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Low-temperature molten salt synthesis and characterization of $\text{Cu}_2\text{ZnSnS}_4$ ultrafine powders

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ABSTRACT

Nano-crystalline particles of $\text{Cu}_2\text{ZnSnS}_4$ have been successfully synthesized by a relatively low-temperature molten salt technique. The reaction of metal chlorides with KSCN at 400°C for 24 h led to the $\text{Cu}_2\text{ZnSnS}_4$ phase. The phase purity of $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals has been confirmed by X-ray diffraction and Raman spectroscopy. The morphology and the crystallite size were evaluated by scanning and transmission electron microscopies. The $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals possess an optical band gap of 1.5 eV, very close to the theoretical optimum for solar energy conversion.

1. Introduction

Quaternary chalcogenides $\text{I}_2\text{-II-IV VI}_4$ compounds have attracted much attention in the past three decades thanks to their interesting optical, electrical, and electronic properties [1–4]. Among them, the quaternary $\text{Cu}_2\text{ZnSnS}_4$ is a good candidate for low-cost terrestrial photovoltaic applications because of its high absorption coefficient of 10^4 cm^{-1} in visible spectrum range. The band gap energy of this semiconductor is in the range 1.45–1.55 eV which is very close to the theoretical optimum for solar energy conversion. In addition, CZTS is consisting of the earth-abundant and non-toxic elements [2–4]. Solar cells based on $\text{Cu}_2\text{ZnSnS}_4$ have reached conversion efficiency as high as 8.4% [1]. However, it is so far below the physical limit, known as the Shockley-Queisser (SQ) limit, of about 31% efficiency under terrestrial conditions [5].

Numerous methods have been developed to prepare this complex chalcogenide, such as laser removal [6], sputtering [4], evaporation [7], electrodeposition [3], nanoparticle or suspension printing [8] pyrolysis of molecular precursors [9] and solvothermal method [10]. However, most of these methods usually require sophisticated instrumentation and some of them use environment-unfriendly reagents such as H_2S , organometallic precursors or toxic solvents.

In the molten state, the mineral salts are ionic liquids where chemical reaction can be carried out as in common solvents. Thus, they enable chemical reactions leading to highly pure inorganic powders. It's known that for the synthesis of mixed oxides from mixtures of parent oxides, the addition of a molten salt decreases the reaction temperature and increases the reaction rate [11]. Thus, various oxide powders, characterized by high specific surface areas with excellent chemical homogeneity, were prepared by reaction of transition metals with oxo-salts of alkali-metals (nitrites, nitrates, carbonates, sulfates,

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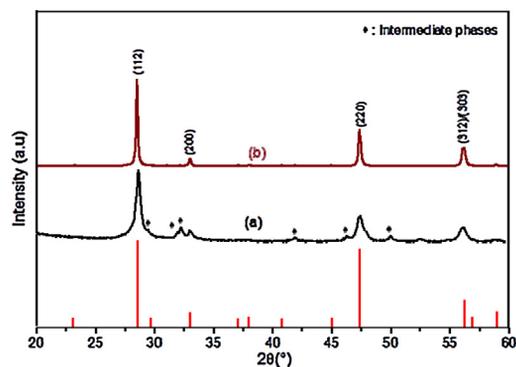


Fig. 1. XRD patterns of samples resultant from 24 h firing at (a) 350 and (b) 400 °C with molar ratio KSCN/Cu = 15. The standard pattern of $\text{Cu}_2\text{ZnSnS}_4$ (JCPDS file no. 26-0575) is provided at the bottom of this figure.

etc.) [11,12]. Recently, high-pure binary and ternary sulfides have been successfully obtained by molten salts synthesis at a temperature lower than 500 °C [13,14].

In this work, we report a simple route for the synthesis of $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles by a molten salt method at a relatively low temperature. KSCN was used as the solvent for the reaction. The structural, morphological, and optical properties of the powder obtained are given.

2. Experimental details

Copper (II) chloride dihydrate ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, sigma-Aldrich), tin (IV) chloride pentahydrate ($\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, Fisher Scientific), and zinc (II) chloride anhydrous (ZnCl_2 , sigma-Aldrich) were used as the metallic sources. Potassium thiocyanate (KSCN, Prolabo) was used both as the solvent and sulfurizing agent.

Copper, zinc and tin sources in appropriate proportions and an excess of KSCN were intimately mixed. Then, the mixture was heated under nitrogen flow in a vertical furnace at 350 and 400 °C for 24 h. The heating and the cooling rates were stated at 2 °C/min. After cooling and solidification of the molten medium, the black precipitate was extracted from the excess of salt by subsequent washings with distilled water and ethanol. The precipitate was dried at 60 °C for 12 h.

The crystal structure and the nature of the phase present in the sample were investigated by X-ray diffraction analysis using a Bruker D4 Endeavor X-ray diffractometer ($\text{CuK}\alpha = 0.154056 \text{ nm}$ and $\text{CuK}\alpha = 0.15404 \text{ nm}$, operating voltage 40 kV and current 40 mA). Raman spectroscopy was performed using a dispersive laser spectrophotometer (Jobin-Yvon Labram HR 800) with an excitation wavelength of 633 nm. The morphology and the particle size were investigated by scanning (Jeol-JSM6400) and transmission (Jeol 2010) electron microscopies.

Optical absorption spectra were recorded on a perkin Elmer Lambda 19 spectrophotometer. Cuvettes used for the experiments are made of Suprasil quartz from Hellma Analytics. In order to avoid artifacts, the cuvettes contribution to the absorption has been systematically subtracted from the raw data.

3. Results and discussion

Fig. 1 shows XRD patterns of the sulfide formed by reaction of metal chlorides in molten KSCN with the molar ratio KSCN/Cu = 15 at 350 and 400 °C for 24 h. At 350 °C, kesterite phase $\text{Cu}_2\text{ZnSnS}_4$ (JCPDS 26-0575) was identified as the main phase besides minor phases which could be binary sulfides. This indicates that the formation of quaternary chalcogenide phase has not completed at 350 °C. On increasing the temperature to 400 °C, the peaks of the minor phases are no longer present in the XRD patterns. This temperature is very close to the MSCN (M = K, Cu, Ag) decomposition temperature reported in the literature [15]. These results demonstrated that the quaternary phase CZTS can be obtained at 400 °C by the present molten salt method. This temperature is lower than that require by other methods [16,17]. The effect of the molar ratio KSCN/CIS on the formation quaternary phase was investigated. The XRD patterns of samples obtained at 400 °C/24 h with various KSCN/Cu ratios are given in Fig. 2. The XRD pattern of powder prepared with SCN/Cu = 5 identifies a main phase CZTS besides minor intermediates phases, indicating incomplete transformation of the metal chlorides. When the molar ratio was 10, the CZTS peaks height increased but significant amounts of intermediates phases still remained. On increasing the ratio to 15, the XRD pattern identifies only CZTS phase, indicating that the formation of CZTS phase had been completed. We note that the full width at half maximum of XRD peaks decrease with the KSCN/Cu molar ratio which signifies that the salt content improves the crystalline quality of CZTS. The lattice parameters calculated according to equation $1/d^2 = (h^2 + k^2)/a^2 + l^2/c^2$ are $a = 5.463$ and $c = 10.943 \text{ \AA}$. These values are close to the reported data (JCPDS 26-0575, $a = 5.434 \text{ \AA}$ and $c = 10.848 \text{ \AA}$). According to the literature, ZnS (JCPDS 5-0566) and Cu_2SnS_3 (JCPDS 89-4714) have a very similar diffraction pattern with $\text{Cu}_2\text{ZnSnS}_4$, consequently, it is not possible to exclude the presence of these phases in our samples. Hence, Raman investigation was performed to fully characterize the sample. The Raman spectrum (Fig. 3) shows a strong peak at 338 cm^{-1} and two secondary

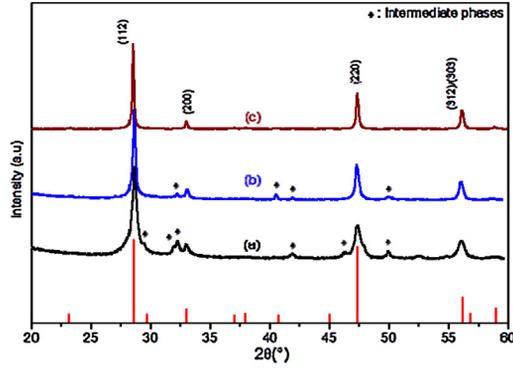


Fig. 2. XRD patterns of samples resultant from 24 h firing at 400 °C with various KSCN/Cu molar ratios: (a) 5, (b) 10, (c) 15. The standard pattern of Cu₂ZnSnS₄ (JCPDS file no. 26-0575) is provided at the bottom of this figure.

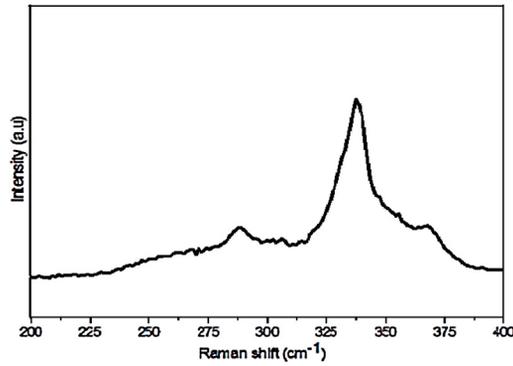
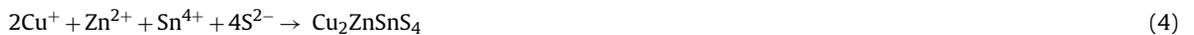


Fig. 3. Raman spectrum of Cu₂ZnSnS₄ nanoparticles.

peaks at 287 and 367 cm⁻¹. Similar Raman spectrum has been described by Altosaar et al. for CZTS [16]. These signals are consistent with the vibration involving the motion of sulfur atoms of quaternary chalcogenides and are attributed to Cu₂ZnSnS₄ structure [2,7,16]. On the other hand, the Raman spectrum does not show any peaks coinciding with the frequency of vibrational modes reported for Cu₂SnS₃, and ZnS compounds [18,19]. This confirms the phase purity of the Cu₂ZnSnS₄ nanoparticles.

In these experiments, the thiocyanate plays four important roles: (1) solvent, (2) reducing agent, (3) chelating agent, and (4) sulfur source. When KSCN was added to the mixture of metal salts, the color turns rapidly. This indicates the formation of metal-thiocyanate (Cu(SCN)_n²⁻ⁿ, Zn(SCN)_m^{2-m}, Sn(SCN)_p^{4-p}) complexes. The pre-formed complexes decompose under temperature effect and release the metal cations and SCN⁻ in the reaction medium. The thiocyanate ions reduce Cu²⁺ into Cu⁺ at a temperature above 173 °C [20]. According to the literature [20], the thermal decomposition of KSCN starts at 275 °C with S²⁻ and (CN)₂ formation. Finally, Cu⁺, Zn²⁺ and Sn⁴⁺ react with S²⁻ to form Cu₂ZnSnS₄. The various reactions involved in this process are given in Eqs. (1) – (4):



SEM observation of the as-synthesized samples (Fig. 4a) shows largely agglomerated particles with a poly-disperse size distribution. The particle sizes varied in the range of 2–3 μm. TEM image (Fig. 4b) shows that these particles are composed of elongated or more or less spherical elementary grains with an average size in the range 40–70 nm. A crystallite size estimate of 50–60 nm was obtained using the Scherrer equation on the X-ray diffraction pattern of Cu₂ZnSnS₄, demonstrating that our nanoparticles are single crystals. The formation of lower grain size suggests a higher nucleation rate due probably to the high concentration of metal cations in the molten medium.

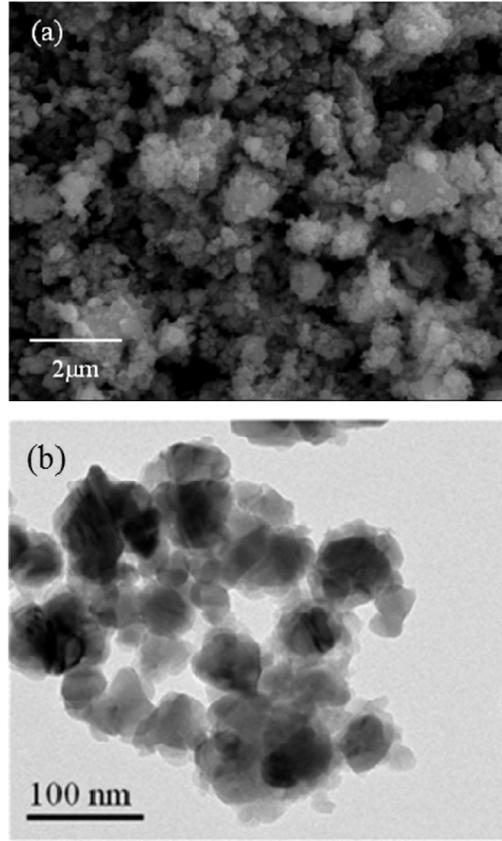


Fig. 4. (a) SEM and (b) TEM micrographs of $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles.

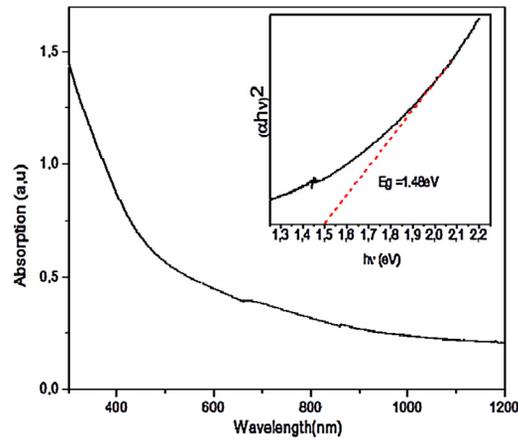


Fig. 5. The UV-vis absorption spectrum of $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles. Inset shows the plot of $(\alpha h\nu)^2$ versus photon energy. The band gap of $\text{Cu}_2\text{ZnSnS}_4$ was estimated to be 1.48 eV. The powder is dispersed in ethanol for recording the spectrum.

UV-vis absorption spectroscopy was used to evaluate the optical properties of the $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals (Fig. 5). It is well known that $\text{Cu}_2\text{ZnSnS}_4$ is a direct gap semiconductor, so the absorption coefficient in the region of strong absorption obeying the equation [21]:

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \quad (5)$$

Where α is the absorption coefficient (cm^{-1}), $h\nu$ the energy of the incident photons (eV) and A a constant. The optical band gap energy of the $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles can be estimated from the $(\alpha h\nu)^2$ versus $h\nu$ graph by extrapolating the linear absorption edge part of the curve. As shown in Fig. 5 (inset), the value is around 1.48 eV, which is very close to the theoretical

optimum for solar energy conversion in a single-band-gap device. This value is in agreement with the ones of the literature, 1.48 eV for samples prepared by solvothermal method [2] and 1.5 eV for $\text{Cu}_2\text{ZnSnS}_4$ films deposited by electrodeposition followed by a sulfuration step [3] or 1.51 eV for samples prepared by RF sputtering from binary compounds (Cu_2S , ZnS and SnS_2) [4]. The band gap of Cu_2SnS_3 and ZnS are 0.96 and 3.41 eV respectively, providing further evidence that these phases are not present in our sample [18,19].

5. Conclusion

In summary, $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles have been successfully synthesized by reaction of CuCl_2 , ZnCl_2 and SnCl_4 with molten KSCN at 400°C with the molar proportion $\text{KSCN}/\text{Cu} = 15$. The phase purity of $\text{Cu}_2\text{ZnSnS}_4$ nanoparticles was confirmed using XRD and Raman spectroscopy. The grain size was in the range 40–70 nm. The optical absorption spectrum shows that the $\text{Cu}_2\text{ZnSnS}_4$ nanocrystals exhibit a band gap of 1.5 eV suitable for application in the photovoltaic conversion of solar energy. This method is a facile and low-cost technique for preparing high-quality chalcogenide nanocrystals.

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