[
\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{2\varepsilon \sin \theta}{\lambda},
\]

where β is the measured full width at half maximum (FWHM) in radians, θ is the Bragg angle of the diffraction peak, λ is the X-ray wavelength, D is the grain size, ε is the effective residual strain. Figure 2 represents a typical plot of \(\beta \cos \theta/\lambda \) vs. \(\sin \theta/\lambda \) for ZnS:Cu nanoparticles. ε and D can be estimated from the slope of the straight line and the intercept on the \(\beta \cos \theta/\lambda \) axis, respectively.

The estimated values for the grain size and the effective residual strain are given in
FIG. 1: X-ray diffraction patterns of the ZnS:Cu (1%, 3%, 5%, 7%, 9%) nanocrystals. The samples have a zinc-blende crystal structure.

Table I.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Grain Size (nm)</th>
<th>Strain</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS:Cu(1%)</td>
<td>12.53</td>
<td>$5.93 \times 10^{-2}$</td>
</tr>
<tr>
<td>CdS:Cu(3%)</td>
<td>14.03</td>
<td>$8.5 \times 10^{-2}$</td>
</tr>
<tr>
<td>CdS:Cu(5%)</td>
<td>15.32</td>
<td>$4.53 \times 10^{-2}$</td>
</tr>
<tr>
<td>CdS:Cu(7%)</td>
<td>16.38</td>
<td>$4.96 \times 10^{-2}$</td>
</tr>
<tr>
<td>CdS:Cu(9%)</td>
<td>18.79</td>
<td>$4.48 \times 10^{-2}$</td>
</tr>
</tbody>
</table>

The most accurate $d$-spacings are those calculated from the high-angle peaks. In this case, the peak of the (111) plane was used and the $d$-spacing for the samples was calculated...
using Bragg’s law:

$$d_{hkl} = \frac{\lambda}{2 \sin \theta}. \quad (2)$$

The lattice parameters $a$ and $c$ were calculated by the relation [25]:

$$d_{111} = \frac{2\pi}{|G_{111}|}, \quad (3)$$

$$\mathbf{G}_{hkl} = h \mathbf{A} + l \mathbf{B} + k \mathbf{C} \quad (hkl) = (111) \quad \mathbf{G}_{111} = \frac{4\pi}{a} j + \frac{2\pi}{c} k, \quad (4)$$

$$\frac{c}{a} = 1.633. \quad (5)$$

Here, $\mathbf{G}$ is the reciprocal lattice vector.
A dislocation is a crystallographic defect, or irregularity, within a crystal structure. The presence of dislocations strongly influences many of the properties of materials. The dislocation density from the relation was also calculated [26]:

$$\delta = \frac{15\epsilon}{aD}.$$ (6)

The calculated $d$-spacing, lattice parameters, and the dislocation of samples are given in Table II.

<table>
<thead>
<tr>
<th>Samples</th>
<th>$d$ (nm)</th>
<th>$a$ (nm)</th>
<th>$c$ (nm)</th>
<th>$\delta$ ($m^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CdS:Cu(1%)</td>
<td>0.3096</td>
<td>0.6476</td>
<td>1.0576</td>
<td>1.72 × 10^{18}</td>
</tr>
<tr>
<td>CdS:Cu(3%)</td>
<td>0.3086</td>
<td>0.6454</td>
<td>1.0539</td>
<td>2.77 × 10^{18}</td>
</tr>
<tr>
<td>CdS:Cu(5%)</td>
<td>0.3091</td>
<td>0.6465</td>
<td>1.0558</td>
<td>1.13 × 10^{18}</td>
</tr>
<tr>
<td>CdS:Cu(7%)</td>
<td>0.3075</td>
<td>0.6433</td>
<td>1.0504</td>
<td>1.67 × 10^{18}</td>
</tr>
<tr>
<td>CdS:Cu(9%)</td>
<td>0.3139</td>
<td>0.6566</td>
<td>1.0722</td>
<td>2.19 × 10^{18}</td>
</tr>
</tbody>
</table>

It is necessary to validate the particle size by a direct measurement such as TEM, which can reveal the size and morphology of the nanoparticles. Figure 3a gives the TEM image of the ZnS:Cu(7%) nanoparticles. As is typically shown in the image, most of the particles are round in shape. The particle size distribution as obtained from the TEM image is demonstrated in Figure 3b. We have taken 100 particles for calculating the particle size distribution. As can be seen from Figure 3b, the diameter of the maximum number of particles lie in the 14–16 nm region, and the average size of the particles is 15.5 nm, as obtained from a log-normal fitting of the particle size distribution.

In Figure 4 the absorption spectra of ZnS:Cu nanoparticles with different molar ratios of Cu to Zn were compared. As shown, the exitonic peak has a red shift when the doping percentage increases from 1% to 9%. In the present study the samples are nanostructured in nature and are expected to reveal a kind of quantum confinement effect that normally causes a blue shift in the optical band gap. The inverse relationship between the cut-off edge and the crystallite size confirms this assumption. In the meantime, the variation of the band gap due to doping may be associated with different phenomenological events occurring with the process. On the one hand, the increase in the band gap or blue shift can be explained by the Burstein-Moss effect [27]. The Burstein-Moss effect results from the Pauli Exclusion Principle, and is seen in semiconductors as a shift with increasing doping of the band-gap defined as the separation in energy between the top of the valence band and the unoccupied energy states in the conduction band. The shift arises because the Fermi energy ($E_F$) lies in the conduction band for heavy n-type doping (or in the valence band for p-type doping). The filled states therefore block thermal or optical excitation. Consequently the measured band gap determined from the onset of interband absorption
FIG. 3: (a) TEM image. (b) The particle size distribution of ZnS:Cu(7%) nanoparticles.
FIG. 4: Absorption spectra of ZnS:Cu nanoparticles for different concentrations of Cu.

moves to higher energy (i.e. suffers “a blue shift”) [28]. On the other hand, band gap shrinkage also happens in doped semiconductors (called band gap renormalization) as a result of mutual exchange and Coulomb interactions between the added free electrons in the conduction band and electron-impurity scattering [29]. Considering the observed red shift of the band gap with Cu content, it would be more plausible to say that the band gap renormalization mechanism is dominant rather than the mentioned Burstein-Moss effect. Meanwhile, the blue shift of the absorption edges and the development of states within the gap were also evident when Cu ions were substituted into the ZnS lattice. This result is in agreement to our previous work [30]. The narrower excitonic band observed for ZnS:Cu(3%) suggests that the particle size distribution is more monodisperse.

From the strong absorption edge, the particle size has been assessed by using the hyperbolic band model [31]:

$$R = \sqrt{\frac{2\pi^2h^2E_{gb}}{m(E_{gn}^2 - E_{gb}^2)}}. \quad (7)$$

Here, $R$ is the quantum dot radius ($2R$ is the diameter and hence the particle size), $E_{gb}$ is the bulk band gap, $E_{gn}$ is the quantum dot band gap (calculated from the strong absorption edge), $h$ is Planck’s constant, and $m*$ is effective mass of the specimen ($3.64 \times 10^{-31}$ Kg
for ZnS [32]). In Table III, the optical size of the samples is given. It can be noted that the particles’ size, determined from UV-vis absorption analysis are in the same size regime as that obtained from the X-ray line width measurements, as described above.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Cu 1%</th>
<th>Cu 3%</th>
<th>Cu 5%</th>
<th>Cu 7%</th>
<th>Cu 9%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical size(nm)</td>
<td>11.06</td>
<td>13.86</td>
<td>14.78</td>
<td>15.63</td>
<td>17.48</td>
</tr>
</tbody>
</table>

FIG. 5: Emission spectra of ZnS:Cu nanoparticles for different concentrations of Cu. The excitation wavelength is 260 nm.

Cu-doped ZnS bulk crystal has two main well-known emission bands, namely the blue band and the green band [33–35]. Peka and Schulz reported on the blue, green, and orange-red light emission for Cu-doped ZnS bulk crystal [36]. These results indicate the complicated energy level structure of Cu-doped ZnS. Some work on Cu doped ZnS nanocrystals showed that the PL spectrum consists of two emission bands which were centered at 460 and 507 nm [37], 450 and 530 nm [9, 38], 420–430 and 490–510 nm [39]. They attributed the blue emission band to a transition from the conduction band (CB) of ZnS to the ‘t$_2$’ state of Cu and the green emission to the transition from the shallow donor (sulfur-vacancy)
to the ‘t$_2$’ state [40]. Peng et al. reported three band emissions at 411–414 nm, 450–455 nm, and 497–512 nm [41]. They attributed the three band emissions to transitions from the shallow donor to the valence band (VB), the CB to the trap states emission of ZnS, related with the native zinc vacancy (V$_{zn}$), and the shallow donor to the ‘t$_2$’ state. These observations are different from those reported by Khosravi et al. [42] and Huang et al. [43]. In their work, a single emission band has been observed in ZnS:Cu nanocrystals. Therefore, it might be inferred that these differences for the emission spectra reported by different authors arise from surface or impurity defect levels [10] and trap states emission of ZnS (V$_{zn}$) [41] in the band gap due to different synthesis techniques. The emission spectra of ZnS:Cu nanocrystals for different concentrations of dopants are illustrated in Figure 5. As shown, the PL spectra consists of four emission bands. On the whole, with regard to the mentioned explanations, it seems that the first peak in the PL spectra (450 nm) arises from the recombination between the shallow donors (sulfur-vacancy) to the valence band. The second peak (462 nm) is attributed to transition from the CB to the ‘t$_2$’ state of Cu$^{2+}$. The third peak (486 nm) is due to recombination between the CB to trap states emission of ZnS (V$_{zn}$). The forth peak (531 nm) arises from the shallow donor (sulfur-vacancy) to the ‘t$_2$’ state.

As shown in Figure 5 the PL intensity increased as the Cu concentration increased from 1% to 5%. When the Cu concentration is 7% and 9%, the PL intensity is diminished. This may be due to the formation of CuS, though the XRD measurement did not detect the existence of the CuS phase. CuS particles not only act as nonradiative recombination centers, but also reduce the number of Cu$^{2+}$ ions that are optically active luminescence.

![FIG. 6: Shematic energy level diagram showing the emission mechanism in ZnS:Cu nanoparticles.](image-url)
centers in ZnS nanoparticles [41]. Therefore the PL intensity is considerably decreased when the Cu$^{2+}$ concentration is 7% and 9%.

The schematic energy level diagram of ZnS:Cu nanoparticles is shown in Figure 6. This figure explains the emission mechanism of the ZnS:Cu nanoparticles and illustrates the above assignment.

IV. CONCLUSIONS

Well dispersed ZnS:Cu nanoparticles were prepared using a wet chemical technique in doubled distilled water solution using MPA as a capping reagent. We investigated the influence of the Cu concentration on the absorption and emission spectra of the samples. The XRD results show that typical ZnS:Cu nanoparticles have the zinc-blend structure. From the TEM image, most of the particles are round in shape, with an average size of about 15.4 nm. The PL spectra consists of four emission bands due to recombination between the shallow donor (sulfur-vacancy) to the valence band, conduction band to the ‘$t_2$’ state of Cu$^{2+}$, conduction band to trap states emission of ZnS ($V_{zn}$), and shallow donor (sulfur-vacancy) to the ‘$t_2$’ state.

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References

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