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Synthesis of CuInS₂ nanometric powder by reaction in molten KSCN

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A B S T R A C T

CuInS₂ was synthesized, with a yield of 70% by reaction in molten KSCN at 400 °C of CuCl₂ and InCl₃ with a ratio KSCN/Cu=15. The homogeneous powder obtained is constituted of nano-sized grains (70–100 nm), with a specific surface area of 6 m²/g and a band gap Eg of 1.5 eV.

Keywords:

Chalcogenide
Semiconductor
Molten salt
Nanoparticles

1. Introduction

An intensive research was carried out on ternary I–III–VI and quaternary I–II–IV–VI₂ chalcogenides of chalcopyrite type structure, characterized by active conductive properties in photovoltaic conversion [1–5]. Among them, the ternary CuInS₂ exhibits a specific interest because of its gap Eg (1.5 eV) very close to the theoretical optimum for solar energy conversion [6,7]. The electron transitions being direct in this sulfide with a high absorption coefficient (10⁵ cm^{−1}), thin films (a few micrometers) [8,9] can be involved for the building of solar devices, minimizing the cost of solar material.

Numerous methods have been developed to prepare this sulfide. The physical ones, laser removal [10], sputtering [11,12], evaporation [13], co-evaporation [14,15] and electrodeposition [6,16,17] are generally expensive and lead to thin layers with micro-sized particles. Among the chemical ones, the solvothermal and organometallic routes are mainly used. They generally lead to homogeneous powders with grain sizes in the range 3–100 nm. The size of particles is dependent upon the nature of the solvents, precursors and temperature of pyrolysis of the precursors [18,19].

In molten state at temperature in the range of 100–800 °C, the salts are ionic liquids where chemical reactions can be carried out as in usual solvents [20–22]. Molten salts may be used as flux. For instance, MgFe₂O₄ can be obtained at temperature as low as 900 °C by reaction of MgO and Fe₂O₃ in the presence of molten

Li₂SO₄–K₂SO₄ eutectic (Eq. (1)), whereas the same transformation in solid state requires a temperature overcoming 1200 °C:

Yet the versatility of the process is considerably improved when molten salts are directly involved in the chemical reaction. For the preparation of oxides, two types of transformations have been often considered [23,24]:

- Reactions between a mixed alkaline oxide and a molten divalent metal chloride likely to lead to the formation of MgFe₂O₄ at temperature as low as 600 °C according to the following equation..

- Reactions between a transition metal salt and a molten alkali nitrate as illustrated by Eq. (3) for the preparation of zirconia can be obtained at temperature as low as 450 °C:

Previous studies on the behavior of transition metal cations in molten potassium thiocyanate demonstrated the possibility to synthesize sulfides [25]. Only a few papers consider the properties of the powders obtained. Geantet et al. [26] presented the hydro-treating properties of a MoS₂ catalyst prepared from thiocyanate melts. Benchikhi et al. [5] proposed a process route to the fabrication of quaternary chalcogenides by reaction in molten KSCN at 400 °C.

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The main advantage of synthesis by reaction in molten salts lies in the chemical homogeneity of the powders obtained and on the control of the particle size.

The present paper describes the synthesis of nano-sized homogeneous powder of CuInS_2 by reaction of CuCl_2 and InCl_3 with molten KSCN at 400°C . The characteristics of the powder obtained are given.

Fig. 1. Structural characterization: (A) XRD patterns of CuInS_2 prepared at 300°C (a) 400°C (b) and 500°C (c). (B) Raman spectrum of CuInS_2 prepared at 400°C .

Fig. 2. Morphology: SEM micrographs of CuInS_2 prepared at 400°C (a) and 500°C (b). TEM micrographs of CuInS_2 prepared at 400°C (c) and 500°C (d).

2. Experimental

CuInS₂ was prepared from the following precursors: InCl₃ (Aldrich) and CuCl₂ · 2H₂O (Sigma). KSCN (Prolabo) was used both as solvent and sulfurizing agent. The equimolar mixture of chlorides was added to KSCN in the molar ratio SCN/Cu = 15. The thermal treatment was performed under nitrogen flow in a vertical furnace at temperatures comprised between 300 and 500 °C for 24 h. The heating and the cooling rates were stated at 2 °C/min. The reaction yield reached 70%.

After cooling and solidification of the molten medium, the sulfides were extracted from the excess of salt by washing with water and drying. The black powders obtained were characterized by XRD (Bruker AXS D4, λCuKα = 1.5418 nm), SEM (JEOL JSM 6400), TEM (JEOL 2010), specific surface area measurement (BET) (Micrometrics Flowsorb II 2300), Raman (Jobin Yvon Labram HR 800) and UV-visible (UV-1601) spectroscopies.

3. Results and discussion

Structural characterization: For the powder prepared at 300 °C, the XRD pattern (Fig. 1Aa) identifies a main phase chalcopyrite CuInS₂ (JCPDS 047-1372) besides minor phases which could be metallic sulfides (In₂S₃, Cu₂S_x). The peaks of the minor phases are no longer present in the patterns of the sulfides prepared at 400 (Fig. 1Ab) and 500 °C (Fig. 1Ac). The decrease of the full width at half maximum of the XRD peaks of the chalcogenide phase, as the synthesis temperature was raised from 300 to 500 °C, is attributed to the increase of primary crystallite sizes.

Raman investigation was performed to fully characterize the samples. The spectrum of the powder prepared at 400 °C (Fig. 1B) exhibits a main peak close to 295 cm⁻¹ and a shoulder close to 314–315 cm⁻¹. These signals are consistent with the vibration involving the motion of sulfur atoms of ternary chalcogenides, principal mode A₁ and secondary mode B₂/E observed in the chalcopyrite phase [27–30].

Mechanism of formation: The formation of CuInS₂ occurs in three steps [21,22,31]: first the thermal decomposition of KSCN starting at 275 °C with S and S²⁻ formation via reactions (4) and (5), then the reduction of Cu²⁺ by SCN⁻ involving the formation of a complex of transition via reaction (6) and lastly the formation of the chalcopyrite phase via reaction (7):

Morphological characterization: SEM observation of the samples synthesized at 400 and 500 °C (Fig. 2a and b) shows largely agglomerated particles with a poly-disperse size distribution. The size of agglomerates increases with increasing temperature synthesis. The agglomerates (Fig. 2c and d) are constituted of nano-sized primary crystallites with more or less elongated shape. It is noticed (Table 1) that the mean sizes of particles calculated from the specific surface area values, assuming mono-disperse spherical particles, are higher than the sizes observed on TEM micrographs. This difference is attributed to the agglomeration of particles.

Measurement of the band gap E_g: The energetic value of the band gap of a semiconductor determines the part of the solar spectrum that could be theoretically absorbed by the material. From the UV-visible absorption spectrum of the sulfide powder

Table 1

Morphological characteristics. (The mean size of particles is calculated from the specific surface area according to the formula $D = 6/dS$, D is the mean diameter, d the density and S the specific surface area.).

Temperature (°C)	Specific surface area (m ² /g)	Grain size (MET) (nm)	Mean grain size (nm)
400	5.9	70–100	200
500	3.5	130–150	340

Fig. 3. UV-visible absorption spectrum of CuInS₂ prepared at 400 °C.

prepared at 400 °C (Fig. 3), the band gap E_g of the semiconductor with a direct transition is determined using the following equation [32]:

$$(\alpha h\nu) = A(h\nu - E_g)^{1/2} \quad (8)$$

Where α is the absorption coefficient (cm⁻¹), $h\nu$ the energy of the incident photons (eV) and A a constant. The E_g value of 1.51 eV is determined by the intersection of the linear part of the curve $(\alpha h\nu)^2$ versus $h\nu$ (inset Fig. 3). This value is in agreement with the ones of the literature, 1.55 eV for single crystals [33] and 1.44 eV for CuInS₂ films deposited by CVD [34] or 1.50–1.52 eV for samples prepared by pulverization of indium and copper followed by a sulfuration step [35].

4. Conclusion

The chalcopyrite phase CuInS₂ was prepared by the reaction in a molten salt. The powder obtained in KSCN medium at 400 °C for 24 h with the ratio KSCN/Cu = 15 is constituted of crystallites with sizes in the range 70–100 nm and exhibits a specific surface area close to 6 m²/g and a gap E_g close to 1.5 eV suitable for application in the photovoltaic conversion of solar energy.

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