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The Role of Fe on Structure, Morphology and Band Gap Energy of $Cu_2Fe_xSn_{1-x}S_3$ Flower-like Nanostructures Synthesized via Solvothermal Method

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Abstract

In this work, quaternary chalcogenite Cu2FexSn1-xS3 (CFTS) flower-like nanostructures (where x=0,0.6,1) have been successfully synthesized by solvothermal approach. The nanocrystals were characterized by means of X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM),Raman Scattering spectroscopy, and UV-Vis-NIR absorption spectroscopy. The nanocrystals sizes are calculated by Deby Sherrer formula to be S1(x=0) 10.71nm, S2(x=0) 8.15 nm and S3(x=1) 22 nm. UV-Vis absorption spectra of as-synthesized CFTS crystals dispersed in ethanol showed the increasing of absorption in visible region of light. The band gap energies of samples were: 1.06 eV for S1 (x=0), 1.37 eV for S2 (x=0.6) and 1.61 eV for S3 (x=1) respectively. As can be seen the optical band gap of samples increases from 1.06 to 1.61 eV by increasing of Fe dopant.

Keywords: Chalcogenides, CFTS, Nanostructures, Semiconducting materials, Solvothermal method;

Introduction

Quaternary Cu2-II–IV–VI4 group semiconductor materials, such as $Cu_2ZnSn(S,Se)_4$ (CZTSSe), due to their abundant and nontoxic elements and excellent photovoltaic and optoelectronic properties (For example, the most representative material of Cu2ZnSnS(Se)4,with high optical absorption efficient ($\geq ۱۰^{۴} cm^{-1}$) suitable band-gap (~1.5 eV), has achieved the power conversion efficiency beyond 11%[3]) have attracted much attention for many photovoltaic applications [1-4]. Among this family, the (CFTS) Cu_2FeSnS_4 Nano crystals with band-gap energy of 1.3-1.5 eV have been synthesized and their applications in photovoltaic cells also have been investigated [1].Cu_2FeSnS_3 (CFTS), a tetrahedrally coordinated semiconductor in which each sulfur anion is bonded to four cations and each cation is bonded to four sulfur anions, is another possible alternative material for photovoltaic (especially in solar cells) applications [1].

Recently, a solvothermal technique, which was carried out at relatively low temperature and did not require organometallic or toxic precursors, was developed as a mild route to synthesize materials. In contrast to conventional synthetic methods, solvothermal technique offers many advantages, including the enhancement of solubility, diffusion, and crystallization as well as the control of the morphologies, sizes and phase transformation, etc [5-7].
The estimated band gap energy is about 1.35 and 0.96 eV for tetragonal and cubic phases respectively, with a high absorption coefficient of 10^4 cm^{-1} in the visible region [8-11].

In this work, quaternary chalcogenite $Cu_2Fe_xSn_{1-x}S_3$ (CFTS) flower-like nanostructures (where x=0, 0.6, 1) with a transition phase from tetragonal to orthorhombic structure have been successfully synthesized by solvothermal approach. So we can change the band-gap energy with tuning the proportion of Fe and Sn in the composite.

Experimental

2.1. Materials

Copper (II) chloride dihydrate ($CuCl_2.2H_2O$), Iron(II) chloride tetra hydrate ($FeCl_2.4H_2O$), Thiourea (TU) (CSN_2H_4) were all analytical grade and purchased from Sigma Aldrich and Merck Company and used as received without further purification.

2.2. Synthesis of CFTS nanostructure powder

In a typical synthesis of Cu_2Fe_x Sn $_{1-x}$ S_3 nanocrystals 2 mmol Copper(II) chloride dihydrate ($CuCl_2.2H_2O$) , x mmol Iron(II) chloride tetra hydrate ($FeCl_2.4H_2O$) (where x=0,0.2, and 0.4) ,1-x mmol $SnCl_2.2H_2O$, 3 mmol Thiourea (TU) (CSN_2H_4) , and 40 ml ethylene glycol (EG) were mixed and then stirred uniformly until a milky suspension was achieved . The resulting suspension was transferred into the Teflon container of a stainless steel autoclave with a capacity of 50 cc then moved into an oven and kept at 220 °C for 24 hours. After that the obtained product was cooled to room temperature then washed with ethanol and DI water for three times isolated by centrifuging with the rate of 8000 rpm. Eventually the sediment was dried in vacuum at 100 °C for 12 hours.

Characterization

Structural phase and crystalline properties of the samples, were examined by X-ray diffraction (XRD) patterns using a diffractometer system (X'Pert Pro MPD) supplied by a Cu-Kα λ=1.5404A° radiation source and high resolution Raman spectroscopy (SENTERRA, λ=785nm). To characterize the ultraviolet absorption spectra of the samples, a double-beam spectrophotometer (UV-4802SOP) was used. The general morphology of the samples was characterized using field-emission scanning electron microscopy (TESCAN) at an acceleration voltage of 15.0 kV.

Results and discussions

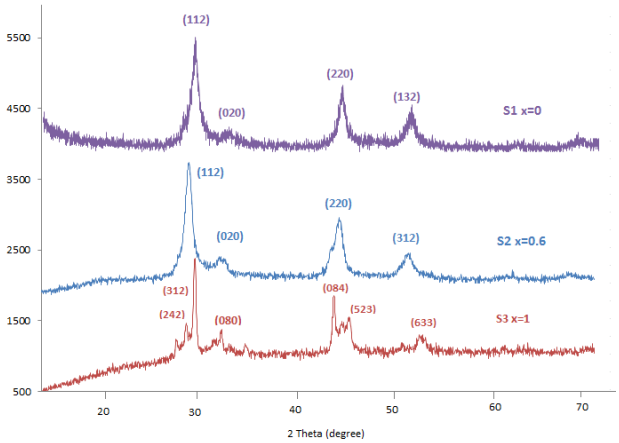

Figure 1 XRD patterns of Cu_2Fe_x Sn $_{1-x}$ S_3 powder.

The size of particles are calculated by DebySherrer Equation (1) where the size of crystallite are 10.71 nm (x=0), 8.15 nm(x=0.6) and, 22 nm (x=1).

$$D = \frac{K\lambda}{\beta cos\theta} \qquad \text{Eq.1}$$

Where K is the shape factor (0.9), λ is the wavelength of X radiation (1.54 Å), β is full width at half maximum (FWHM), and D is the crystallite size.

For S2 The main peaks at 2θ = 28.49°, 33.29°, 47.07°, and 55.93° were respectively indexed to planes (112), (020), (220), and (312) in XRD spectra, indicating presence of tetragonal unit cell with space group I-42m (ICDD no. 00-035-0582).

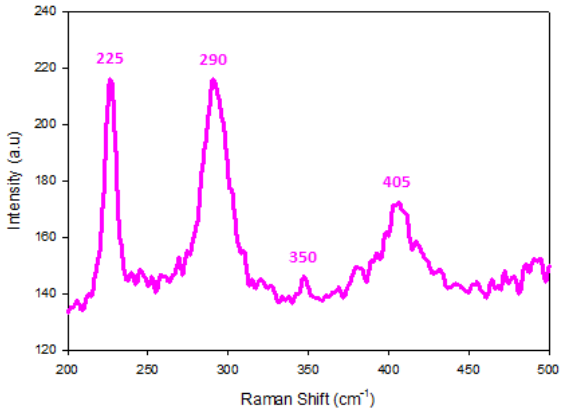

Figure2. Raman spectrum of S3 nanoparticles.

Figure 2 illustrates Raman spectra of the CFS nanoparticles for S3 (x=1). The main Raman peaks here observed is at 225 and 290 cm^{-1}.

The band gap can be calculated by extrapolating the linear region of the plots $(Ahv)^2$ vs. hv on the energy axis (Figure 3-6). The estimated values are 1.06 for S1, 1.37 for S2, and 1.61 eV for S3.

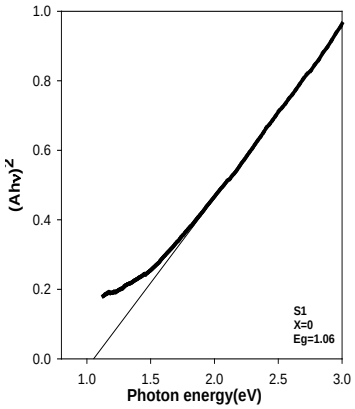

Figure 3 UV-Vis absorption spectra of S1

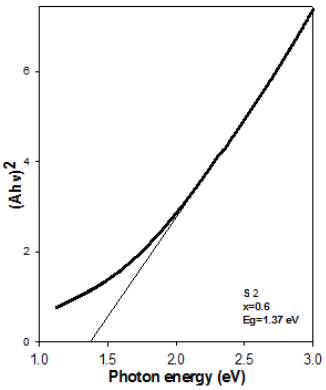

Figure 4 UV-Vis absorption spectra of S2

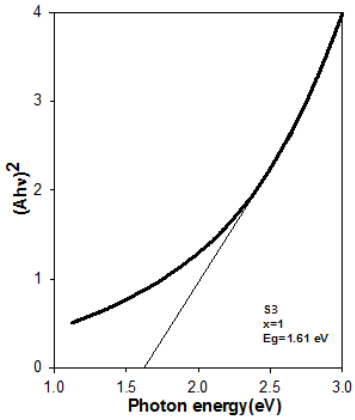

Figure5. UV-Vis absorption spectra of S3

Figure 6 shows FESEM images of S1, S2 and S3 .

The morphologies of the final products were investigated by FESEM, as shown in Figure 6 the uniform flower-like shape with an average size of ~ 1-5 μm could be observed. From higher-magnification

Figure 6 FESEM images of S1, S2 and S3

FESEM image demonstrates that several flower-like particles connect with each other. Interestingly, each flowerlike's surface is composed of numerous ultrathin nanoflakes with an interval of around 20-30 nm.

Conclusions

From all the XRD spectra of as-synthesized $Cu_2Fe_xSn_{1-x}S_3$ nanoparticles we can conclude that in the sample S1 with absent of Fe the structure was tetragonal. Then at sample S3 with presence of Fe and absent of Sn the crystallite structure is most likely to be in orthorhombic phase in accordance with ICDD no.00-042-0586, but further investigation is needed to specify the exact crystallite phase of sample 3 .

In addition from the UV-Vis spectra of samples decrease in the band gap energy of the CFTS nanostructures with increasing Sn content can be interestingly observed. which can be result of

different atomic radius between Fe (194 pm) and Sn (217 pm).with decreasing the size of Nano crystals ,the estimated band gap increased to 1.61eV; which is almost the optimum band gap suitable for photovoltaic applications.

References

[1] Meng Cao, Chao Li, Binlei Zhang, Jian Huang, Linjun Wang, Yue Shen , *Journal of Alloys and Compounds* 622 (2014) 695–702 .

[2] K. Tanaka, M. Kato, H. Uchiki, J. *Alloys Comp*. 616 (2014) 492–497.

[3] T.K. Todorov, J. Tang, S. Bag, O. Gunawan, T. Gokmen, Y. Zhu, D.B. Mitzi, *Adv. Energy. Mater*. 3 (2013) 34–38.

[4] F. Aslan, A. Tumbul, J. *Alloys Comp*. 612 (2014) 1–4.

[5] G. Demazeau, *J. Mater. Chem*. 8 (1999) 15.

[6] Y. Xie, Y.T. Qian, W.Z. Wang, S.Y. Zhang, Y.H. Zhang, *Science* 272 (1996) 1926.

[7] Xiangying Chena, XiongWanga, Changhua Ana, JianweiLiua, YitaiQia ,*Journal of Crystal Growth* 256 (2003) 368–376.

[8] P.A. Fernandes, P.M.P. Salom, A.F. da Cunha. *J. Phys. D Appl. Phys*. 43, 215403 (2010).

[9] M. Bouaziz, J. Ouerfelli, S.K. Srivastava, *J.C. Berne`de, M.Amlouk. Vacuum* 85, 783 (2011)

[10] T. Kuku, O. Fakolujo .*Sol. Energy Mater*. 16, 199 (1987).

[11] N. R. Mathews • J. TamyBenı´tez •F. Paraguay-Delgado • M. Pal • L. Huerta .*J Mater Sci: Mater Electron* (2013) 24:4060–4067.