Structural and Optical Properties of $\text{ZnO}_{1-x}\text{S}_x$ Nanoparticles

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We describe a method for synthesis of semiconductor $\text{ZnO}_{1-x}\text{S}_x$ (ZOS) nanoparticles by reaction of hydrogen sulfide with a mixture of ethanol solutions of zinc acetate and sodium hydroxide salts. The nanoparticle composition, structure and optical properties are investigated for different ratios of the salt content in the mixture. Structure of ZOS nanoparticles changes from pure wurtzite ($x \leq 0.1$) to sphalerite ($0.5 \leq x \leq 1$). Between $x = 0.1$ and $0.5$ wurtzite and sphalerite phases coexist. According to the transmission electron microscopy as prepared nanoparticles have spherical shape and size of 10–20 nm in diameter. Cathodoluminescence spectra show the emission peaks in the UV- and the green wavelength regions. The band gap of ZOS nanoparticles nonlinearly depends on the sulfur content as was evaluated from the diffuse reflectance measurements.

Keywords: Zinc Oxide, Nanoparticles, Sulfur Doping, Solid Solutions, Luminescence.

1. INTRODUCTION

Nanostructures based on zinc sulfide (ZnS) and zinc oxide (ZnO) have attracted considerable interest due to their unique electronic and optical properties. Bulk crystals of ZnS and ZnO are characterized by wide direct band gaps, i.e., $E_g(\text{ZnO}) = 3.3$ eV and $E_g(\text{ZnS}) = 3.6$ eV$^1$ and large exciton binding energies, i.e., $E_{\text{X}1}(\text{ZnO}) = 60$ meV, $E_{\text{X}1}(\text{ZnS}) = 40$ meV$^2$. A strong exciton emission in ultraviolet (UV) spectral region is observed for such compounds even at a room temperature$^{1,2}$. Nanocrystalline ZnS and ZnO are promising for fabrication of optoelectronic devices emitting in the UV and visible ranges. The substitution of oxygen or zinc in ZnO by isoelectronic anions or cations changes the band gap position. For example, the replacement of Zn by Cd ($\text{Zn}_1-x\text{Cd}_x\text{O}$) and by Mg ($\text{Zn}_1-x\text{Mg}_x\text{O}$) modifies the band gap clearly toward lower ($x = 0.33$, $E_g = 3$ eV) and higher energies ($y = 0.07$, $E_g = 4$ eV), respectively$^3$. Anion doping in ZnO, i.e., replacing oxygen by sulfur or selenium, has been reported recently$^4-9$. Due to the large differences of electronegativity and Bohr radius between O and S (Se) the band gap of $\text{ZnO}_{1-x}\text{S(Se)}_x$ would be possible to adjust in a wide energy range with low fraction of S or Se in ZnO for emission in the UV-visible range.

Basically, the synthetic procedure of the solid solutions $\text{ZnO}_{1-x}\text{S}_x$, described in the literature, concerns with the synthesis of thin films. For example, $\text{ZnO}_{1-x}\text{S}_x$ films ($x = 0 \div 1$) were fabricated by supplying ZnS species from laser ablation of a ZnS target during ZnO growth$^7$. It has been established that the band gap energy can be adjusted down to $2.6 \pm 0.1$ eV for $x = 0.45$. Similar dependence was observed for $\text{ZnO}_{1-x}\text{S}_x$ nanophosphors grown by solvothermal autoclave technique at $225$ °C and 1000 psi of N$_2$ pressure$^8$.

However, the most simple and economic synthetic procedure of ZnO-based nanomaterials is a synthesis from alcohol solutions$^{10-12}$ where the growth of nanoparticles is slow and controllable. It is carried out at a room and even lower temperatures and does not require any special equipment. So, in the present work the synthesis of ZnO-based nanoparticles over a wide composition range is described and structural and optical properties of the nanoparticles as well as the composition dependence of the band gap energy in the ternary system are investigated.

2. EXPERIMENTAL SECTION

ZOS nanoparticles were prepared via a wet chemical method. Zinc acetate dehydrate ($\text{Zn(CH}_3\text{COO)}_2 \cdot 2\text{H}_2\text{O}$, 99.9% purity), iron (II) sulfide (FeS, 99.9% purity),...
sodium hydroxide (NaOH, ≥ 98% purity, pellets, anhydrous), hydrochloric acid (HCl, 37%), absolute ethanol (≥ 99.8%) were used.

A typical preparation process was as follows: ν(Zn(CH₃COO)₂·2H₂O) = 0.005 mole and separately ν(NaOH) = 2(0.05 – x) mole were dissolved in 100 ml of ethanol under vigorous stirring at room temperature respectively. It should be noted that amount of sodium hydroxide was not sufficient for complete reaction with zinc acetate and was varied aiming to change the S/O molar ratio in the ZOS nanoparticles. Sodium hydroxide alcohol solution was slowly added into the zinc acetate solution aiming to change the S/O molar ratio in the ZOS nanoparticles. Sodium hydroxide alcohol solution was slowly added into the zinc acetate dehydrate solution. Then as-prepared clear solution was slowly added into the zinc acetate solution. Sodium hydroxide alcohol solution was slowly added into the zinc acetate dehydrate solution. Then as-prepared clear solution was slowly added into the zinc acetate solution. Sodium hydroxide alcohol solution was slowly added into the zinc acetate dehydrate solution. Then as-prepared clear solution was slowly added into the zinc acetate solution. Sodium hydroxide alcohol solution was slowly added into the zinc acetate dehydrate solution. Then as-prepared clear solution was slowly added into the zinc acetate solution.

Compared to ZnO, ZnS has a lower solubility, which can make fast reducing rate of zinc cations, which can be used to control the growth of nanoparticles. At the first stage, when the alcohol solution of NaOH was added to the alcohol solution of Zn(CH₃COO)₂·2H₂O, the formation of Zn-OAc primary nanoparticles occurs. Then, during the H₂S bubbling through the solution the growth of primary nanoparticles is promoted by non-reacted zinc acetate and thus ZnO₁₋ₓSₓ nanoparticles are formed.

TGA experiments were performed by using a Perkin Elmer Pyris Diamond thermal analyzer. Crystal structure identification was obtained by x-ray diffraction (XRD) method using a Rigaku D/Max 2500 diffractometer with CuKα radiation in the 2θ range from 10° to 80°. Transmission electron microscopy (TEM) was carried out by using a LEO912 AB OMEGA electron microscope. Energy dispersive X-ray microanalysis was performed by using a SUPRA system. UV-visible diffuse reflectance spectra were recorded with a Lambda 35 spectrometer in the range of wavelength from 200 to 800 nm. Cathodoluminescence spectra were measured by using an XL 30S FEI high resolution scanning electron microscope (HRSEM) with MonoCl spectroscopy system.

### 3. RESULTS AND DISCUSSION

XRD patterns of ZO, ZOS5, and ZOS10 samples (Fig. 1, curves a, b, and c, respectively) show only peaks of the ZnO wurtzite structure (w-ZnO). Increasing the sulfur content from 0 to 10 molar% resulted in a shift the peaks to the lower angles. The XRD pattern of ZOS30 sample (Fig. 1(d)) shows peaks of both wurtzite and sphalerite phases (sph-phase). The XRD patterns of ZOS50 and ZS samples (Fig. 1, curves e, f) show only sph-phase peaks. The XRD data are used to determine lattice parameters of the samples, which are presented in Table I.

According to the TEM results (see Fig. 2) the prepared ZOS nanoparticles are characterized by mainly spherical shape with the average radius of about 10–20 nm, which is not sensitive to the sulfur content. All crystallographic planes in the electron diffraction pattern of ZOS5 sample correspond to those of ZnO (see inset in Fig. 2).

The sulfur content in the ZOS samples was determined by two methods, i.e., TGA and energy-dispersive X-ray analysis (EDX). Results of the quantitative analysis are presented in Table I. Figure 3 presents TGA curves for ZOS5 and ZS samples. At the first stage in the range from 50 to 300 °C the removal of adsorbed water and acetate groups from the surface of nanoparticles occurs. Then, in the range from 450 °C to 1000 °C ZnS is oxidized on air with the formation of ZnO. The sulfur content was determined from the mass loss taken in the temperature range

### Table I. Notation and data on the investigated samples: lattice parameters, a, c; the sulfur contents, x(S), obtained by means of EDX, TGA; the band gap, E_g, from the data of UV-visible spectroscopy.

<table>
<thead>
<tr>
<th>Notation of sample</th>
<th>Nominal content (Å)</th>
<th>x(S) by EDX (%)</th>
<th>TGA (%)</th>
<th>E_g (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZO</td>
<td>ZnO</td>
<td>3.253(2)</td>
<td>5.212(2)</td>
<td>3.25(2)</td>
</tr>
<tr>
<td>ZOS5</td>
<td>ZnOₓSₓ</td>
<td>3.252(7)</td>
<td>5.212(9)</td>
<td>4 ± 2</td>
</tr>
<tr>
<td>ZOS10</td>
<td>ZnOₓSₓ</td>
<td>3.252(7)</td>
<td>5.207(9)</td>
<td>3.01(2)</td>
</tr>
<tr>
<td>ZOS50</td>
<td>ZnOₓSₓ</td>
<td>3.24(6)</td>
<td>—</td>
<td>3.27(2)</td>
</tr>
<tr>
<td>ZS</td>
<td>ZnS</td>
<td>5.38(4)</td>
<td>—</td>
<td>100</td>
</tr>
</tbody>
</table>

![Fig. 1](image) XRD patterns of samples ZOS5 (a), ZOS10 (b), ZOS30 (c), ZOS50 (d), and ZS (e).
of the oxidation of ZnS in accordance with the following reaction:

\[
\text{ZnO}_{1-x}\text{S}_x + 1.5x\text{O}_2 = x\text{SO}_2 + \text{ZnO}
\]  

(1)

Note that the sulfur content of ZOS5 sample determined from TGA agrees with the nominal content with ±2 molar % accuracy (see Table I).

The band gap dependence on the sulfur content of ZOS nanoparticles was evaluated by analyzing the diffuse reflectance spectra. Figure 4 shows the corresponding absorption coefficient spectra for samples ZOS5 and ZOS10. For allowed direct transitions the spectrum of optical absorption coefficient, \(\alpha(h\nu)\), is known to be described by the following equation:

\[
(\alpha h\nu)^2 = A(h\nu - E_g)
\]  

(2)

where \(h\nu\) is the photon energy, \(E_g\) is the band gap, and \(A\) is a constant, which depends on type of the optical transition.

The absorption spectra shown in Figure 4 demonstrate typical edges associated with the direct absorption in semiconductor materials. By extrapolating the linear part of \((\alpha h\nu)^2\) to the energy axis the value of \(E_g\) can be estimated. Figure 5 shows the optical band gap of ZOS nanoparticles as a function of the sulfur content. The value of \(E_g\) decreases with increasing the sulfur content from \(x = 0.05\) to 0.3. For ZOS nanoparticles with sphalerite structure, ZOS50 sample, the band gap is equal 3.27 that more than bandgap values of ZOS samples with wurtzite structure., indicating that the band gap decreases with increasing the sulfur concentration for the sample of \(w\)-ZOS and increases for ones with \(sph\)-ZOS. It is also seen from Figure 5 that the band gap energy of \(w\)-ZOS decreases greatly when a small amount of sulfur incorporate into \(\text{ZnO}\), implying that ZOS nanoparticles are suitable material for preparation of \(\text{ZnO}\)-based blue light emitters.

![Fig. 2. TEM image of ZOS10 sample. Inset shows a section of the corresponding ED pattern.](image)

![Fig. 3. TGA curves for samples ZOS5 (a) and ZS (b).](image)

![Fig. 4. UV-visible absorbance spectra of samples ZOS5 (a) and ZOS10 (b). Inset shows the same spectra, which are plotted as functions of \((\alpha h\nu)^2\) versus \(h\nu\).](image)

![Fig. 5. Band gap energy of ZOS nanoparticles determined from the UV-visible spectra as a function of the sulfur content. Vertical dashed lines mark edges of the region of mixed \(w\)- and \(sph\)-phases.](image)
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Fig. 6. Cathodoluminescence spectra of samples of ZOS5 (a) and ZOS10 (b).

Figure 6 shows cathodoluminescence (CL) spectra of ZOS5 and ZOS10 samples. Two CL peaks at 386 nm (3.21 eV) and at 500–560 nm (2.5–2.2 eV) are detected for the both samples. The first peak is obviously the excitonic peak which is close to the band gap of ZnO and its spectral position correlates with the band gap value estimated from the diffuse reflectance measurements (see Table I). The “green” CL peak at 500–560 nm can be attributed to the light emission mediated by anion vacancies. The increasing in sulfur content of $w$-phase leads to the disappearance of UV-emission and the shift of luminescence to the visible range (Fig. 6(b)). Moreover the CL intensity of the peak at 500–560 nm increases with an increase of sulfur concentration. It indicates that incorporation of sulfur in ZnO leads to the anion vacancy formation, shifting the luminescence spectrum to the blue-green visible range.

4. CONCLUSIONS

ZnO$_{1-x}$S$_x$ nanoparticles are synthesized without any surfactants in ethanol solvent. Their crystalline structure was determined by using X-ray and electron diffraction experiments. ZnO$_{1-x}$S$_x$ nanoparticles with $x = 0–0.1$ are characterized by the wurtzite structure, while those with $x \geq 0.5$ possess the sphalerite structure. According to the transmission electron microscopy results the particles have spherical shape with size of 10–20 nm in diameter. The optical absorption and cathodoluminescence spectra of the investigated samples indicate that ZnO$_{1-x}$S$_x$ nanoparticles could be used as nanophosphors in the blue-green wavelength region.

References and Notes


Received: xx Xxxx xx. Accepted: xx Xxxx xx.