Available online at www.sciencedirect.com

SCIENCE DIRECT

Materials Letters 59 (2005) 3535 – 3538

materials letters

www.elsevier.com/locate/matlet

Morphology controlled solvothermal synthesis of copper indium sulphide powder and its characterization

S. Gorai [a], S. Bhattacharya [b], E. Liarokapis [c], D. Lampakis [c], S. Chaudhuri [a,*]

[a] *Department of Materials Science, Indian Association for the Cultivation of Science, Kolkata-700032, India*
[b] *Department of Electronic Engineering, The Queen's University, Belfast BT7 1NN, United Kingdom*
[c] *Department of Physics, National Technical University of Athens, Athens, GR157 80, Greece*

Received 10 January 2005; accepted 11 June 2005
Available online 18 July 2005

Abstract

Copper indium sulphide powders were synthesized via a simple and convenient solvothermal route. The morphological patterns of the products, namely, woolen ball-like porous micro sphere and micro rods composed of interconnected flakes were revealed from scanning electron microscopy. The products were also characterized by XRD, fluorescence and Raman studies. Compositional analyses of the powders were done by XRF.

Keywords: Copper indium sulphide; Solvothermal route; Porous micro rods and spheres; Fluorescence; Raman spectroscopy

For the past few years [1–5] multinary chalcogenides have been the subject of intense research. The ternary semiconducting materials like $CuInS_2$ and $CuInSe_2$ have drawn much attention because their band gaps match well with the solar spectrum leading to photovoltaic applications [6,7]. In the past, much effort was devoted to study the fundamental properties of $CuInSe_2$ with a view to prepare device. Although very high efficiencies have already been reported [8] with copper indium gallium selenide as the absorber layer, the ternary semiconductor containing selenium is harmful due to the toxicity of selenium. Therefore, $CuInS_2$, an equally important but environmentally benign solar cell material has great importance in current PV research. Solar cells fabricated with $CuInS_2$ thin films have already exhibited an efficiency of ~16% on an area of 1 cm^2 [9].

There are various techniques [10–31] for the synthesis of $CuInS_2$ powders and thin films with different nano and microforms, such as nanoparticles [23,24], nanorods [25,26], nanotubes [27], foam like nanocrystallites [28] and porous microspheres [29]. Previously we have reported the synthesis of stoichiometric $CuInS_2$ powder by wet chemical route [19]. In the present work, we propose a convenient solvothermal method to synthesize woolen ball-like micro spheres of $CuInS_2$ and also rods-like structures, containing interconnected flakes. The products were characterized by fluorescence and Raman study.

1. Experimental

In this typical synthesis, copper (II) chloride dihydrate (99%, E. Merk), indium (III) chloride and thiourea (Spectrochem, India) were used. Indium chloride was prepared from indium metal (Plasma Materials, U.S.A., 99.999%) and hydrochloric acid (International chemicals, L.R.). At first, after dissolving 2 mM copper chloride in 30 ml ethanol, 2.8 mM ascorbic acid was added to the solution and it was stirred to dissolve. Secondly, 2 mM indium chloride was added to the above solution and stirred for a few minutes. In the next step 3.5 mM of thiourea was added to the above solution and stirred for 10 min. Then the whole

* Corresponding author.
E-mail address: subhadra_chaudhuri@yahoo.com (S. Chaudhuri).

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2005.06.023

Table 1
Variation of stoichiometry and morphology of copper indium sulphide with reaction conditions

Sample no.	Compositions	Reducing agent	Solvent	Molar ratio of Cu : In precursor	Morphology
Ia	$Cu_{1.06}In_{0.9}S_{2.1}$	Ascorbic acid	Ethanol	1 : 1	Woolen ball-like microsphere
IIa	$Cu_{1.7}In_{0.64}S_{1.7}$	–	Ethanol	1 : 1	Microspheres composed with network of interconnected flakes
IIIb	$Cu_{1.26}In_{0.8}S_{1.97}$	–	Ethanol	1 : 1.25	Rods composed with network of interconnected flakes
IVa	Copper indium sulphide + excess indium sulphide	–	Water	1 : 1	–

mixture was kept into a Teflon-lined stainless steel autoclave. The autoclave was filled with ethanol upto 65% of its total volume (110 ml). Finally the autoclave was placed at 180 °C for 16 h and after completion of the reaction it was cooled down to room temperature. The black precipitate was filtered and washed with distilled water and ethanol. The precipitate was dried at 100 °C for 5 h in vacuum. The same experiment was repeated without using ascorbic acid and the products were collected by the same procedure as indicated above. Two sets of experiment (a and b) were performed with different Cu/In ratio (a-Cu : In : S = 1 : 1 : 3.5, b-Cu : In : S = 1 : 1.25 : 3.5). The products synthesized from 1 : 1 molar solutions of copper and indium salts with and without using ascorbic acid were named as sample Ia and IIa, respectively. The product obtained from indium rich solution (no ascorbic acid was used) was named as sample IIIb. The above experiment was repeated again using water instead of alcohol taking the molar ratio of Cu : In : S = 1 : 1 : 3.5. No ascorbic acid was used in this case. The product thus obtained was named as sample IVa. For clarity all were incorporated in Table 1.

All the products were characterized by XRD (Seifert, 3000P) using monochromatic CuKα radiation (Ni filter). Elemental analysis of the samples were done by JSX-3202M Element analyzer. Morphologies of the samples were investigated by SEM (Hitachi, S-2300). The room temperature fluorescence spectra of the powders were recorded by Luminescence Spectrometer (Perkin Elmer, LS 55) with excitation wavelength of 350 nm. The Raman spectra were recorded at room temperature in back scattering geometry with a T64000 Jobin–Yvon triple spectrometer using the green line of an Ar^+ laser ($\lambda = 514.5$ nm).

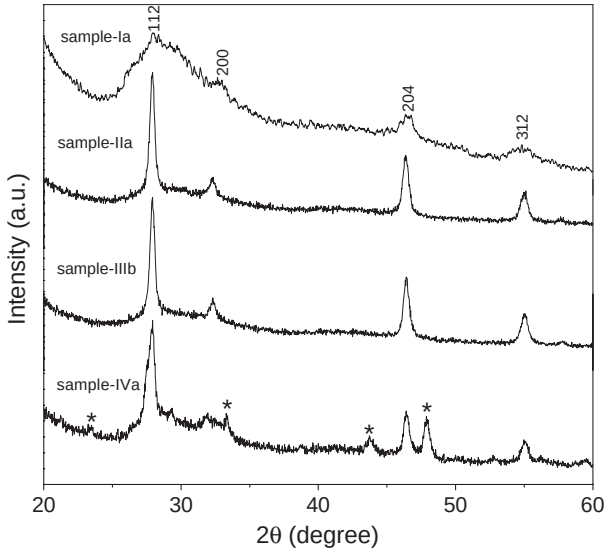

Fig. 1. XRD patterns for copper indium sulphide powders synthesized at 180 °C for 16 h. (* indicates the formation of In_2S_3 phases).

2. Results and discussion

Typical XRD patterns of the products are shown in Fig. 1. All the peaks of the samples Ia to IIIb match well with the standard JCPDS (27-0159) pattern of $CuInS_2$. No impurities can be detected from this figure. But the XRD spectrum of the product (sample-IVa) obtained by using water as the solvent indicates the formation of indium sulphide (represented by *) along with $CuInS_2$. Therefore, in our system water is not appropriate for the synthesis of pure copper indium sulphide. It is also revealed from this figure that when ascorbic acid is used in the reaction system (for sample Ia), the diffraction peaks become broad whereas sharp peaks indicating good crystallinity of the samples (sample IIa and IIIb) are observed in absence of ascorbic acid. The broad peaks arising in case of sample Ia is due to the poor crystallinity as well as the smaller size of the particle, which is evident from SEM picture (Fig. 4, discussed later). In case of sample IIa, the particle size increases and hence the sharp peaks appeared.

The compositions of the products were investigated by XRF. The results are shown in Table 2, which indicates that when ascorbic acid is used, the composition of the product obtained from the equimolar solution of copper–indium was $Cu_{1.06}In_{0.9}S_{2.1}$ whereas when ascorbic was absent, compositions of the products obtained from the equimolar solution of copper–indium and indium rich solution were $Cu_{1.7}In_{0.64}S_{1.7}$ and $Cu_{1.26}In_{0.8}S_{1.97}$ respectively. The results indicate that nearly stoichiometric copper indium sulphide was formed from equimolar solution of copper–indium in the presence of ascorbic acid.

In Fig. 2 typical room temperature emission spectra are shown for the three synthesized samples (sample Ia–IIIb). For all the samples a broad emission band in the region ~833–850 nm (i.e. ~1.49–1.46 eV) is revealed. It is also observed that for copper rich samples slight red shift of this emission band occurs with respect to the nearly stoichiometric sample.

Table 2
XRF analysis of the products

Sample no.	Cu (at.%)	In (at.%)	S (at.%)
Ia	26.63	22.51	52.52
IIa	42.51	16.01	42.54
IIIb	31.52	20.05	49.25