

THE INFLUENCE OF ANNEALING TEMPERATURE ON COPPER SULPHIDE Cu_xS OBTAINED BY CHEMICAL PRECIPITATION

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Abstract

Copper sulphide (Cu_xS) powders were obtained by chemical precipitation from aqueous solutions composed of: copper chloride II ($CuCl_2 \cdot 2H_2O$) as source of (Cu^{2+}), thiourea [$(NH_2)_2CS$] as a source of sulphide ions (S^{2-}) in the presence of complexing agents: ammonia (NH_3) and trietanolamine (TEA). Precipitation process occurred at room temperature for 6 days. The obtained precipitate was filtered with a vaccum pump (707.76 cm Hg) using a 4G ceramic filter and then was rinsed with distilled water. To study the influence of the heat treatment on the copper sulphide powders the precipitate was divided in three. Two of the samples were treated in an oven at 100°C for 2 hours, respectively at 200°C for 3 hours. The third sample was dried at the room temperature. The optical and structural properties of the Cu_xS and copper sulphate powder were determined using the UV-Vis spectroscopy and X- ray diffraction (XRD).

Keywords: chemical precipitation, copper sulphide, UV-Vis spectroscopy, energy band gap

INTRODUCTION

Transition metals chalcogenides represents a great attraction for researchers due to their optical and electrical properties. The first scientific discovery regarding the photovoltaic properties of Cu_xS dates from 1980 and describes the deposition of a Cu_xS/CdS films, having an efficiency of 10%. The copper- sulphure system received a special attention due to its application in solar cells [1-3], solar control coating [4], gas sensors [5], antireflection coating [6].

The copper-sulphur system is a complex system, with five stable phases most common in nature: covellite (CuS), anilite ($Cu_{1.75}S$), digenite ($Cu_{1.8}S$), djurleite ($Cu_{1.95}S$) and chalcocite (Cu_2S) [7].

General chemistry presents the copper sulphide as Cu_xS ($2 > x > 1$) due to its stable and metastable phases of Cu-S system. Chemists have an important contribution on the formation and characterization of copper sulphides with special properties (mechanical, optical, magnetical and morphological). The copper sulphide (Cu_xS) powders can be obtained through various methods including solid state reaction, high temperatures processes and hydrothermal methods. Xuelian Yu et al. obtained Cu_2S nanowires by hydrothermal synthesis [8]. Copper sulphide nanopowders were synthesized by Lida Fotouhi using the electrochemical synthesis [9].

Complexity of this material favors the formation of mixed phases throughout the obtaining process by different methods. Many researchers use only a single copper sulphide phase for their applications, fact which led to the use of simplified methods and selective production of copper sulphide.

This paper presents the influence of heat treatment on optical properties and on formation of Cu_xS ($2 > x > 1$) phases.

EXPERIMENTAL DETAILS

In a flat bottomed flask of 100 ml was prepared a solution containing 20 ml CuCl₂*2H₂O (0.009 M) as Cu²⁺ source, 4.545 gr TEA, 10 ml NH₃ - 25%, 20 ml [(NH₂)₂CS] (TU, thiourea), 0.65 M, for S²⁻ source, and 45 ml water. By adding TU a change on color solution held from blue to olive-green. The solution was left to precipitate at room temperature for six days. During the precipitate formation we observed a change in color from purple - silver to black. The obtained precipitate was filtered with a vacuum pump (707.76 cm Hg) using a ceramic filter, then was rinsed with distilled water and dried in air, at room temperature. Then the precipitate was divided in three melting pots, two of them were treated at different temperatures as follows: 100°C for 2 hours and at 200°C for 3 hours. After the heat treatment the powders were cooled at room temperature in the presence of air.

Characterization of Cu_xS powder

Optical properties of Cu_xS powders were determined on a Lambda 35 spectrometer (Perkin Elmer), the absorption spectra were performed at wavelengths between 300 - 1100 nm. The structural properties were determined by X-ray diffraction (XRD), with a XRD 6000 Shimadzu diffractometer equipped with a Cu-K_α radiation ($\lambda = 1.5418 \text{ \AA}$).

RESULTS AND DISCUSSIONS

X-ray diffraction

The phase composition of Cu_xS powder was identified by X-ray diffraction. The X-ray diffraction patterns of Cu_xS are presented in figure 1. One can see that the obtained powders contains a mixture of copper sulphide and copper sulphate phases: (1) CuS Covellite (JCPDS: 06-0464); (2) Cu₉S₅ Digenite (JCPDS: 26-0476); (3) Cu₉S₈ Yarrowite (JCPDS:36-0379); (4) Cu_{1.81}S Digenite (JCPDS:41-0959); (5) Cu_{7.2}S₄ Digenite (JCPDS:24-0061); (6) Cu₄SO₄(OH)₆ Bronchantite -O (JCPDS:13-0398); (7) Cu₄SO₄(OH)₆*2H₂O Posnjakite (JCPDS:43-0676).

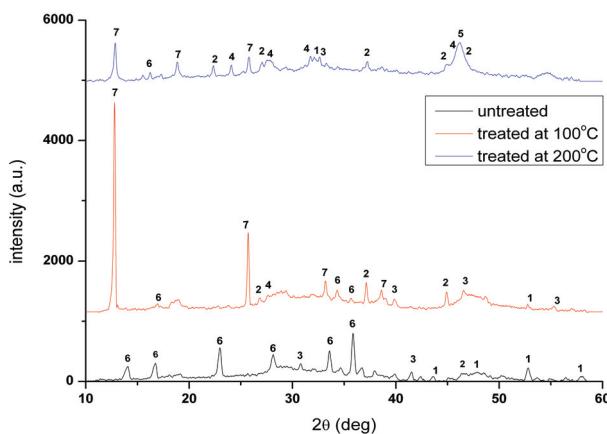


Fig.1. X-ray diffraction patterns of Cu_xS and copper sulphate for as prepared and thermal treated samples.

Predominant phases for the untreated powder are $\text{Cu}_4\text{SO}_4(\text{OH})_6$ (Bronchantite -O) and CuS (covellite). For the powder treated at 100°C for 2 hours it can be observed the transformation of $\text{Cu}_4\text{SO}_4(\text{OH})_6$ (Bronchantite -O) in $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ (Posnjakite) and a decrease in intensity. Also a mixture of posnjakite, yarrowite and digenite was identified by XRD analysis on powder treated at 100°C for 2 hours. X-ray diffraction analysis on powder treated at 200°C (3 hours) confirmed the formation of a mixture of copper sulphides with Cu_9S_5 and $\text{Cu}_{1.81}\text{S}$ as predominante phases. Such mixture phases were also reported in the literature data for powders [10] and copper sulphides films [11,12].

Optical properties

Absorption curves of the powders obtained from $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ at room temperature by chemical precipitation method are presented in Fig.2. Absorption curves presents a liniar decrease of absorption at wavelengths between 417 – 948 nm, the curves presents a shift of minima absorption to infrared domain, with increasing of the annealing temperature. Fig.3. shows the transmission curves for Cu_xS powders.

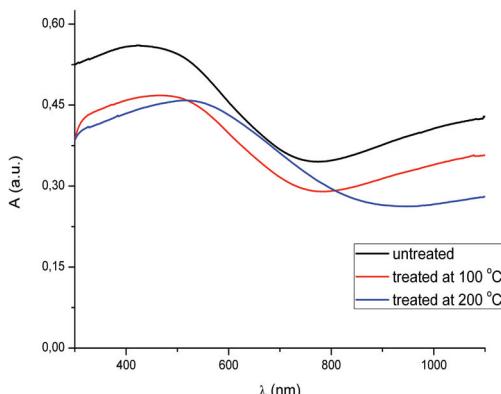


Fig.2. Absorption curves for Cu_xS powders before and after heat treatment

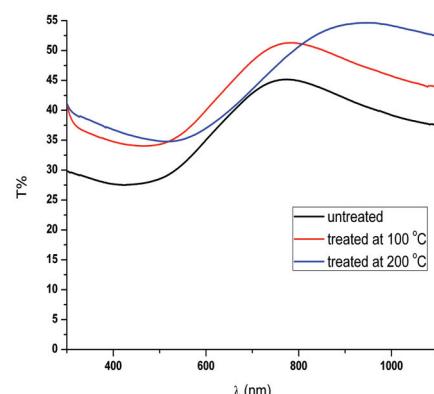


Fig.3. Transmission spectra of Cu_xS powders before and after heat treatment

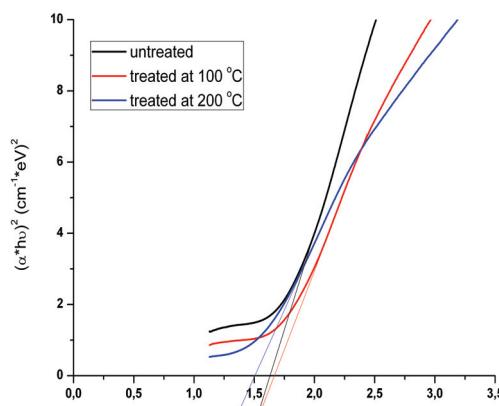


Fig. 4. The variation of $(\alpha \cdot h\nu)^b$ vs. $h\nu$, $b = 2$ (direct transition).

Xiuwen Zheng and Qitu Hu obtained similar results for Cu₉S₈ and CuS prepared at 100°C for 4 hour using different solvents [13].

The energy band gaps for the Cu_xS powders obtained at room temperature for 6 days can be seen in Fig.4. The values were determined by extrapolation of the linear portion of $(\alpha h\nu)^b$ vs. hν, for b = 2 (direct transition).

The energy band gap values for the obtained Cu_xS are given in Table 1. We can conclude that the powder treated at 200°C shows a smaller energy band gap comparing to the samples treated at 100 °C.

Tab.1. Energy band gaps of Cu_xS.

Sample	Temperature/time [°C/ h]	Eg [eV]
Untreated	-	1.63
Treated	100°C /2h	1.66
Treated	200°C/3h	1.50

The values of energy band gap (direct transition) of Cu_xS powders are in good agreement with the literature data [11,14].

CONCLUSIONS

In this paper we reported the variation of copper sulphide phases, obtained by chemical precipitation. The optical and structural properties of the copper sulphides mixture were found to be closely related to the thermal treatment. The values of energy band gap are specific for semiconductors.

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