JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 10, October 2008, p. 2700 - 2702

Synthesis and characterization of Cu_7S_4 (anilite) obtained from copper:thiosulfate system

C. M. SIMONESCU*, O. CARP[a], L. PATRON[a], C. CAPATINA[b]

Department of Inorganic Technology and Environmental Protection, Faculty of Applied Chemistry and Materials Science, University "Politehnica" of Bucharest, Polizu Street, No. 1-7, RO-011061, Bucharest, Romania

[a]*Institute of Physical and Chemical "Ilie Murgulescu", Splaiul Independentei Street, No.202, Bucharest, Romania*

[b]*Department of Environmental Engineering, University "Constantin Brancusi", Genova Street, No. 3, RO-210152, Targu-Jiu, Romania*

The system $Cu(CH_3COO)_2{\cdot}H_2O$ and $Na_2S_2O_3{\cdot}5H_2O$ in a molar ratio 1:1, in 50 mL H_2O at room temperature (25 °C) was used to obtain the thiosulfate complex compound ($\{Na[Cu(S_2O_3)]\}_n$). After the thiosulfate compound separation, the obtained filtrate was submitted to hydrolytic decomposition at 80°C and pH==11-11.5.The non-stoichiometric copper sulfide Cu_7S_4 nanocrystallites obtained by hydrolytic decomposition of filtrate were characterized by chemical elemental analysis, X-ray powder diffraction, scanning electron microscopy and IR spectroscopy. The average diameter of the obtained particles varied between 80-110 nm. Their thermal stability in air, studied by nonisothermal techniques together with IR spectroscopy in order to identify phases from different thermal decomposition stages was also investigated. It was established that Cu_7S_4 is converted to $Cu_{1.8}S$ which is stable in a relatively large temperature range 103-240°C. Furthermore, a five-stepped oxidation to $0.42CuSO_4$ $0.52CuO{\cdot}CuSO_4$ occurs. At temperatures higher than 635ºC the formed oxysulfates decompose to CuO. Comparative with the thermal stability of CuS [1] the oxidation process of lower sulfur content sulfides to oxysulfates starts with ~70ºC lower.

(Received April 25, 2008; accepted August 14, 2008)

Keywords: Anilite, Synthesis, Physico-chemical characterization, Thermal oxidation

1. Introduction

Copper sulfides have attracted considerable attention in recent decades due to their interesting optical and electrical properties [2-6]. Since the historic discovery of the photovoltaic properties of Cu_xS thin films in contact with CdS films [7], the copper-sulfur systems have received particular attention related to the achievement of solar cells [8,9], solar control and solar absorber coatings [10-12]. Oxidation processes of different copper sulfides were received the considerable interest due to the great importance of them in copper pyrometallurgy [13-19].

The natural copper sulfides were extensively studied respect to their thermal behaviour [13-15, 20], but in case of copper sulfides synthesized there are a few articles concerning the thermal behaviour of them [16-18]. Until now it wasn't studied the thermal decomposition of Cu_7S_4. In case of Cu_7S_4 it was reported some method of synthesis and its characterization [21-26]. In many cases Cu_7S_4 it was obtained in mixture with other copper sulfides.

In this article is presented the obtaining and characterization of Cu_7S_4 from copper acetate and thiosulfate system. This non-stoichiometric copper sulfide obtained was investigated in order to establish its thermal properties.

2. Experimental

The non-stoichiometric copper sulfide obtaining made part from a series of experiments conducted to copper sulfide CuS obtained [25, 26]. In this case it was used the filtrate obtained after the separation of the thiosulfate complex compound $\{Na[Cu(S_2O_3)]\}_n$. This complex compound was obtained from system $Cu(CH_3COO)_2{\cdot}H_2O$ and $Na_2S_2O_3{\cdot}5H_2O$ (reagent quality-Merck) in a molar ratio 1:1, in 50 mL H_2O at room temperature (25 °C). The filtrate was diluted to 200 mL. At this solution it was added 20 mL of 25% NH_4OH solution. This experiment was realized at 80°C, and the medium pH was 11-11.5. After 4 hours of stirring at this temperature it was obtained a black precipitate which was washed and dried at room temperature.

The sample obtained from this system was characterized by IR Spectroscopy, X-ray powder diffraction (XRD), SEM – scanning electron microscopy. The elemental chemical analysis was performed by an Electronics SPD 1200A ICP emission analyzer with a pump flow of 1.85 $mL{\cdot}min^{-1}$ and a flow rate of the auxiliary gas (Ar 99.99%) of 0.5 $L{\cdot}min^{-1}$. The sulfur content was determined by gravimetric analysis. The IR spectra (KBr pellets) of compounds were recorded on a Bio-Rad-FTS-135 spectrophotometer in the 400 - 4000 cm^{-1} region. Powder X-ray diffraction (XRD) was used to characterize the sample. Data were collected on a Philips Xpert X-ray Diffractometer with CuKα radiation (λ = 1.54178 Å). A scan rate of $0.05°s^{-1}$ was applied to record the patterns in the 2θ range of 20-80°. Scanning electron microscopy (SEM) was applied to determine the morphology of the prepared products by using an electron microscope Hitachi S2600N. Thermal measurement was performed on a Q-1500 Paulik-Paulik-Erdey derivatograph, at heating rates of 2.5-5 K/min and with sample mass of ~20 mg.

3. Results and discussion

The chemical analysis of as-prepared product confirmed the non-stoichiometric copper sulfides Cu_7S_4 formation.

X-ray pattern recorded for this sample obtained at pH = 11-11.5 presented as single phase Cu_7S_4 (ASTM Files No. 72-617 [27], anilite with orthorhombic structure (Fig. 1)).

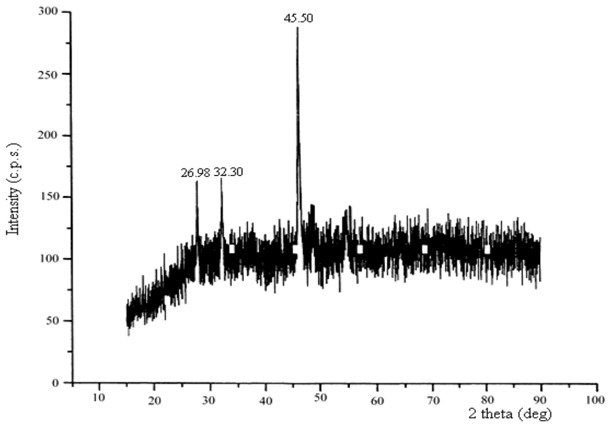

Fig 1. X-ray pattern of Cu_7S_4 obtained from the filtrate resulted after separation of thiosulfate complex compound treated at pH = 11 – 11.5

SEM image for this sample is shown in Fig. 2. The average diameter of particles varied between 80-110 nm.

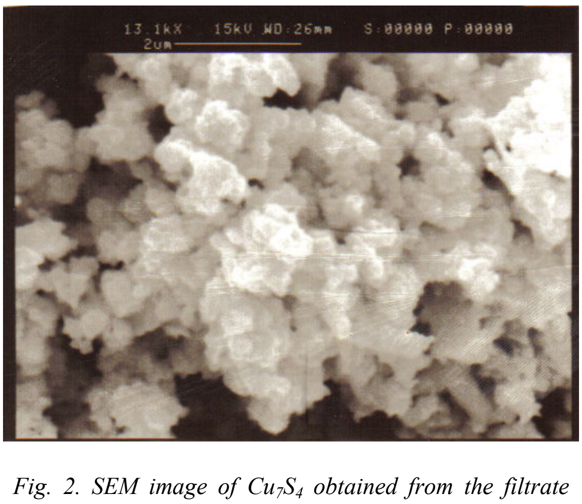

Fig. 2. SEM image of Cu_7S_4 obtained from the filtrate resulted after separation of thiosulfate complex compound treated at pH = 11 – 11.5.

No infrared activity was detected in the FTIR spectrum (Fig. 3), which is characteristic for sulfides IR spectra recorded on this sample [28].

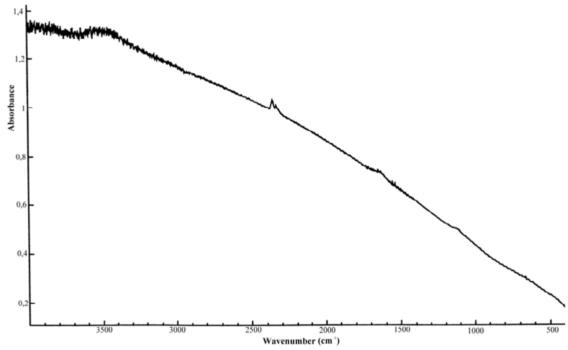

Fig. 3. UV –VIS spectrum of Cu_7S_4 obtained from the filtrate resulted after separation of thiosulfate complex compound treated at pH = 11 – 11.5.

The thermal decomposition curves (TG, DTG and DTA) of the Cu_7S_4 is presented in figure 4. A first decomposition step (103-193ºC), characterized by a small weight loss represents $Cu_7S_4 \rightarrow Cu_{1.8}S$ conversion (weight loss exp./theor.=0.78/0.71%). Formation of lower sulfur content sulfides up to 450ºC is mentioned also by other investigations [29]. The formed sulfide, characterized like the unreacted Cu_7S_4, by no infrared active phases, is stable in the temperature range (103-240ºC). Due to the stability on a such a large temperature range, the thermal decomposition of Cu_7S_4 can be used to obtain $Cu_{1.8}S$. The next stage, which occurs in the temperature range (240-584ºC), is a five stepped weight gain (weight gain=51.8%) , assigned to $Cu^+ \rightarrow Cu^{2+}$ and $S^{2-} \rightarrow SO_4^{2-}$ oxidation, with formation of an oxysulfate with proposed molecular formula $0.42CuSO_4$ $0.52CuO \cdot CuSO_4$. The presence of SO_4^{2-} anion is identified by IR investigations. The oxysulfates stable in the temperature range (435-652ºC), decompose via two endothermic steps on further heating (584-636°C) to CuO. Comparative with the thermal stability of CuS [1] the oxidation process of lower sulfur content sulfides to oxysulfates starts with ~70ºC lower.

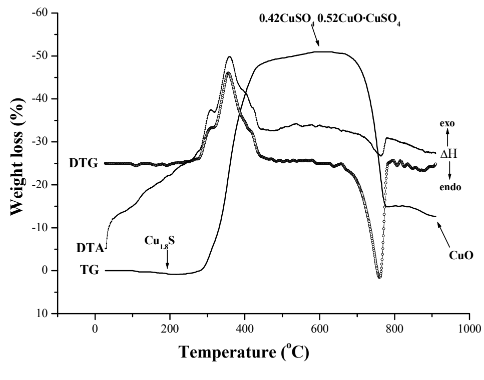

Fig. 4.TG, DTG and DTA curves obtained for Cu_7S_4 obtained from the filtrate resulted after separation of thiosulfate complex compound at pH = 11 – 11.5 (heating rate=5°/min).

4. Conclusions

Filtrate obtained after the separation of the thiosulfate complex compound $\{Na[Cu(S_2O_3)]\}_n$ resulted from system $Cu(CH_3COO)_2 \cdot H_2O$ and $Na_2S_2O_3 \cdot 5H_2O$ in a molar ratio 1:1, in 50 mL H_2O at room temperature (25 ºC), was diluted to 200 mL and treated. After the treatment process it was obtained a non-stoichiometric copper sulfide Cu_7S_4. This copper sulfide obtained was characterized by chemical elemental analysis, X-ray powder diffraction, scanning electron microscopy and IR spectroscopy. The average diameter of the obtained particles varied between 80-110 nm.

From thermal decomposition it was established that Cu_7S_4 is converted to $Cu_{1.8}S$ which is stable in a relatively large temperature range 103-240ºC. Due to this fact Cu_7S_4 can be used to $Cu_{1.8}S$ obtained. The next stages of thermal decomposition are similar with those involved in CuS thermal decomposition. Comparative with the thermal stability of CuS [1] the oxidation process of lower sulfur content sulfides to oxysulfates starts with ~70ºC lower.

Acknowledgements

The authors (Claudia Maria Simonescu, Oana Carp, Luminita Patron, Camelia Capatina) acknowledge the Ministry of Education and Research (Romania) for financial support (CEEX Program No. 6113/12.10.2005 "Methods and mechanisms for crystalline nanoparticles with shape and dimensions controlled for applications in bionanotechnology, sensors, plating and catalysis synthesis).

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*Corresponding auhto: claudiamaria_simonescu@yahoo.com