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Structural and optical properties of Cu_2M (M: Zn, Fe, Co, Ni) $SnSe_4$ nanoparticles synthesized *via* heating up method

Z. Dehghani[a,*], Z. Shadrokh[b]

[a] Department of Physics, University of Neyshabur, Neyshabur, P. O. Box 9319774400, Iran
[b] Department of physics, Tarbiat Modares University, Tehran, P. O. Box 14115-175, Iran

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ABSTRACT

Quaternary semiconductor Cu_2M (M: Zn, Fe, Co, Ni) $SnSe_4$ nanoparticles have been successfully synthesized by one-step simple wet chemical heating up method. All samples display aggregated sphere-like with a range of 20–80 nm but in $Cu_2FeSnSe_4$ can be seen micrometer particles with hexagonal shape that EDS analysis confirm presence of CuSe. The Structure of $Cu_2ZnSnSe_4$, $Cu_2FeSnSe_4$, $Cu_2NiSnSe_4$ and $Cu_2CoSnSe_4$ are tetragonal kesterite, tetragonal stannite, similar to ZnSe wurtzite and resemble to ZnSe zinc blende respectively. The band gap energy of these samples was 1.27–1.69 eV that $Cu_2FeSnSe_4$ was greater value of band gap energy due to formation of CuSe in it. Broad, weak and asymmetric PL peaks for all samples indicate presence of defects that create centers of non-irradiative. Cu_2M (M: Zn, Fe, Co, Ni) $SnSe_4$ thin films show photoresponse behavior, indicating that these nanoparticles have a potential application in low cost thin film solar cells.

1. Introduction

$Cu_2ZnSn(S,Se)_4$ (CZT(S,Se)) has demonstrated suitable optical and electrical properties with low-cost, earth abundant and non-toxic elements which have to potential for thin film solar cells [1–3]. Moreover, CZT(S,Se) has display rang of direct band gap from 1 to 1.6 eV with high absorption coefficient ($\alpha > 10^4$ cm^{-1}) [1–3]. CZT(S.Se) nanocrystals have been prepared by various solutions-based including solvothermal [3], hot injection [2,4], and microwave [5]. As well as, solution deposition for CZT(S.Se) are attractive for large-scale and inexpensive fabrications [4]. There are many operative can be affected on the quality and power conversion efficiency of thin film solar cells, such as shape and size, annealing process, precursor type, concentration and ratio, solvent and *etc* [1–7]. One of the challenges in wet chemical process is organic molecules that can be decrease of electronic properties (such as olylamine with long ligand of carbon) [8]. Tajima et al. [9] preparation CZTS thin film by two processes of deposition of ZnS/Sn/Cu and sulfurization and generated two-layer of CZTS consecutive. They reported that open-circuit voltage (V_{OC}) was improved and the best CZTS cell showed a conversion efficiency of 8.8%. Lee et al. fabricated CZTSe thin film by co-evaporation and achieved power conversion efficiency of 11.6% [10]. To compare between Tajim and Lee works, presence of Se cause to decrease of band gap energy, but can be affected on quality of the layer. The Se atom (1.98 Å) is larger than the S atom (1.84 Å) therefor, can be an expansion of volume lead to decrease of void in thin film. Therewith CZT(S, Se), quaternary $Cu_2MSn(S, Se)_4$ (M = Co^{2+}, Fe^{2+}, Ni^{2+}) compounds can be important materials for solar cell due to resemble of structure to CZT(S, Se) (kestrite, stannite and wurzite), direct band gap, large absorption coefficient and large magneto-optical effects [11–14]. To date, there are a few reports on the synthesis and characterization of $Cu_2FeSnSe_4$ (CFTSe) and there is not any reports on synthesis of $Cu_2CoSnSe_4$ (CCTSe) and $Cu_2NiSnSe_4$ (CNTSe) by wet

* Corresponding author.
E-mail address: zahra.dehghani@neyshabur.ac.ir (Z. Dehghani).

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chemical methods. Quintero et al. [15] synthesized sixteen polycrystalline samples of Cu_2-II-IV-S_4(Se_4) (II: Mn, Fe, Co; IV: Si, Ge, Sn) magnetic semiconductor compounds by the melt and anneal technique. They reported about differential thermal analysis (DTA) and crystallographic parameters of above compound. Their results showed that compounds formed to stannite (I-42 m), pseudo-cubic (P-4), wurtzite ($Pmn2_1$) and orthorhombic (F222) structures which more compounds generated to stannite structure.

Herein, first, we synthesized Cu_2MSnSe_4 (M = Zn, Fe, Co, Ni) nanoparticles via cost effective and simple heating up method for first time and characterized these compound.

2. Experimental methods

At first, 4 mmol of selenium powder were mixed with 10 ml of oleylamine and the mixture was stirred on a heater/stirrer at 100 °C until selenium was completely dissolved and a light grey solution was obtained. 2 mmol of copper (II) chloride dihydrate ($CuCl_2{\cdot}2H_2O$) and 1 mmol of zinc chloride (nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), cobalt nitrate hexahydrate ($Co(NO_3)_2{\cdot}6H_2O$), and iron chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$)) were separately mixed with 1 mmol of tin chloride dihydrate ($SnCl_2{\cdot}2H_2O$) and 10 ml of oleylamine, and the mixture was stirred on a heater/stirrer at 100 °C. After the substances were dissolved in oleylamine, the selenium-containing oleylamine solution prepared in the first step was also added and the resulting solution was maintained at 200 °C for 10 h. Next, it was allowed to be cooled naturally, and then acetone was added to it and it was centrifuged at 9000 rpm for precipitation. The process of washing with acetone was repeated several times in order to obtain a powder without any significant impurities. Next, the obtained powder was annealed in a furnace at 100 °C for 4 h to be completely dry. Thin films of the samples were prepared via the drop casting of the nanocrystals' ink prepared through dissolving the nanoparticles' powder in ethanol by ultrasonication. The prepared films were first heated at 200 °C for 2 h in the vacuum, and they were next annealed in a furnace at 400 °C for 30 min in the presence of argon flow.

In this study, in order to characterize the crystal structures, X-ray diffractometry analysis (X'Pert Pro MPD, Cu-kα λ = 1.54 Å) was performed. UV–vis absorption spectra were recorded by a double-beam spectrophotometer (UV-4802SOP) with a resolution of 0.5 nm in order to calculate the band gap energy of the nanoparticles. Photoluminescence (PL) measurements were performed by using a fluorescence GILDEN photonics device (fluoroSENS) with an excitation wavelength 500 nm. The particle size, shape, and morphology were studied by field emission scanning electron microscopy (FESEM, Zeiss, ΣIJMA-VP), and energy dispersive spectroscopy (EDS) analysis was employed in order to find the substance chemical ratio and purity.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of CZTSe, CNTSe, CCTSe, and CFTSe with zinc blende and wurtzite structures. The zinc blende structure of the CZTSe and CFTSe samples matches with reports [5,8,14]. In the CFTSe sample, the peaks at 2θ = 27.63, 45.41, 55.32° correspond to the planes of (112), (204), (116) matched to the tetragonal stannite structure (PDF No. 52-0998) [5,8]. In the CZTSe sample, the peaks at 2θ = 27.71, 45. 63, 55.42° correspond to the planes of (112), (204), (312) matched to the tetragonal kesterite structure (PDF No. 052-0868) [14]. No reports have been made on the CCTSe and CNTSe samples yet. Therefore, we analyzed the structured by X´pert software. Our results indicate that the XRD pattern of the CCTSe sample shows a more match with the ZnSe zinc blende structure and the XRD pattern of the CNTSe sample matches with the ZnSe wurtzite structure (PDF No. 15-0105). Thus we can state that in this structure, sulfur anions arrangement is like a close-packed hexagonal structure and all metal ions randomly occupy the Zn sites.

Table 1 shows the XRD analysis results. The mean crystallite sizes and the lattice strains were calculated by the Williamson-Hall relation (Eq. (1)) [6] and the lattice constant of the tetragonal lattice was calculated by the Eq. (2) [6] and the lattice constant of the hexagonal structure was calculated by the Eq. (3) [16]. In Eq. (1), λ is the wavelength of copper (1.54 Å), K is the form factor (0.9), D is crystallite size, β is the peak FWHM, and ε is lattice strain. In Eqs. (2) and (3), d is the distance between planes, (hkl) are miller

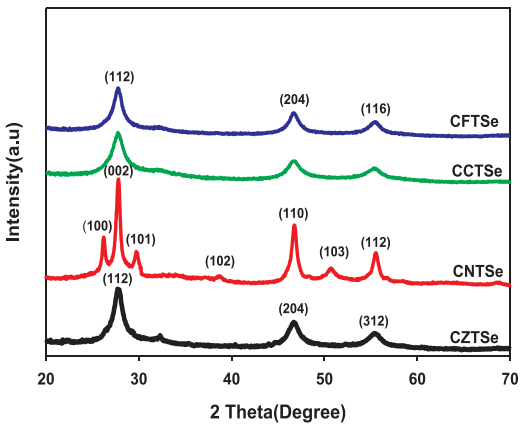

Fig. 1. XRD pattern of the as-synthesized CM(Zn, Ni, Co, Fe)TSe samples.