Journal of Thermal Analysis, Vol. 53 (1998) 355-364

Dedicated to Professor Ferenc Paulik on the occasion of his 75th birthday

THERMAL DECOMPOSITION OF COPPER(I) THIOCARBAMIDE CHLORIDE HEMIHYDRATE

M. Krunks[1,3], *T. Leskelä*[1], *R. Mannonen*[2] *and L. Niinistö*[1]*

[1]Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology FIN-02015 Espoo
[2]Laboratory of Concrete Technology, Helsinki University of Technology, FIN-02015 Espoo Finland
[3]Institute of Materials Technology, Tallinn Technical University, EE-0026 Tallinn, Estonia

Abstract

Two combinations of simultaneous thermoanalytical techniques (TG+DTA and TG+EGA) were used to study the thermal decomposition of the title compound in order to gain a better insight into the spray pyrolytic processes leading to $Cu_{2-x}S$ and $CuInS_2$ thin films. After dehydration a complex sequence of reactions starts above 220°C leading through several intermediates to the formation of CuO in air at 1000°C. In an inert atmosphere Cu_2S is formed which in helium above 800°C partly decomposes to Cu. XRD and FTIR were used to identify the intermediate solid phases which in air included CuCl, Cu_2OSO_4, Cu_2OCl_2 and $CuSO_4$. EGA-FTIR confirmed the complex reaction mechanism with NH_3, HCl, H_2O, COS, CO_2 and some HCN as main gaseous products under oxidative conditions.

Keywords: copper thiocarbamide complex, DTA, EGA, spray pyrolysis, TG

Introduction

Aqueous solutions of cadmium, copper and indium chlorides containing thiocarbamide (tu) are used to deposit binary and ternary metal sulfide thin films by the spray pyrolysis process [1–6]. Spray pyrolysis is an attractive method due to the possibility to deposit large area films with low cost. It is often used to produce thin film gas sensors, conductive electrodes and photovoltaic solar cells. It was shown in the earlier studies that the formation of metal sulfides in a spray process involves the thermal decomposition of the complex compounds formed in the starting solution [2–4, 7].

* Author to whom all correspondence should be addressed.

1418–2874/98/ $ 5.00

Akadémiai Kiadó, Budapest
Kluwer Academic Publishers, Dordrecht

In the present study we have investigated the thermal behavior of 1:1 complex formed in an aqueous solution of copper chloride and (tu) in order to study the thermal decomposition mechanism leading to $Cu_{2-x}S$ and $CuInS_2$ thin films. The main reaction is the reduction of Cu^{2+} to Cu^{+} followed by complexation [4, 7, 8]. The resulting complexes of Cu^{+} with (tu) have high stability constants [8]. The interaction of (tu) with copper ions has been known since last century [9] and it has found practical application in removal of copper deposits encrusting power boilers, corrosion prevention of steel, treatment of metalliferous industrial wastewaters [10] and metal plating [8]

Thermogravimetric studies of solid copper chloride – thiocarbamide complexes in air show that in all cases the thermal degradation is a complex multistep process [4, 7]. The formation of copper sulfide has been detected after the first decomposition stage [4, 7, 11] while CuO is the final decomposition product [4]. In the present study, the solid complex $Cu(tu)Cl \cdot 1/2H_2O$ (**1**) [9, 12] was chosen as a model compound for the spray pyrolytic process. It was expected that the results of the thermoanalytical study would provide data for better understanding of the deposition process and properties of the resulting metal sulfide films. Furthermore, the data could also be important in developing occupational safety measures for the deposition process.

Experimental

Synthesis and characterization of the precursor

The title compound $Cu(tu)Cl \cdot 1/2H_2O$ (**1**) was prepared by mixing 0.2 mol dm^{-3} water solutions of $CuCl_2$ and $SC(NH_2)_2$ in the ratio of 1:2. Analytical grade copper(II) chloride dihydrate and thiourea were used as initial chemicals for synthesis. The blue color typical for $CuCl_2$ solution changed through green up to colorless when solution of $SC(NH_2)_2$ was added and white precipitate consisting of fine needle-shaped crystals formed in solution with enhanced acidity (pH=2.8). The precipitate was filtered, rinsed with deionized water and dried in a thermostat at 50°C. The compound (**1**) was identified by IR [7, 13, 14], chemical analysis (Cu by AAS 35.3 %; calc.: Cu 34.5 %) and by its X-ray diffraction pattern [4, 15].

IR spectra were obtained in the region 4000–400 cm^{-1} with a Nicolet Magna FTIR 750 Spectrometer using the KBr pellet technique. The X-ray diffraction (XRD) patterns of the precursor and its decomposition intermediates and products were recorded by a Philips MPD 1880 diffractometer using CuK_α radiation. The phases were identified using reference samples and JCPDS files.

Thermoanalytical measurements

For the thermoanalytical studies a Seiko simultaneous TG/DTA 320 instrument was used. The sample mass was 15–30 mg and the heating rate 10°C min^{-1}

The measurements were carried out in the flowing air and nitrogen (99.5 %) atmospheres (flow rates in both cases 80 cm^3 min^{-1}). For comparison one experiment was made in pure helium (99.9995 %) with the same flow rate. Some additional heat treatments of the precursor with sample mass of 50–100 mg were made isothermally. For isothermal heating in air a Nabertherm furnace and in flowing nitrogen a Carbolite furnace were used. The heating temperatures were determined on the basis of the dynamic TG runs.

The evolved gas (EGA) studies were carried out in a Bomem TG/Plus instrument consisting of a DuPont 951 thermobalance coupled to a Bomem MB 102 FTIR spectrometer. The samples (50–100 mg) were heated at 10°C min^{-1} in He (99.9995%) and (He+10% O_2) up to 700°C at flow rates 230 cm^3 min^{-1}. The spectra were recorded every 30 s. The identification of the molecules was based on reference spectra or on a characteristic frequency.

Results and discussion

The TG and DTA curves of the samples heated up to 220°C in both inert and oxidative atmospheres are very similar but show different behavior at higher temperatures (Figs 1 and 2).

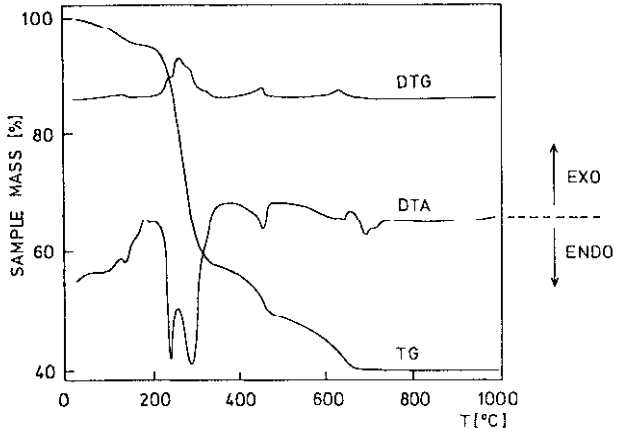

Fig. 1 TG, DTG and DTA curves of $Cu(SCN_2H_4)Cl \cdot 1/2H_2O$ recorded in flowing nitrogen at the rate of 10°C min^{-1}. The sample mass is 25.4 mg

Thermal analysis in the range 20–220°C

The mass loss determined by TG curve in the temperature range 20–200°C is ~5.5%. It is accompanied by an endothermic effect at 140°C in inert as well as in oxidative atmosphere. For the sample heated in air at 150°C for 100 min the mass loss was about 6%.

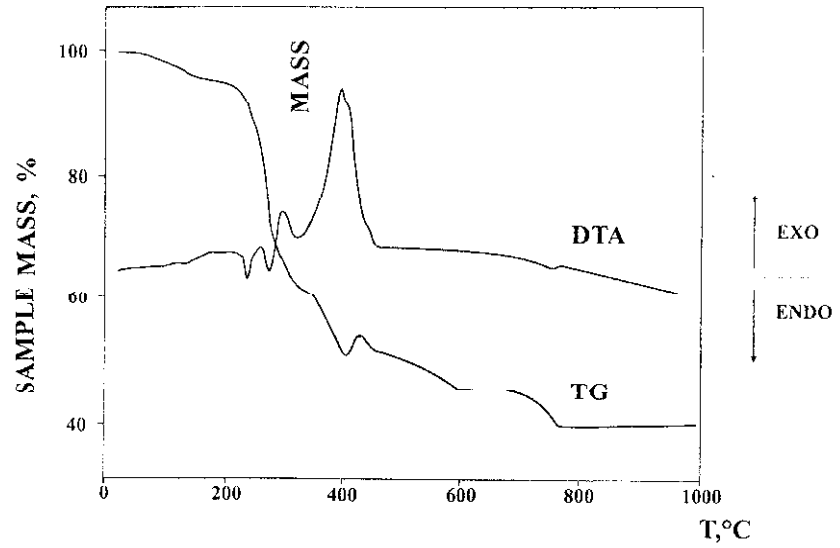

Fig. 2 TG and DTA curves of $Cu(SCN_2H_4)Cl \cdot 1/2H_2O$ recorded in flowing air at the rate of $10^{\circ}C\ min^{-1}$. The sample mass is 20.5 mg

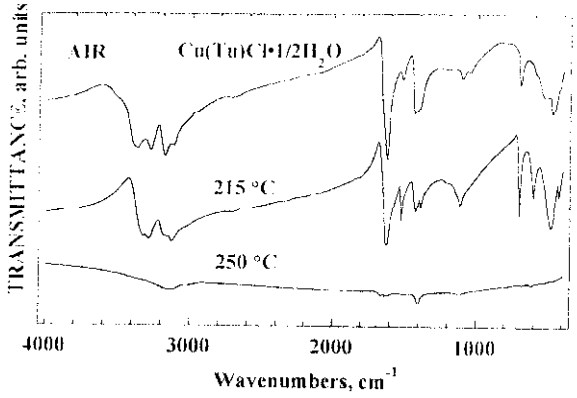

Fig. 3 FTIR spectra of $Cu(SCN_2H_4)Cl \cdot 1/2H_2O$ (air, 215, 250°C)

The IR spectra for the sample heated at 215°C are rather similar to the IR spectra of the starting material (Fig. 3). The difference is that IR spectrum for the material heated at 215°C exhibits very sharp and strong vibrations at 700 and 604 cm^{-1}, corresponding to ν(CS) in sulfur-coordinated thiourea [7, 13, 14, 16]. The absorption bands at 1510–1520 and 1100 cm^{-1} are due to the vibrations of the CN group belonging to the coordinated thiocarbamide molecule [7, 13, 14]. In the precursor (**1**) ν(CN) absorption bands were detected at 1510 and 1105 cm^{-1} but after heating at 215°C they are shifted to the higher wave numbers 1525 and

1117 cm^{-1}, respectively (Fig. 3). On the basis of IR measurements it can be concluded that in the heated material thiocarbamide molecule is still coordinated to the copper atom through the sulfur donor atom but there are some differences in bonding distances and energies with respect to the precursor (**1**).

XRD patterns of the sample heated at 215°C in air and in inert atmosphere are identical but differ from the diffraction pattern of the precursor (**1**) (Fig.4). The strongest lines in the XRD pattern of the sample heated at 215°C are at interplanar distances d=9.67, 4.84, 3.33, 3.29 and 3.22 Å which correspond to the reflections reported for Cu(tu)Cl in the literature [15]. Cu(tu)Cl is highly crystalline and similarity of the diffraction patterns suggests a possible structural relationship with (**1**).

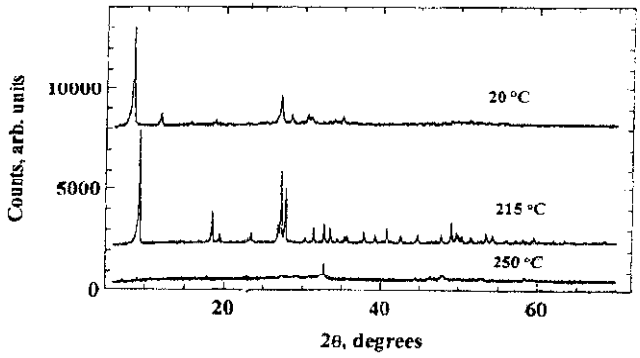

Fig. 4 X-ray diffraction patterns of $Cu(SCN_2H_4)Cl{\cdot}1/2H_2O$ (20, 215, 250°C)

The formation of Cu(tu)Cl (**2**) was confirmed by EGA. Evolution of water in the temperature range 50–180°C was detected by FTIR *in situ* (Fig. 5a) and the measured mass loss of ~5% (calc. 4.9%) corresponds to the dehydration process of (**1**):

$$Cu(tu)Cl{\cdot}1/2H_2O\ (s) \rightarrow Cu(tu)Cl\ (s) + 1/2H_2O\ (g) \qquad (1)$$

Thermal analysis in the range 220–1000°C

Inert atmosphere

TG curve shows in nitrogen atmosphere 3 mass loss maxima at approximately 270, 460 and 650°C (from DTG peaks) (Fig. 1). The first and the second mass loss processes are endothermic. The first decomposition is a two-step process shown by two endothermic peaks at 240 and 290°C. The third decomposition step contains both endo- and exothermic reactions at 650 and 665°C, respectively. The exothermic effect at 665°C could be correlated with oxidation processes due to the quality of nitrogen (99.5%) used in this TG run.

The sample mass has a constant value from 670°C and the end product is Cu_2S according to XRD (Table 1). The total mass loss in the temperature region 20–1000°C is 59% which is 2% higher than calculated on the basis of the assumption that all copper in precursor will be converted into Cu_2S.

In pure helium the DTG curve shows 4 mass loss maxima, three at approximately 265, 440, 640°C and fourth one at 820°C (Δm=3%). All processes are endothermic in He. The total mass loss in the temperature region 20–1000°C is 62.5%. According to XRD data, Cu_2S and metallic Cu are the final products of the thermal decomposition. The fourth peak is due to the partial decomposition of Cu_2S to Cu.

Table 1 Solid decomposition products of $Cu(tu)Cl \cdot 1/2H_2O$ at different temperatures

Nitrogen			Air		
T/°C	phases	reference JCPDS files	*T*/°C	phases	reference JCPDS files
220	Cu(tu)Cl	–	215	Cu(tu)Cl	–
240	CuS, (Cu_7S_4)	6–464, (33–489)	250	CuS, unidentified phase	6–464
330	CuS, (Cu_7S_4)	6–464, (33–489)	320	CuCl	6–344
390	$Cu_{1.8}S$	23–962	420	Cu_2OSO_4 Cu_2OCl_2 $CuSO_4$	13–189 35–679 15–775
460	$Cu_{1.8}S$	23–962	620	Cu_2OSO_4 CuO	13–189 5–661
650	Cu_2S	33–490	770	CuO	5–661
1000	Cu_2S	33–490	1000	CuO	5–661

Oxidative atmosphere

In air the TG curve shows three decomposition steps (Fig. 2). The first decomposition step of (**2**) at temperatures 220–320°C contains both an endothermic and exothermic reaction with mass loss maximum (from DTG curve) at 270°C. Two separate endothermic processes can be distinguished at 240 and 280°C and the exothermic reaction takes place at 300°C. The second decomposition step (330–440°C) is highly exothermic due to the formation of sulfate phases (Table 1). From the TG curve it can be seen that the mass decreases up to 400°C. After that there is a small mass gain up to 420°C after which the mass decreases again. The third decomposition step between 700–760°C is an endothermic process. The total mass loss is 60%. In the temperature interval 20–1000°C CuO is the final product of thermal decomposition.

IR data and X-ray diffraction patterns of the solid residues (Figs 3, 4) confirm a complete degradation of (**2**) at temperatures higher than 220°C. Copper sulfides are the main crystalline phases at 250°C both in air and in nitrogen. Additionally the reflexes of an unidentified phase are present on the diffractogram of the sample treated at 250°C in air (Fig. 4). The stoichiometry of copper sulfides (CuS, $Cu_{1.8}S$, Cu_2S) in nitrogen atmosphere depends on the temperature (Table 1). In air, CuS, CuCl, $CuSO_4$, Cu_2OSO_4, Cu_2OCl_2 and CuO are the main solid crystalline products observed at different decomposition stages.

Evolved gas analysis in oxidizing environment

The spray pyrolytic process is normally carried out in the ambient without strict exclusion of air. Therefore EGA studies were focused on the decomposition under oxidative conditions (He+10% O_2). Comparative studies were also made in inert atmosphere (He).

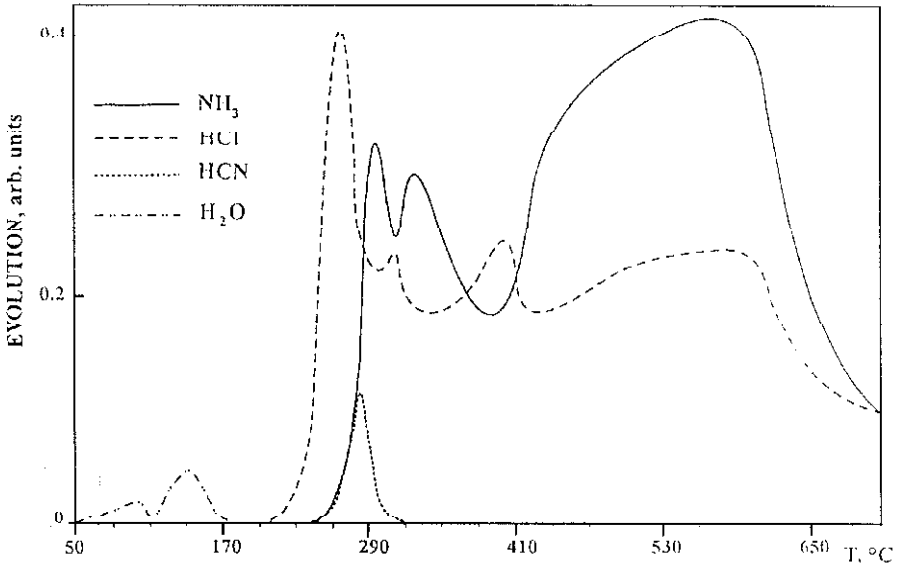

Fig. 5a The evolved gases from $Cu(SCN_2H_4)Cl{\cdot}1/2H_2O$ in a (He+10% O_2) mixture

Evolved gas analysis by FTIR (EGA-FTIR) shows also the complexity of the thermal processes. Figures 5a and 5b summarize the evolution of gaseous species when the sample is heated in a (He+10% O_2) mixture. In Table 2 the gases are grouped accordingly to the temperature intervals.

According to EGA, hydrogen chloride (Fig. 5a) starts to evolve after the dehydration. This helps to interpret the first endothermic decomposition reaction at

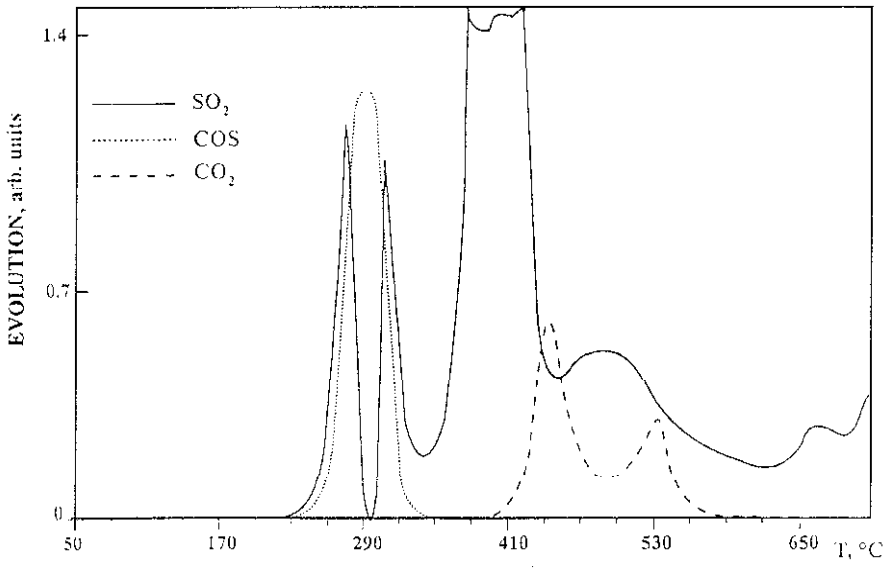

Fig. 5b The evolved gases from $Cu(SCN_2H_4)Cl \cdot 1/2H_2O$ in a (He+10% O_2) mixture

240°C also in the case of an inert atmosphere (Figs 1 and 2). According to the TG curve the mass loss in this step is less than 10% meaning that part of chloride is still left in (**2**).

Evolution of SO_2, COS, NH_3, HCN (Figs 5a, 5b) in an oxidative atmosphere starts at 30°C higher temperature than the evolution of HCl. The evolution of a very small amount of highly reactive H_2NCN was detected during the same decomposition step. This gas was present in a higher concentration in He runs. Also CS_2 and HNCS were detected (Table 2). The gases evolved after HCl are decomposition products of thiocarbamide ligand [2]. Hydrogen isothiocyanate (HNCS) and ammonia (NH_3) have also been found earlier as gaseous thermal decomposi-

Table 2 EGA results of $Cu(tu)Cl \cdot 1/2H_2O$ in a (He+10% O_2) mixture. Gases in parenthesis were detected in trace amounts only

Temperature interval/°C	Evolved gases
50–200	H_2O
220–330	HCl, SO_2, COS, NH_3, HCN, (CS_2, H_2NCN, H_2O, HNCS)
330–400	SO_2, HCl, NH_3
400–470	CO_2, SO_2, NH_3, HCl, H_2NCN
470–560	SO_2, CO_2, NH_3, HCl
560–680	SO_2, NH_3, HCl

tion products of thiourea in the case of the free compound and zinc butyrate thiourea complex [17]. The evolution of NH_3 and HCl continues up to the end of the EGA experiment (680°C)

Thus, taking into account the results of the two simultaneous modes of thermal analysis (TG+DTA, TG+EGA by FTIR) together with the *ex situ* XRD and IR data, the main reactions occurring between 220–400°C can be presented as follows:

$$Cu(SCN_2H_4)Cl\ (l) \rightarrow CuCl\ (s) + SC(NH_2)_2\ (l) \quad (2)$$

$$SC(NH_2)_2\ (l) \rightarrow HNCS\ (g) + NH_3\ (g) \quad (3)$$

$$2SC(NH_2)_2\ (l) \rightarrow CS_2\ (g) + H_2NCN\ (l,g) + 2NH_3\ (g) \quad (4)$$

$$HNCS\ (g) + O_2\ (g) \rightarrow HCN\ (g) + SO_2\ (g) \quad (5)$$

$$2CS_2\ (g) + 3O_2\ (g) \rightarrow 2COS\ (g) + 2SO_2\ (g) \quad (6)$$

The formation of CuS and liberation of HCl from CuCl is possible by the following reaction:

$$CuCl\ (s) + SC(NH_2)_2\ (l) + O_2\ (g) \rightarrow \rightarrow CuS\ (s) + HCl\ (g) + NH_3\ (g) + 1/2\ N_2\ (g) + CO_2\ (g) \quad (7)$$

However, nitrogen cannot be detected by EGA-FTIR which is a drawback of the method compared to EGA-MS [18].

Copper chloride formed in the reaction (2) may oxidize to oxochloride.

$$2CuCl\ (s) + 1/2O_2\ (g) \rightarrow Cu_2OCl_2\ (s) \quad (8)$$

Evolution of SO_2 is very intensive at temperatures 350–420°C in air and it continues up to 680°C. The highly exothermic process at 350–450°C and increase of sample mass by TG curve between 400–420°C is connected with the oxidation of copper sulfide. The formation of the oxidation products such as $CuSO_4$ and Cu_2OSO_4 was confirmed by XRD (Table 1).

Evolution of CO_2 at 400–560°C and presence of small amount of H_2NCN at 400–470°C in air indicate decomposition and oxidation of the condensed organic species. Oxidative atmosphere contributes the degradation of the organic part at lower temperatures than in inert atmosphere.

The last major decomposition step between 700–760°C is endothermic in air and can be attributed to the decomposition of copper oxosulfate leading to CuO as a final decomposition product at 770°C:

$$Cu_2OSO_4\ (s) \rightarrow 2CuO\ (s) + SO_3\ (g) \quad (9)$$

This reaction generates sulfur trioxide [19] but because it takes place beyond the temperature range of our EGA study SO_3 was not detected.

Conclusions

As seen in the present study, simultaneous use of several thermoanalytical techniques enhances the information content of results obtained from a single thermoanalytical measurement. Evolved gas analysis (EGA) is especially powerful in yielding complimentary data. However, in order to interpret the decomposition and oxidation processes it is necessary to analyze the solid state intermediates and products. This can be done only by *ex situ* measurements (XRD, IR) and chemical analysis but even then the results in the case of a complex process can be ambiguous.

A relevant result for the development of spray pyrolytic processes obtained in the present study is that oxygen must be excluded in order to obtain pure copper sulfides. Also special safety measures need to be considered for the process because small amounts of HCN are among the evolved gases.

* * *

A scholarship from the Nordic Council of Ministers to M. K. and support from the Estonian Scientific Foundation (grant no. 2841) are gratefully acknowledged. Prof. János Madarász is thanked for compiling the reference database for EGA by FTIR.

References

1 S. Mathew, P. S. Mukerjee and K. P. Vijayakumar, Thin Solid Films, 254 (1995) 278.
2 M. Krunks, J. Madarász, L. Hiltunen, R. Mannonen, E. Mellikov and L. Niinistö, Acta Chem. Scand., 51 (1997) 294.
3 B. Brown and C. Bates, Thin Solid Films, 188 (1990) 301.
4 M.Krunks, E.Mellikov and O.Bijakina, Phys. Scripta, T69 (1997) 189.
5 M. Ortega-Lopez and A. Morales-Acevedo, Proceedings IEEE Photovoltaic Spec. Conf. 25th (1996) 1009.
6 H. Bihri, C. Messaoudi, D. Sayah, A. Boyer, A. Mzerd and M. Abd-Lefdil, Phys. Stat. Solidi, 129 (1992) 193.
7 Y. A. Ugai, V. Semenov and E. Averbakh, Russian J. Inorg. Chem., 26 (1981) 147.
8 M. H. Hölzle, C. W. Apsel, T. Will and D. M. Kolb, J. Electrochem. Soc., 142 (1995) 3741.
9 B. Rathke, Ber. Deutsch. Chem. Ges., 17 (1884) 297.
10 C. J. Doona and D. M. Stanbury, Inorg. Chem., 35 (1996) 3210.
11 Y. Shibutani and K. Shinra, Chem. Express, 4 (1989) 321.
12 A. Rosenheim and W. Loewenstamm, Z. Anorg. Chem., 34 (1903) 62.
13 Y. Kharitonov, V. Brega, A. Ablov and N. Proskina, Russian J. Inorg. Chem., 19 (1974) 1187.
14 M. Krunks, E. Mellikov and O. Bijakina, Proc. Estonian Acad. Sci., Eng., 2 (1996) 98.
15 G. W. Watt and J. S. Thompson Jr., J. Inorg Nucl. Chem., 33 (1971) 1319.
16 K. Swaminathan and H. M. N. H. Irving, J. Inorg. Nucl. Chem., 26 (1964) 1291.
17 K. Györyová, V. Balek and J. Kovárova, Thermochim. Acta, 269/270 (1995) 425.
18 T. Leskelä, M. Lippman, L. Niinistö and P. Soininen, Thermochim. Acta, 214 (1993) 9.
18 J. Paulik, Atlas of Thermoanalytical Curves, G. Liptay (Ed.), Vol.I, Heyden & Son Ltd., London, 1971, p. 24.