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Solvothermal Synthesis and Characterization of Flower-Like β-In_2S_3 Microparticles

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Flower-like β-In_2S_3 particles have been successfully synthesized *via* solvothermal process by using acetylacetone-water solvent mixture. The products were characterized by X-ray diffraction, scanning electron microscopy, reflectance spectra. X-ray diffraction analysis confirms the formation of cubic β-In_2S_3. Microstructural investigation with SEM indicated that the particle size increases with increasing reaction time. The optical band gap determined from reflectance spectra was found to have values within the range of 2.34-2.49 eV.

Keywords: β-Induim sulphide, Solvothermal synthesis, Acetylacetone-water solvent system, Microstructure, Optical properties.

INTRODUCTION

β-Induim sulphide (In_2S_3), a wide band gap (2-2.45 eV) n-type semiconductor, is an important material for optoelectronic and photovoltaic applications [1]. It is used for many technological applications due to its stability, wider band gap and photoconductive behaviour [2,3]. It can be used as an effective nontoxic substitute for cadmium sulfide (CdS) in Cu(In,Ga)Se_2 based solar cells [4]. Besides, it has applications for preparation of green and red phosphors for the manufacture of picture tubes for colour televisions [5,6].

As the unique properties of material are highly dependent on their size and shape, various techniques were used for the synthesis of morphology controlled bulk and nanoforms of β-In_2S_3 [1,7-12]. In the present work, we propose a convenient solvothermal method to synthesize flower-like β-In_2S_3 microparticles by using acetylacetone-water solvent mixture at 180 °C for 12-18 h. The products were characterized by microstructural and optical study.

EXPERIMENTAL

Indium(III) chloride and thiourea were used as the precursor materials of In and S, respectively. Indium chloride was prepared from indium metal (Plasma Materials, USA, 99.999 %) and hydrochloric acid (International Chemicals, L.R.). About 3 mM of indium chloride and 6 mM of thiourea were added into a Teflon-lined stainless steel autoclave, which was filled up to 90 % of the total volume (85 mL) with a 50:50 mixture of acetylacetone and water solution. The autoclave was maintained at 180 °C for 10-18 h and cooled at room temperature. According to the reaction time, such as 10, 12 and 18 h, the synthesized samples were named as I, II, III. After solvothermal treatment, the obtained yellow precipitate was washed with water and absolute alcohol for several times. The washed precipitate was dried at 100 °C for 3 h in vacuum. The synthesized samples were characterized by XRD (Seifert, 3000P) using monochromatic CuK_α radiation (Ni filter). The morphology and particle size of the samples were investigated by SEM (Hitachi, S-2300). The powder samples were uniformly dispersed in ethanol for deposition on glass substrate and their reflectance spectra were recorded by a spectrophotometer (Hitachi U-3410).

RESULTS AND DISCUSSION

Fig. 1 shows the XRD spectra of In_2S_3 powders synthesized at different reaction times (10 to 18 h). It may be observed that all the spectra matches well with the standard JCPDS data [22] of β-In_2S_3 indicating that it is crystallized with a cubic symmetry. The XRD spectrum for the sample-I synthesized for10 h reaction time shows nearly an amorphous-like nature containing a broad diffraction peak at the diffraction angle 2θ = 47.9°. With increase of time, the intensity of the diffraction peaks increases, which corresponds to the increase of crystallinity of the samples with reaction time prolonging from 10 to 18 h. No characteristic peaks for impurities were detected.

Fig. 2(a-f) shows the SEM pictures of the synthesized samples which revealed the flower-like morphology of the obtained product. It may also be mentioned here that when the reaction time was 10 h, the flake-like or petal-like patterns within the spherical microparticle was not observed properly

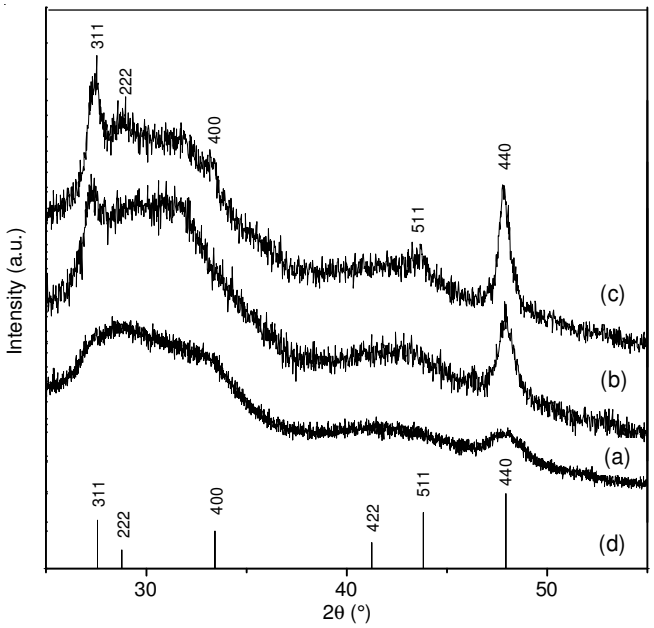

Fig. 1. X-ray diffraction patterns for β-In_2S_3 powders synthesized at 180 °C for different reaction times (a) 10 h, (b) 12 h, (c) 18 h; (d) standard cubic (JCPDS Card 32-0456) spectrum of In_2S_3

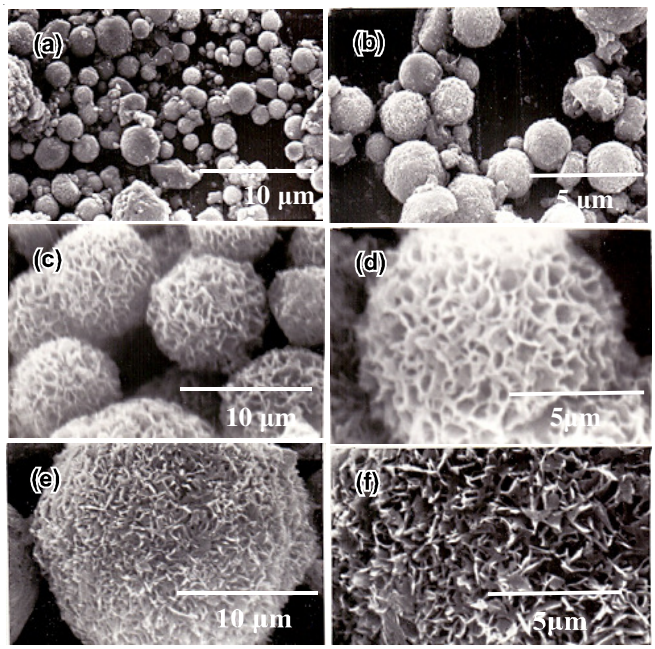

Fig. 2. SEM micrographs of β-In_2S_3 powders synthesized at 180 °C for 10 h (a) lower magnification, (b) higher magnification (flower-like form not generated properly); for 12 h (c) lower magnification, (d) higher magnification (uniform flower-like particle); for 18h (e) lower magnification, (f) higher magnification image

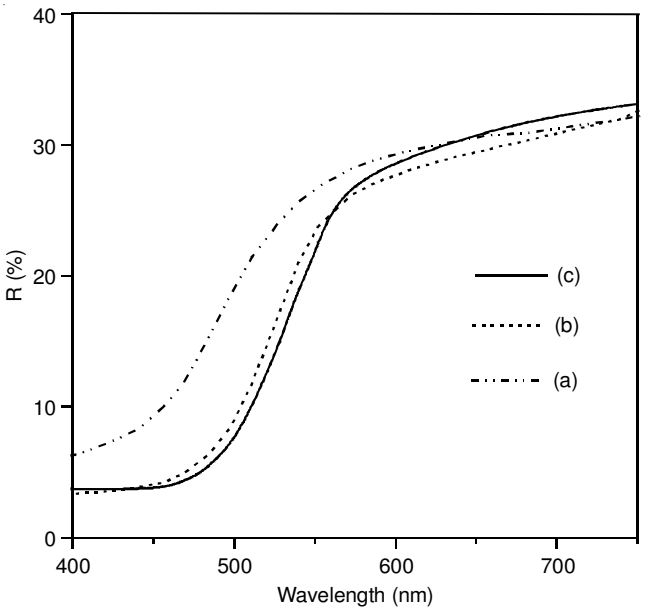

Fig. 3. Optical reflectance (% R) *vs*. wavelength (λ) traces for β-In_2S_3 particles corresponding to different reaction times: (a) 10 h, (b) 12 h and (c) 18 h

value from sample III to II to sample I. The band gaps of the materials were determined from the differential reflectance spectra [18]. Fig. 4 shows the differential reflectance spectra. The calculated band gaps of the samples obtained from these spectra were varied from 2.34-2.49 eV. The increase of band gap of In_2S_3 with the decrease of reaction times occurs due to the decrease of size of In_2S_3 particle.

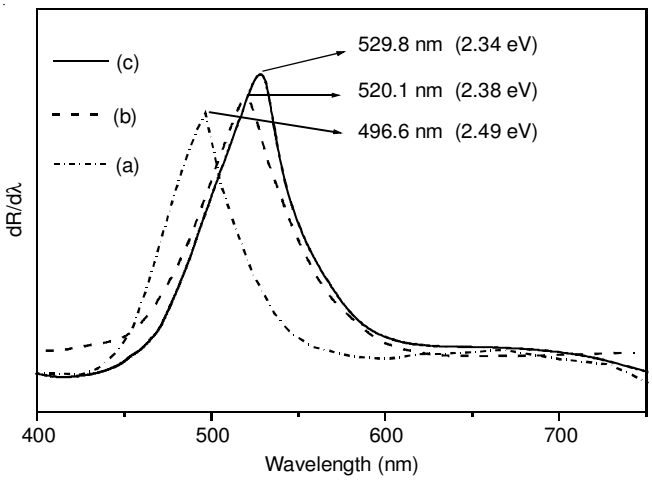

Fig. 4. Plot of [d(R)/d(λ)] *vs*. λ for β-In_2S_3 particles corresponding to different reaction times: (a) 10 h, (b) 12 h and (c) 18 h

but with the increase of reaction time flower-like structure of these spherical particles became prominent. The average particle size of In_2S_3 was calculated from the SEM. From these figures it is revealed that the average sizes of the particles increases from about 2 to 9.7 to 23.3 μm with the increase of reaction times from 10 to12 h to 18 h, respectively.

Fig. 3 shows the reflectance-wavelength spectra of the samples I-III prepared at 180 °C for different reaction times. From this figure it is observed that the band-edge of the reflectance spectra slightly shifted towards lower wavelength

Solvent plays an important role in controlling the shapes of the material. Acetylacetone (Hacac) was used as the solvent because of its special properties like strong chelation and solubility in some cases. It shows weak acidity due to presence of active methylenic hydrogen and was thought that reaction of acetylacetone with metal hydroxides or hydrated basic metal oxides would lead to an acid-base type reaction, thereby formation of metal acetylacetonate complex [23]. Similarly when the hydrated indium salt reacts with acetylacetone, the ligand binds In^{3+} ion in a bidentate manner and forms a five-membered

chelate ring [23]. It is believed that the complex ion with bidentate ligand may form self-assembly under solvothermal condition which facilitates the oriented growth [15] of the flower-like molecule. After a certain time of reaction at elevated temperature and pressure the stability of the complex decreased and S^{2-} (obtained by the dissociation of thiourea at high temperature) immediately reacted with the aforesaid complexes to form In_2S_3 microsphere; the volatile organic ligand was gradually lost (as the boiling point of acetylacetone is 140 °C at normal pressure and temperature). Flake-like pattern (inside the flower) may be explained by considering a non-equilibrium growth phenomenon *via* a diffusion-limited monomer-cluster aggregation [24,25]; this concept matches well with the progressive formation of each flake-like pattern as a function of reaction time (12 h as compared to 10 h). The structure-directing ability of acetylacetone obviously helps in this growth phenomenon.

Conclusion

Flower-like β-In_2S_3 microparticles were successfully synthesized *via* solvothermal route. Acetylacetone-water solvent mixture helps to control the morphology of the prepared indium sulphide powders. This simple method might be generalized for the preparation of other metal-sulphide compounds.

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