OPTICAL PROPERTIES OF CU$_X$S NANO-POWDERS

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Cu$_x$S nano-powder with hexagonal structure was obtained by chemical precipitation method. The solution prepared for the obtaining of the precipitate contains copper chloride (CuCl$_2 \cdot$2H$_2$O) as Cu^{2+} ions source, thiourea (CH$_4$N$_2$S) as S^{2-} ions source, complexing agent EDTA, NaOH and water. Precipitate formation occurs in warm bath at a temperature of 50 ° C for 2 hours. Structure was determined by X-ray diffraction and optical properties by UV-VIS spectroscopy. Cu$_9$S$_8$ (yarrowite) nano-powder with hexagonal structure was obtained. The powder can be used to obtain composite materials with special optical properties.

1. Introduction

Semiconducting chalcogenides as powders or films have been received special interest among researchers due to their special optical and electrical properties, leading to various possible applications. Copper sulphide as powders or films can be used in very diverse fields, such as solar cells [1-9], electroconducting layer at the surface of polymers [10-32], gas sensors [33] or catalyst [34] materials for photochemical conversion of solar energy [35- 38], thermoreflecting coatings [39], eyeglass coatings, antireflection coatings [40], solar control coatings [39].

Cu$_x$S (x=1–2) - in bulk form – has many forms at room temperature: chalcocite (orthorombic Cu$_2$S), djurleite (monoclinic – prismatic, Cu$_{1.95}$S), digenite (Trigonal - Hexagonal Scalenohedral, Cu$_{1.8}$S), anilite (Orthorhombic – Dipyramidal, Cu$_{1.75}$S), covellite (Hexagonal - Dihexagonal Dipyramidal, CuS), spionkopite (Trigonal - Ditrigonal Pyramidal, Cu$_{1.4}$S or Cu$_{39}$S$_{28}$), yarrowite (Trigonal - Ditrigonal Pyramidal, Cu$_9$S$_8$ or Cu$_{1.12}$S) [41-43].

All phases of Cu$_x$S have been identified as p-type semiconducting materials because of the copper vacancies within the lattice [44, 45].

Cu$_x$S materials shows different values of the energy band gap for each phase. Cu$_2$S is both an indirect and direct band gap material, with E_g bulk $\approx$ 1.2 eV and 1.8 eV, respectively [44, 45, 51]. Tabel 1. provides a summary of energy bands gaps of the literature data.

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Table 1. Summary of energy bands gaps of the literature data.

Phase	Energy band gap	Reference
Cu_2S	1.5 eV	46
$Cu_{1.95}S$	1.3 eV (direct)	47
$Cu_{1.8}S$	2.3 eV	48
$Cu_{1.75}S$	2.54 eV	49
$Cu_{39}S_{28}$	1.96 eV (indirect)	33
CuS	1.27 – 1.75 eV (direct)	50

Mixed phases are also known in an intermediate composition [23].

Several phases of copper sulfides are metastable, but these may convert to the thermodynamically more stable ones. For example, after a few hours, the high digenite ($Cu_{1.805}S$) began to convert into the low digenite ($Cu_{1.765}S$), which, in turn, converts to anilite ($Cu_{1.750}S$) [52, 53]. At 41 °C, anilite decomposes into CuS and low digenite, whereas low digenite transforms into high digenite around 82 °C [52, 54].

Nanocrystalline powders of Cu_xS can be obtained by chemical and physico-chemical methods, such as chemical bath deposition (CBD) [41,55,42], hidro- and solvo- thermal methods [57], precipitation [55] or electrical synthesis [64].

Wang W. et al. [34] described the deposition of copper sulfide hollow nanospheres in aqueous solution at room temperature. Behboudnia M. and Khanbabaee [49] obtained nanocrystalline copper sulfide Cu_7S_4 by ultrasonic radiation technique. Copper sulfide nano-crystals of novel morphologies were prepared by Zou Jing et al. [65] using a hydrothermal process at low temperature. Cu_xS powders were obtained in our laboratory by chemical precipitation. Cu_xS powders can be used to obtain thin films or composites materials.

An important issue regarding the copper sulphide is the influence of the process parameters (temperature, concentration, pH) on the optical properties of the obtained powders.

The aim of this paper was the obtaining and characterization of Cu_xS powders, using X ray diffraction and UV-VIS spectroscopy, in order to evaluate the stability of Cu_xS during thermal treatment at low temperature.

2. Experimental details

2.1. Preparation of Cu_xS nano-powder

Cu_xS nanocrystalline powders have been prepared starting from copper chloride ($CuCl_2 \cdot 2H_2O$) – as Cu^{2+} source and thiourea (TU) (CH_4N_2S) for S^{2-} generation, in an alkaline (NaOH) environment, using ethylenediaminetetraacetic acid (EDTA) as a complexing agent. The solution was prepared in a 50 ml Berzelius beaker adding 2.5 ml $CuCl_2 \cdot 2H_2O$, 0.05mol/l; 5 ml TU, 0.065 mol/l, 5ml complexing agent, EDTA, 0.045 mol/l; 14.3 ml NaOH, 0.10 mol/l and water up to 50 ml. The precipitation solution was maintained at a constant temperature of 50 °C for 2 hours in a thermostatic bath (arex, Velp SCIENTIFICA). The obtained precipitate was filtered with a vacuum pump (707.76 cm Hg) using a 4G ceramic filter and then was rinsed with distilled water. After filtration the obtained product was divided in two. One of the samples was introduced in an electric oven (Memmert) and dried at 100 ° C for 30 minutes. The other one was dried in air, at the room temperature.

2.2. Characterization of Cu_xS nano-powder

X-ray diffraction data (XRD) was performed on a XRD 6000 Shimadzu diffractometer using a monochromatic Cu-K_α radiation (λ= 1.5418Å). Diffraction data were recorded in a $\theta2$ range of 10 - 60°, the tube current of 30 mA, tube voltage of 40 kV, scan speed of 2.0000 (deg/min) and precision angle reproductibility of ± 0.001°.

For the study of the absorption spectra of the samples it's been used a Lambda 35 spectrometer (Perkin Elmer) at wavelengths of 190 – 1100 nm.

3. Results and discussions

3.1 X-ray diffraction

The X-ray diffraction patterns of the CuxS powders are presented in Figure 1. These shows that the obtained powder is a complex mixtures of copper sulfides with the following composition: CuS (covellite) and Cu_9S_8 (yarrowite). From the XRD spectra (figure.1) it can be observed that the obtained copper sulfide powder contains also Na_2S_3 impurities.
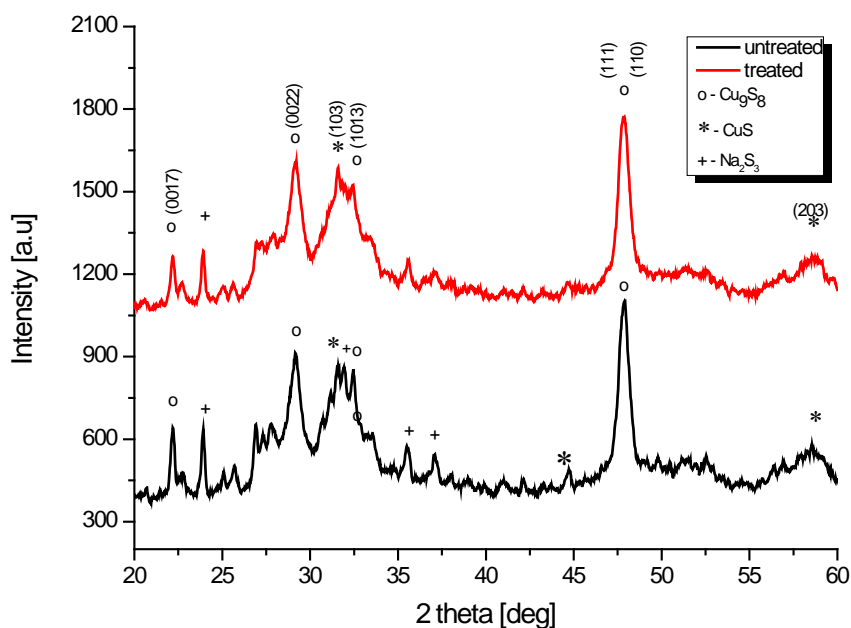

*Fig. 1. X-ray diffraction patterns for Cu$_x$S for as prepared and thermal treated samples ** *CuS (covellite), o Cu$_9$S$_8$ (yarrowite) + Na$_2$S$_3$*

Goble reported in his paper the resemblance between XRD patterns of the Cu$_x$S phases: covellite and yarrowite. This resemblance is given by the unit cell which shows cells parameters nearly equals for covellite (a= 3.79 Å and c= 16.36 Å) and yarrowite (a= 3.80 Å and c= 16.81 Å) The deviation of yarrowite unit cells is given by the double reflection near the covellite indices ((105), (205), (108) and (208)) [66].

From the XRD patterns of the Cu$_x$S powder we can observe that the thermal treatment leads to a phase transition from Cu_9S_8 to CuS.

The literature data show different values of the average crystallite size calculated using the Scherrer formula. For example the value of the average crystallite size of the CuS films treated at 200 ºC by M. Ali Yldirim et al. [58] was about 13.1 nm while the average crystallite size for the Cu$_2$S phase reported by Yu and An [46] was about 110 nm. Simionescu et al [55] obtained Cu$_9$S$_8$ nanocrystallites, by chemical precipitation at 90ºC, with an average crystallite size biggest than 500 nm. Usually the heat treatment induces an increase in network parameter (a$_o$). When it has been a decrease of this parameter a phase (1) form another phase (2), transition phase change material content. The majority phase (1) (before heat treatment) becomes the majority phase (2) after heat treatment, while a decrease of crystal lattice parameter for phase 1 takes places. Transition phase change the composition (volume) of the sample: the majority phase 1 (before treatment) reduces its volume, while phase 2 increase in volume due to the phase 1. After heat treatment the lines corresponding to CuS increased in intensity and become narrower (FWHM),

the crystallite size increases, while the intensity of Cu_9S_8 lines decreased. A part of Cu_9S_8 transformed in CuS. In the mean time the intensities of the lines of Na_2S_3 decreased.

3.2 Optical properties

Optical properties such as absorption (Figure 2.) and transmittance (Figure 3.) of the copper sulphide powder are presented.
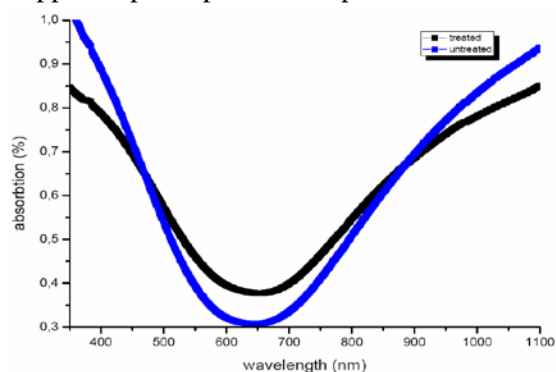

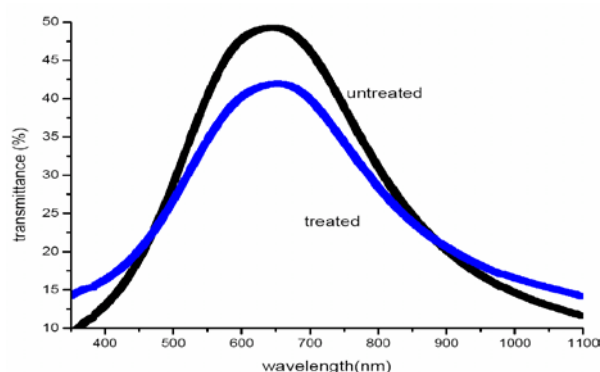Fig. 2. *Absorption spectra for samples of Cu$_x$S before and after heat treatment*

Fig. 3. *transmission spectra for Cu$_x$S before and after heat treatment*

The temperature influence on the adsorption and transmission of the Cu$_x$S samples can be observed in figure 2 and 3 respectively. A thermal treatment leads to the widening of the adsorption band. Absorption peak has been slightly displaced toward higher wavelength (from 644 nm to 650 nm). Adsorption edge also suffered a red shift, from about 525 to 620 nm, after thermal treatment.

Similar results were obtained by H.T. Zhang et.al [59] for covellite (CuS) nanoflakes, prepared at different temperatures. For example, he obtained an absorption edge at 640 nm for the CuS nanoflakes synthesized at 107°C and respectively an absorption edge at 700 nm for the covellite nanoflakes synthesized at 145°C.

The energy band gap for the Cu$_x$S powder has been estimated from the adsorption spectra using the Tauc's law:

$$\alpha h\nu = A (h\nu - E_g)^m \tag{1}$$

where: α is the absorption coefficient; hν- photon energy; E_g- energy band gap; A – a constant; m – a constant for a given transition (m= ½ for direct transition and m= 2 for indirect transition).

The optical band gap of Cu$_x$S can be estimated from the extrapolation of the linear portion of the $(\alpha h\nu)^2$ and respectively $(\alpha h\nu)^{1/2}$ plots versus hν to $\alpha = 0$ (figure 4).
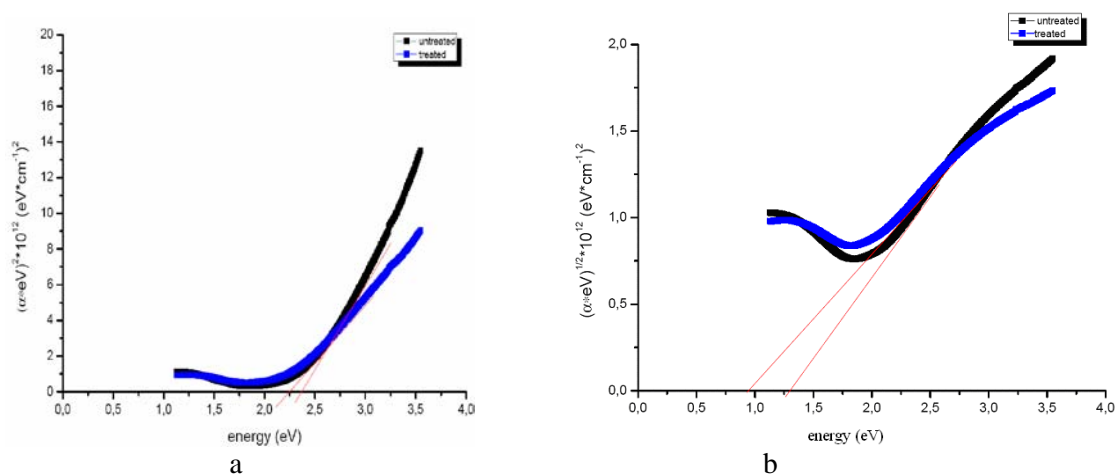
Fig. 4. Graphical determination of energy band gap a) indirect band gap and b) direct band gap

The values of the energy band gap for the Cu_xS powders obtained in our laboratory are presented in Tabel 3. It can be observed the influence of thermal treatment on the energy band gap of Cu_xS powders. We observed that for the treated sample the energy bang gap decrease from 1.30 eV to 0.9 eV, for the indirect transition, and from 2.37 to 2.25 eV in the case of the direct transition. One can see that the value of band gap decreased following the heat treatment. We suppose that the decreasing of band gap can be correlated to a slight change in Cu_xS phases and (also) with the quantum size effect of the nanometer range mean crystallite size.

Table 3. Thermal treatment influence on energy band gap of Cu_xS

Sample	T (°C)	Energy band gap (E_g)	
		m=1/2	m= 2
untreated	-	1.30 eV	2.37 eV
treated	100	0.9 eV	2.25 eV

X. Yu et al. obtained for the Cu_2S powders prepared at 120°, an energy band gap of 1.5 eV [46]. A similar value of the energy band gap (1.22 eV) was obtained by Zhao et al [57] for the Cu_2S synthesized at 180°C. Other values of the energy band gap given in the literature data are 2.54 eV for the Cu_7S_4 obtained at 60 °C by M. Behboudnia [49], 2.96 eV [63] for the Cu_2S obtained by M. Yang using the thermal decomposition at 450°C, respectively 1.25 – 1.75 eV for the CuS powders reported by Raevskaya et al. [50].

Grozdanov [61] determined the energy band gap for Cu_xS films, using various methods. Ploting $(\alpha h\nu)^2 = f(h\nu)$ he obtained the following values: 2.40 eV for Cu_2S; 2.55 eV for $Cu_{1.8}S$; 2.5 eV for $Cu_{1.4}S$ and 2.58 eV for CuS.

According to a recent study made by Sagade and Sharma [33], the optical band gaps (Eg) of thin Cu_xS films are 1.26 eV for CuS, 1.96 for $Cu_{1.4}S$, and 2.31 for Cu_2S.

One can see that the values obtained for Eg by different authors were not the same. Because the determinations were made on films, not on bulk material, the value of band gap was influenced also by the particle size.

In the literature the values of energy band gap for Cu_xS varies from 1.05 – 1.21 eV for the indirect transition, for samples obtained by CBD method by Y. Rodriguez-Lazcano [47] and 2.15 - 2.53 eV for direct transition in the case of Cu_xS obtained with photochemical deposition by J. podder [62].Similar values of the energy band gap were obtained by Obawa et al. for the ternary chalcogenide thin films deposited by CBD method, respectively 2.45 eV for the untreated film, 2.20 eV for the film treated at 373 K and 2.35 eV for the one treated at 473 K [67].

4. Conclusions

In this paper we reported the preparation of the Cu_xS nanopowder using the chemical precipitation method. The structural and optical characteristic of the Cu_xS were found to be closely related to the thermal treatment. Complex mixtures of copper sulfides with the following composition were obtained: CuS (covellite), $Cu_{39}S_{28}$ (spionkopite) and Cu_9S_8 (yarrowite).Resemblance of the three phases indices and the double reflection near covellite indices will be studied next. The values of the energy band gap obtained for the as-prepared Cu_xS powder are in good agreement with the literature data.

Acknowledgment

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