Synthesis of AgInS$_2$ semiconductor nano crystals by solvothermal method

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Abstract. A solvothermal route was proposed to synthesis nanocrystalline silver indium sulfide (AgInS$_2$) using ethylenediamine as a solvent. The reaction was carried out in an autoclave in the temperature of 200 °C with AgCl, Indium (In) and sulfur (S) as reactants. Powder X-ray diffraction studies show that the synthesized nano crystals belongs to orthorhombic phase AgInS$_2$ with cell parameters $a=7.001$ Å, $b=8.278$ Å, and $c=6.698$ Å. High resolution scanning electron microscope (HR-SEM) and Energy Dispersive X-ray (EDX) analyses have been carried out for the synthesized nano crystals to find the surface morphology and composition respectively. The band gap of the synthesized nano crystals was determined from UV-Vis spectrum and photoluminescence spectrum. The melting point of the AgInS$_2$ nano crystals was found to be 956°C using differential thermal analysis (DTA).

1. Introduction

AgInS$_2$ is a semiconductor compound of the I–III–VI$_2$ groups, which crystallizes in chalcopyrite and orthorhombic ordered phases. It might be used in light emitting diodes, nonlinear optics and solar cells [1]. Semiconductor materials, such as AgInS$_2$, CuInS$_2$ and CuInGaSe$_2$ have been broadly investigated for photovoltaic device applications [2, 3]. So far, substantial attempts were made to the preparation of AgInS$_2$ thin films and single crystals [4]. As a potential different, AgInS$_2$ based chalcopyrite semiconductor is also likely to make a good solar-cell absorber layer because of its large absorption coefficient [5]. To realize large amounts of size-controlled semiconductor nanoparticles, chemical synthesis methods are suitable, and are mainly well developed for type II–VI semiconductor nanoparticles. Indeed, the optical properties of CdS nanoparticles have been studied for a long time [6]. However, conventional binary-compound semiconductors contain toxic elements such as Cd, Hg, Pb, Te, Se and As. Hence, nontoxic and semiconducting materials are required for the perspective of control of hazardous substances, such as I–III–VI$_2$ chalcopyrite semiconductors mainly CuInS$_2$, AgGaS$_2$, AgInS$_2$ etc, are the promising and alternative materials. Much interest has been decided on chalcopyrite semiconductors as an applicant for solar cell materials, because they have direct band gaps with energies well matched to the solar spectrum, high absorption coefficients and high environmental stability [7, 8]. In the present work solvothermal method has been adopted for the synthesis of AgInS$_2$ nano crystals using ethylenediamine as a solvent. We discuss the formation of AgInS$_2$ nano crystals, optical and thermal properties.

2. Experimental

2.1. Synthesis of AgInS$_2$ nano crystals

Analytical grade of Silver chloride (AgCl), Indium (In) and Sulphur (S) were selected as the reactants. In a characteristic procedure 1:1:2 mole ratio of AgCl, In and S were put into a stainless steel...
The autoclave was then filled with ethylenediamine up to 85% of the total volume. The autoclave was maintained at 200 °C for 8 hrs and allowed to cool to room temperature. The precipitate was separated by filtration and then washed sequentially with carbon disulfide, absolute ethanol and distilled water to remove residual impurities such as S and Cl. A dark brown color AgInS$_2$ powder was obtained after drying at 80 °C for 2 hrs. The final products were collected and subjected to further investigation by using powder X-ray diffractometer (SEI FERT) JSO DEBYEFLEX 2002 model with CuK$_\alpha_1$ radiation (1.541 Å). The accelerating voltage and the applied current were 40 kV and 30 mA respectively. The surface morphology of as synthesized samples was investigated using FEI Quanta FEG 200 HR-SEM. The chemical compositions of the samples were studied using EDX system connected with a HR-SEM operating at an accelerating voltage of 30 keV. UV-Vis absorption spectrum has been carried out using Cary 5E high resolution spectrophotometer. The emission spectrum was recorded using JOBIN - YUON Flurolog-3-11spectroflurometer and DTA analysis was carried out by using Netzsch STA 409 c/cd thermal analyzer at the heating rate of 10°C/min in the Nitrogen atmosphere.

3. Results and discussion

3.1. X-ray diffraction

Figure 1 shows the XRD pattern of as synthesized AgInS$_2$ nano crystals by solvothermal method. All the diffraction peaks could be indexed to the orthorhombic AgInS$_2$ phase with cell parameters $a$ = 7.001 Å, $b$ = 8.278 Å and $c$ = 6.698 Å in agreement with reported data in the literature (JCPDS, 25-1328). The XRD peak intensity of (002) plane was relatively higher than the other planes. Whereas, no characteristic peaks of other impurities such as In and Ag$_2$S were observed. The broad peak indicates polycrystalline behaviour of the particles. From this pattern, the scherrer’s equation gives the crystalline size 21.31 nm of (002) plane.

![Figure 1. XRD pattern of AgInS$_2$.](image)

3.2. Surface morphology analysis

The surface morphology of as synthesized nano crystalline AgInS$_2$ are shown in figure 2. It can be seen that nano crystalline AgInS$_2$ consist of agglomerate like flower structure. The diameter of the particles is in the range around 20-30 nm in accord with the XRD result.
3.3. Composition analysis
Figure 3 Shows the typical EDX spectrum of as synthesized nano crystalline AgInS$_2$. The results showed that the sample was composed of only Silver (Ag), Indium (In), Sulfur (S) elements are in the following molar ratio 24.85: 26.37: 48.85, which is more close to the stoichiometric composition. No apparent impurities like chloride and elemental sulfide could be detected in the samples.

3.4. UV-Vis absorption spectrum
Figure 4 shows the UV-Vis absorption spectrum of as synthesized AgInS$_2$ nano crystals and the absorption edge was observed at approximately 590 nm. Inset of the figure 4 shows $\alpha(h\nu)^2$ versus photon energy examined by absorption spectrum, with $\alpha$ and $h\nu$ being the absorption coefficient and photon energy respectively. Band energy ($E_g$) 2.08 eV can be calculated using the following equation $(\alpha h\nu)^2 = (h\nu - E_g)$. As compared with bulk band gap of 1.98 eV the band gap of obtained nano crystals was widened approximately 0.1 eV due to quantum size effect [9].

3.5. Photoluminescence (PL) spectrum
The photoluminescence spectrum of the synthesized nano crystals were obtained at the excitation wavelength of 590 nm using xenon as a source and it is shown in the Figure 5. An emission peak
located around 620 nm (1.99 eV) were approximately 0.09 eV smaller than the optical band gap it is due to the electron hole recombination pair.

3.6. Differential thermal analysis (DTA)
As synthesized AgInS$_2$ nano crystalline powder was carried out using DTA in nitrogen atmosphere with a gas flow rate of 50 cm$^3$/min. The heating rate was 10 °C/min. Al$_2$O$_3$ was used as a standard to measure the absolute value of temperature reading. DTA curve of AgInS$_2$ indicates only one sharp endothermic peak at 956 °C corresponding to the melting point of the material.

![DTA curve of AgInS$_2$](image)

**Figure 6.** Differential thermal analysis of AgInS$_2$.

4. Conclusions
Ternary AgInS$_2$ nano crystals were synthesized by solvothermal method using ethylenediamine as a solvent. The formation of nano crystals were confirmed with powder XRD studies and the cell parameter shows that these nano crystals possess orthorhombic system. HR-SEM analysis indicates the as synthesized nano crystals consist of flower like structure. The stoichiometric composition of the synthesized AgInS$_2$ nano crystals was determined using EDX analysis. UV-Vis absorption spectrum of AgInS$_2$ nano crystals show an absorption peak around 590 nm. The emission band appears at 620 nm (1.99 eV) were determined from PL spectrum is due to the electron hole recombination pair. The melting point of the AgInS$_2$ was found to be 956°C using DTA.

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