Materials Letters 207 (2017) 202–205

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Effects of alloying on band gap and morphology of iron pyrite nanoparticles

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ARTICLE INFO

Article history:
Received 9 June 2017
Received in revised form 18 July 2017
Accepted 19 July 2017
Available online 20 July 2017

Keywords:
Iron pyrite
Alloy nanoparticles
Morphology
Band-gap
Raman

ABSTRACT

Here, we report the effects of zinc alloying in iron pyrite (FeS_2) nanoparticles (NPs). The NPs were synthesized by a hot-injection method using oleylamine (OAm) only, with no other ligand. The band-gap and morphology were found to be strongly dependent on the relative amount of zinc incorporated in the nanoparticles. A blue shift was observed in Raman active modes for FeS_2 upon Zn incorporation which has been ascribed to the change in the bond length of $(S_2)^{2-}$ dumbbells in the pyrite structure. According to the optical absorption measurements the band-gap (E_g) of NPs increased linearly with the mole fraction of Zn in the precursor solution (Zn_i) for the NP synthesis, and an enhancement of ~0.08 eV was achieved for Zn_i = 40%. Also, the shape of NPs varied from cubic to quasi-cubic with the increase in the mole fraction of Zn in the precursor.

1. Introduction

FeS_2 is a promising material which has been used for many applications including photovoltaics (PV), photoelectrochemical cells, lithium ion battery, and photodetectors [1]. In addition to its non-toxicity and earth-abundance, its strong light absorption ($\alpha > 10^5$ cm^{-1} for $h\nu > 1.3$ eV), good mobility (>300 cm^2 V^{-1} s^{-1} in single crystal form) and a high minority carrier diffusion length (100–1000 nm) make it very attractive for solar PV. However, the power conversion efficiencies of pyrite based PV devices have been low, largely due to the low open-circuit voltages (V_{oc}) (<200 mV). Although large short-circuit current densities (30–42 mA cm^{-2}) and quantum efficiencies as high as 90% have been reported for these devices [2]. The possible main reasons for low V_{oc} may be bulk defects, intrinsic surface states, and the presence of secondary phases [2–4]. The optimum band gap for which the theoretical energy conversion efficiency is 31% is 1.3 eV according to Shockley-Queisser theory [5]. The band-gap of FeS_2 is 0.95 eV and it can absorb an ample range of solar spectra [2]. To advance its use in PV devices, tunability of band-gap is necessary like other materials [6,7] for which FeS_2 NPs radii should be smaller than its exciton Bohr radius (~1.3 nm) [8], however, FeS_2 NPs smaller than its exciton Bohr radius have not been obtained experimentally. Also, by alloying/doping with the substitution of cation or anion [9,10], the band-gap can be changed. Alloying of FeS_2 with different elements has been explored theoretically [11] as well as experimentally [12] and a bowing effect in the energy band-gap has been reported. Among these, since the zinc chalcogenide (ZnS_2) has pyrite crystal structure with a band-gap of 2.0–2.5 eV [9] and zinc is less toxic and abundant in nature, all this makes it the best choice among transition metals for alloying FeS_2 [13]. Eyert et al. have shown that alloying of zinc in FeS_2 changed the S—S bond length in $(S_2)^{2-}$ dumbbells thereby causing an upshift in the conduction band minima (CBM) and thus an increase in the band-gap [13]. Also, modification in cationic arrangement and phonon subsystem due to zinc alloying may affect the optical properties of alloyed FeS_2 nanoparticles [14]. Recently, Mao et al. have synthesized zinc alloyed ternary FeS_2 NPs and observed an increment in the band-gap without any bowing effect; they also used these NPs in photodetectors [15]. Alloyed FeS_2 NPs have shown potential for other applications also [13,16].

In this work, we report the first time synthesis of $Zn_xFe_{1-x}S_2$ NPs using OAm only which acts as both the ligand and the solvent. Further, the effects of Zn alloying on the optical and morphological properties of FeS_2 have been discussed.

2. Experimental method

All analytical grade chemicals were purchased and used without further purification. We used zinc stearate and iron chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$) as the starting chemicals and elemental

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http://dx.doi.org/10.1016/j.matlet.2017.07.083
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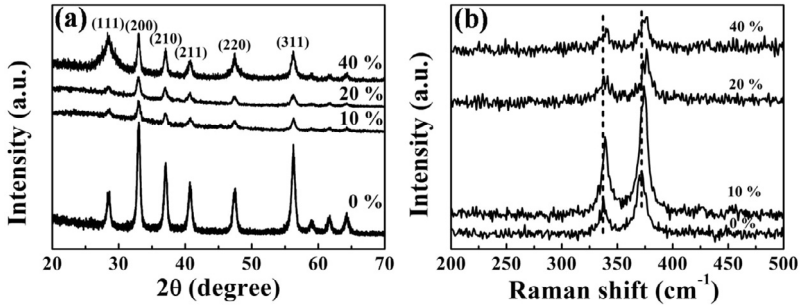

Fig. 1. (a) XRD pattern, and (b) Raman spectra of $Zn_xFe_{1-x}S_2$ alloy NPs for Zn_i = 0%, 10%, 20% and, 40%.

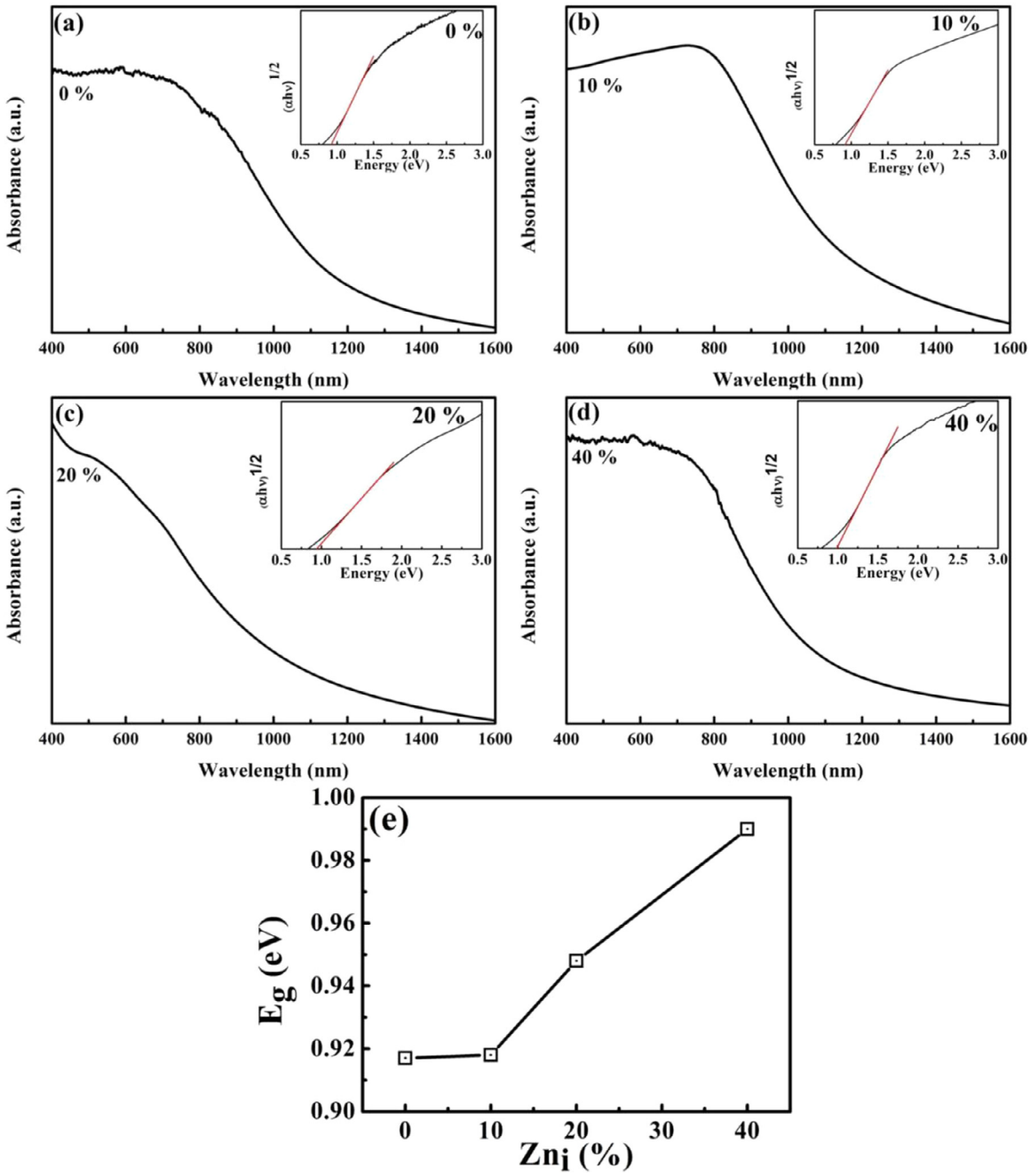

Fig. 2. UV–Vis–NIR spectra of $Zn_xFe_{1-x}S_2$ NPs for different initial mol% (a) 0%, (b) 10%, (c) 20%, and (d) 40% of Zn precursor. (e) Change in indirect band-gap Eg (eV) with different amounts of Zn_i.