Synthesis of chalcogenides of I, II and IV groups using a wet-chemistry route

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Abstract: *The objective of the present work is to study the synthesis of sulphide nanoparticles using a wet-chemistry route. More specifically, copper, zinc and tin sulphides were prepared by diluting the metallic salts in various polar solvents. During precipitation, synthesis parameters like temperature, time, and atmosphere were controlled, and their influence analysed. Different sources of sulfur were used, such as thiourea, dimethyl sulfoxide and elemental sulphur. The influence of these parameters on microstructure and composition of the powders has been investigated.*

Key words: *Wet-chemistry, sulphides, kesterite, nanoparticles.*

INTRODUCTION

Chalcogenides are important semiconductors, presenting unique optical, electrical and chemical characteristics. Due to this wide range of properties, in the last years chalcogenides have attracted the attention of the scientific community, particularly in thin films technology due to their applications in nonlinear optical materials [1], Infrared sensors and lenses [2], and solar energy conversion, being the layer heavily impulsed by the growing interest in CIGS and CZTS - based solar cells [3, 4]. Many processes were used to synthesise binary, ternary and quaternary chalcogenides. Binaries were obtained using a wide variety of routes, from microwave irradiation [5] to solvothermal methods [6, 7]. The growing interest in $CuInSe_2$ and $Cu_2ZnSnSe_4$ - based solar cells in the last decades encouraged the study of ternary sulfides and selenides. Chalcopyrite solar cells are mainly deposited by physical methods [8, 9], but chemical methods [4, 10, 11] are gradually gaining attention.

OBJETIVES

This paper aims the synthesis of binary and quaternary sulfides of copper (Cu), tin (Sn) and zinc (Zn) through soft chemistry methods by using various salts and solvents.

EXPERIMENTAL

All syntheses were performed using the following basic procedure: Firstly, metallic salts and sulfur sources were dissolved in the different solvents and put under magnetic stirring. Afterwards, the obtained solutions/suspensions were mounted on a reflux system and heated during different times and atmospheres. Obtained suspensions were then centrifugated and the precipitated powder left to dry at room temperature for 1 day. The procedures of synthesis could be described in detail, as follows:

***Binary coumpounds*.** Experiments were performed in air, using 12ml of DMSO as solvent and 1,6 mmol of thiourea as sulfur source. Metal salts quantities, synthesis temperatures and times are presented in Table 1.

Table 1. Binaries synthesis conditions

Element	Cu	Sn	Zn
Concentration (mol) x 10^{-3}	1.6	0.9	1.1.
Temperature (°C)	90	90	90
Time (hours)	4	24	24

Quaternary compounds. Two different synthesis were made to obtain quaternary materials, using (Q1) DMSO as solvent in oxidizing atmosphere, and (Q2) ethylenediamine as solvent in a reducing atmosphere. Details on both syntheses are explained below:

Experiment Q1. 0.8 mmol of $Cu(NO_3)_2.3H_2O$, 0.45 mmol of $SnCl_4.5H_2O$ and 0.55 mmol of $Zn(NO_3)_2.6H_2O$ were added to 20 ml of DMSO and 3.2 mmol of thiourea. The obtained solution was placed in reflux system for 24h at 100°C.

Experiment Q2. 3.2 mmol of $Cu(NO_3)_2.3H_2O$, 1.8 mmol of $SnCl_4.5H_2O$ and 2.17 mmol of $Zn(NO_3)_2.6H_2O$ were added to 20 ml of ethylenediamine and 20 mmol of thiourea.obtained solution was placed in reflux system under an atmosphere of N_2 5% H_2 for 6h at 110 °C.

RESULTS AND DISCUSSION

Binary compounds Only Cu and Sn binary synthesis resulted in a precipitated powder. No precipitation was observed for Zn binary synthesis after 24h. FESEM micrographs of Cu binary showed flower - shaped crystals of CuS and are presented in Fig.1. a relation very near to 1:1 between Cu and S was observed by EDX analysis. XRD spectrum (Fig.2) showed diffraction peaks of the covellite CuS (PDF# 99 - 101 - 0173).

Also, minor, unidentified peaks were observed.

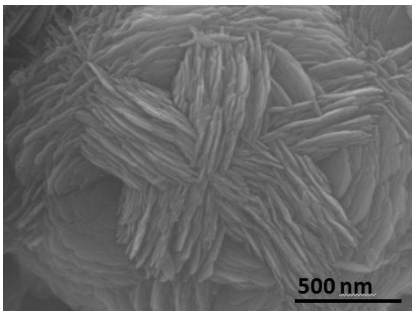

Fig 1. Flower – shaped particles of the as – obtained Cu binary synthesis

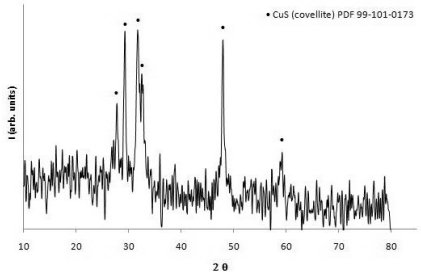

Fig.2. XRD spectrum of Cu binary powder presenting CuS covellite reflections.

Sn binary micrographs presented crystal with a diameter of around 1 μm (Fig. 3). EDX analysis revealed a high quantity of oxygen besides Sn and S. XRD spectrum (Fig.4) showed a broad amorphous band, and revealed the presence of SnS SnS (PDF#99 -200-4045), but also SnO_2 (PDF#99---200---0062) and sulphur (PDF #99 - 101 - 2503).

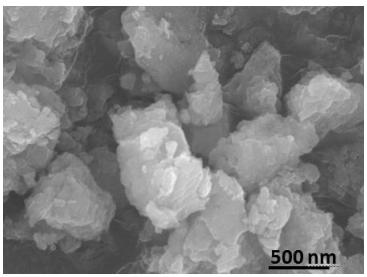

Fig.3. FESEM micrographs of the Sn binary as – synthesized power.

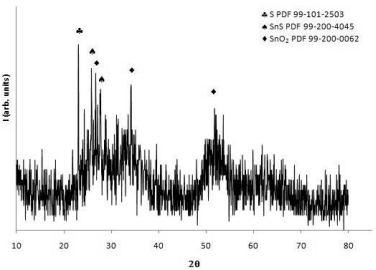

Fig. 4. XRD spectrum of Q2 powder showing

Quaternary compounds EDX analysis of Q1Experiments shows the absence of Zn, and the presence of Sn in a very low quantity. Due to this, DMSO was substituted by ethylenediamine for Q2, since it is a good medium for metallic sulphides precipitation [7]. Also, for Q2 a reductant atmosphere was used to avoid oxygen presence. FESEM micrograph of Q2 is presented in Fig. 5. EDX analysis indicated the presence of all three metals (Cu, Sn and Zn) homogeneously distributed in the powder. Metal ratios were verified to be very near to the initially added composition. XRD spectrum (Fig. 6) presented broad peaks, which is in agreement with the small crystals observed by FESEM. SCII, these peaks matched with the most intense reflections of kesterite

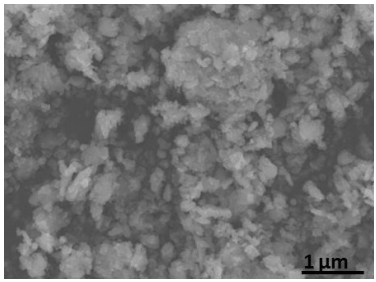

Fig.5 Q2 particles with all added elements in a ratio near to the initial.

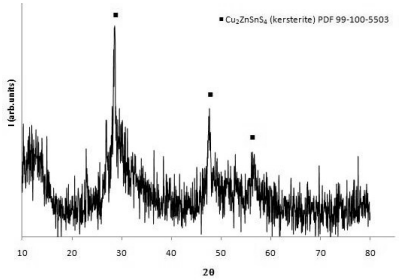

Fig.6. XRD spectrum of Q2 powder showing Diffraction peaks of kesterite (PDF #99 - 100 - 5503.)

CONCLUSION

In this contribuston we presented a path to obtain binary and quaternary chalcogenides from group I, II and IV. Near stoichiometric quaternary sulphide was obtained using ethylenediamine as solvent and thiourea as sulphur source. The low crystalinity of the synthesized powders is a problem yet to be solved, but this is a promising route to obtain multinary chalcogenides.

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