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STUDY OF ZINC THIOCARBAMIDE CHLORIDE, A SINGLE-SOURCE PRECURSOR FOR ZINC SULFIDE THIN FILMS BY SPRAY PYROLYSIS

M. Krunks[1*], *J. Madarász*[2], *T. Leskelä*[3], *A. Mere*[1], *L. Niinistö*[3] *and G. Pokol*[2]

[1]Institute of Materials Technology, Tallinn Technical University, EE-19086 Tallinn, Estonia
[2]Institute of General and Analytical Chemistry, Budapest University of Technology and Economics, Szt. Gellért tér 4, H-1521 Budapest, Hungary
[3]Laboratory of Inorganic and Analytical Chemistry, Helsinki University of Technology, P.O. Box 6100, FIN-02015 Espoo, Finland

Abstract

Thermal decomposition of the title compound, $Zn(tu)_2Cl_2$ (*tu*=thiourea), was studied up to 1200°C in dynamic inert (N_2) and oxidative (air) atmospheres using simultaneous TG/DTA techniques. In addition, XRD and IR were employed *ex situ* to resolve the reaction mechanism and products. Cubic ZnS (sphalerite) is formed below 300ºC in both atmospheres and is observed until 760ºC, whereafter it transforms in nitrogen to the hexagonal ZnS (wurtzite). EGA by FTIR revealed the complexity of the decomposition reactions involving also the evolution of H_2NCN, which reacts to form hexagonal $ZnCN_2$ as shown by an XRD analysis.

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

Introduction

Aqueous solutions containing cadmium, zinc, tin, copper or indium chlorides together with thiourea (*tu*) have been used to deposit binary and ternary metal sulfide thin films by the spray pyrolysis technique [1–5]. It has been shown that from thiourea solutions of Cd, Zn, Cu and Sn halogenides several complexes with different stoichiometry and water content could be obtained [1, 4, 6–8]. The formation of $Zn(tu)_2Cl_2$ in an aqueous solution of thiourea and $ZnCl_2$ and its use as a precursor for ZnS films has been only briefly reported earlier [9, 10]. On the other hand, the thermal decomposition of Cd and Cu chloride complexes with thiourea has been investigated in detail by applying TG, DTA and EGA methods [1, 6, 7].

In the present work, thermal decomposition of $Zn(tu)_2Cl_2$ in dynamic inert and oxidative atmospheres has been studied and compared to that observed under static air [4]. The research has been initiated to obtain a better understanding of the process

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[*] Author for correspondence: E-mail: malle@staff.ttu.ee

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of producing ZnS films by the spray technique which has extensively been studied during the last years as an inexpensive chemical alternative to produce thin films especially for large-area applications [2–4, 10–13].

Experimental

$Zn(tu)_2Cl_2$ (**1**) was prepared at room temperature by mixing of 1 mol dm^{-3} $ZnCl_2$ and tu aqueous solutions in a molar ratio of 1:2. The solution was let to slowly evaporate under ambient conditions. The crystalline precipitate was formed in a couple of days and it consisted of well-shaped transparent prisms with sizes up to some millimetres. The crystals were decanted and dried in the ambient. The compound was characterized by chemical analysis to confirm the composition of $Zn(tu)_2Cl_2$: Zn by AAS 22.5 mass%, calc. 22.7 mass%; C and N by organic elemental analysis (OEA) 8.3 and 19.2 mass%, calc. 8.3 and 19.4 mass%, respectively. The formation of **1** was also confirmed by recording its FTIR spectrum and comparing it with the literature data [14].

For TG/DTA/DTG studies of **1**, a Seiko simultaneous TG/DTA 320 analyser, a Setaram Labsys simultaneous TG/DTA 16 instrument and a TA Instruments STD 2960 simultaneous TG/DTA instrument were used. A sample mass of 14–28 mg was used for the experiments applying heating rate of 10ºC min^{-1}. The measurements were carried out in dynamic air and nitrogen (99.99%) atmospheres using gas flow rates of 80 in Seiko and 30 mL min^{-1} in Setaram instrument. Some additional heat treatments of **1** were made isothermally at temperatures determined on the basis of the dynamic TG runs. In air the experiments were performed in a laboratory oven while in the case of inert atmosphere the treatments were made in the quartz tubes under an argon flow.

The evolved gas analysis (EGA) was performed in a TA Instruments TGA 2050 thermogravimetric analyzer coupled to a Biorad Excalibur Series FTS 3000 FTIR spectrometer equipped with a TG/IR accessory unit. The samples (20–30 mg) were heated at a rate of 10°C min^{-1} up to 800°C in an air flow of 130 mL min^{-1}. The interferograms were collected at every 30 s and transformed to absorbance spectra in the range of 4000–650 cm^{-1}. The identification of the gaseous molecules was based on reference spectra or on a characteristic wavenumber.

FTIR and powder diffraction were used ex situ to characterize the precursor as well as intermediates and final products of the thermal decomposition. IR spectra were recorded in the region 4000–400 cm^{-1} with a Perkin Elmer GX1 spectrometer using the KBr pellet technique. The X-ray diffraction (XRD) patterns were recorded in a Bruker AXS D5005 diffractometer with monochromatic CuK_α radiation. The phases were identified using JCPDS files.

Results and discussion

Thermal analysis

Thermal behaviour of **1** was studied in pure nitrogen and synthetic air up to 1200ºC. According to the TG curves there was no mass loss up to 200ºC in either atmosphere

(Figs 1 and 2). The first endothermic effect at 160ºC corresponds to the melting of the compound, also observed visually by heating the crystals of **1** in a laboratory oven.

The TG curves show no well-defined mass loss steps during the first decomposition stages in either atmosphere but instead indicate overlapping processes. According to the DTG curves, 5 mass loss steps could be distinguished in both atmospheres (Figs 1 and 2).

Table 1 Mass of the final solid residue of $Zn(tu)_2Cl_2$ in TG runs in air and nitrogen atmospheres at heating rate of 10°C min^{-1} using different sample mass and gas flow rate on different TG apparatures

Atmosphere	Sample mass/mg	Gas flow rate/ mL min^{-1}	Final temp./ °C	Mass of the final residue/%	TG apparatus
Air	24.12	80	800	16.6	Seiko
	22.38	80	800	16.0	Seiko
	10.48	130	800	20.0	TA Instr.
	14.20	30	800	21.0	Setaram
N_2	28.10	30	1000	20.8	Setaram
	21.45	80	1000	12.7	Seiko
	21.45	80	1200	0	Seiko

In nitrogen, all decomposition processes are endothermic and the mass loss up to 1000ºC is 87.3%. According to XRD, ZnS (wurtzite) is the final decomposition product. No residue remained when the heating was extended up to 1200ºC. In air, both endo- and exothermic processes could be observed (Fig. 2). ZnO was the final decomposition product at 770ºC, confirmed by XRD. The total mass loss shown by the TG curve is 83.4%.

The final residual mass was found to be dependent on the experimental parametres including the TG apparatus, initial sample mass and gas flow rate as presented in Table 1. Assuming that all Zn present in the precursor is still incorporated in the final product, the theoretical residue in air, where ZnO is formed, is 28.2% while it is in an inert medium 33.8% for ZnS. It was found, however, that the mass of the final residue is significantly smaller than the theoretical value, independent on the experimental conditions (Table 1), likewise also when heating in static air [4]. Consequently, a part of Zn must have escaped the sample during the heating and probably $ZnCl_2$, having the highest vapour pressure among the Zn compounds in the system, is responsible for the Zn loss as concluded also recently in [4]. The sublimation of ZnS leads to an empty crucible if heating is continued up to 1200ºC in nitrogen.

The temperature ranges of the decomposition steps, temperatures of DTA and DTG maxima as well as the observed mass losses are presented in Table 2. The first decomposition step in both atmospheres involves a sequence of reactions as discussed above. In nitrogen, the decomposition steps 2–4 are single decomposition processes while the decomposition step 5, clearly distinguishable on the TG curve (Fig. 1), consists of two endothermic processes.

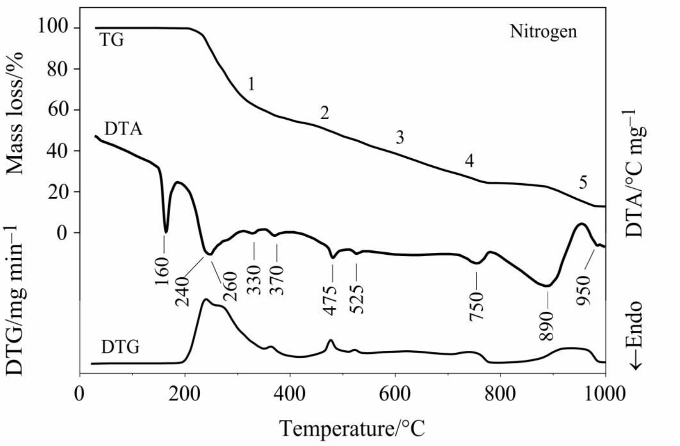

Fig. 1 TG, DTA and DTG curves of $Zn(tu)_2Cl_2$ recorded in flowing nitrogen of 80 mL min^{-1} at the heating rate of 10°C min^{-1} on Seiko TG/DTA 320 instrument. The sample mass is 21.45 mg

In air, the decomposition step 1 contains at least two endothermic reactions (Fig. 2, Table 2) but the overall effect is exothermic whereupon a considerable amount of heat evolves around 300ºC. The decomposition steps 2 and 3 in the range of 340–500ºC are endothermic processes followed above 500ºC by exothermic reactions of step 4. The final decomposition step (No. 5) is again exothermic. Air at 700–770ºC is an oxidative process which changes to endothermic decomposition above 750ºC (Fig. 2 and Table 2).

The largest mass loss occurs during the first decomposition step and at temperatures close to 500ºC approximately half of the initial mass has been lost in both atmospheres.

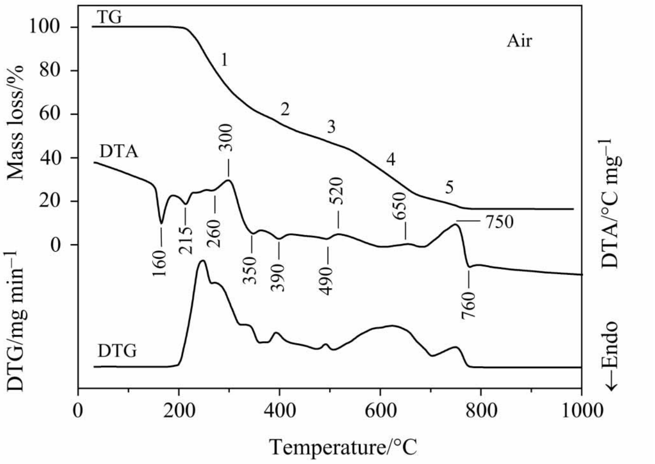

Fig. 2 TG, DTA and DTG curves of $Zn(tu)_2Cl_2$ recorded in flowing air of 80 mL min^{-1} at the heating rate of 10°C min^{-1} on Seiko TG/DTA 320 instrument. The sample mass is 24.12 mg

Table 2 Mass losses, temperatures of DTA and DTG peaks as recorded on Seiko TG/DTA 320 instrument and identification of the crystalline phases in different decomposition steps of Zn(tu)$_2$Cl$_2$

Atmosphere	Step	Temperature range/°C	DTA peak temperature/°C	DTG max temperature/°C	Mass loss/%	Crystalline phases in the decomposition step, ICDD file No.
Nitrogen	1	200–390	240 endo 260 endo 330 endo 370 endo	245 260 – 365	44.9	ZnS (S*, 05-0566)
	2	390–500	475 endo	475	6.8	ZnS (S, 05-0566)
	3	500–700	525 endo	525	18.8	ZnS (S, 05-0566) Unidentified phase
	4	700–760	750 endo	750	5.7	ZnS (S, 05-0566) Unidentified phase
	5	820–980	890 endo 950 endo	930	11.1	ZnS (W**, 36-1450)
Air	1	200–340	215 endo 225 exo 260 endo 300 exo	240 270 330 –	37.0	ZnS (S, 05-0566)
	2	340–460	350 endo 390 endo	– 390	13.5	ZnS (S, 05-0566) (ZnCO$_3$ (08-0449)
	3	460–510	490 endo	490	4.1	ZnS (S, 05-0566) ZnO (36-1451) ZnCl$_2$·4Zn(OH)$_2$·H$_2$O (07-0155) Unidentified phase
	4	510–700	520 exo 650 exo	620	24.2	ZnS (S, 05-0566) ZnO·ZnCl$_2$·2H$_2$O (45-0819) ZnO (36-1451) Unidentified phase
	5	700–770	750 exo 760 endo	750	4.8	ZnO (36-1451)

* S – sphalerite, ** W – wurtzite

IR study of solid decomposition products

IR spectra of the precursor and the products in the first decomposition step are presented in Fig. 3. A comparison of IR spectra of $Zn(tu)_2Cl_2$ and those of a sample heated up to 200°C confirms the rearrangement of **1**. The strong absorption peak at 2094 cm^{-1}, assignable to the stretching vibrations of both thiocyanate (SCN) groups and hydrogen bonded RNH_3^+ groups, suggest isomerisation of thiourea into ammonium thiocyanate. IR spectra of the decomposition product at 230°C show the disappearance of the characteristic vibrations of **1** as well as the overlapping ν(SCN) and $\nu(NH_4^+)$ vibration bands, confirming the destruction of the initial compound during the first decomposition step (Fig. 3).

IR spectra of the solid residues prepared by heating of **1** at temperatures of 300–500°C in air in a laboratory oven are similar to those recorded for the sample heated at 230°C (Fig. 3). Only small changes could be detected if the samples were prepared at higher temperatures, viz. close to 500°C.

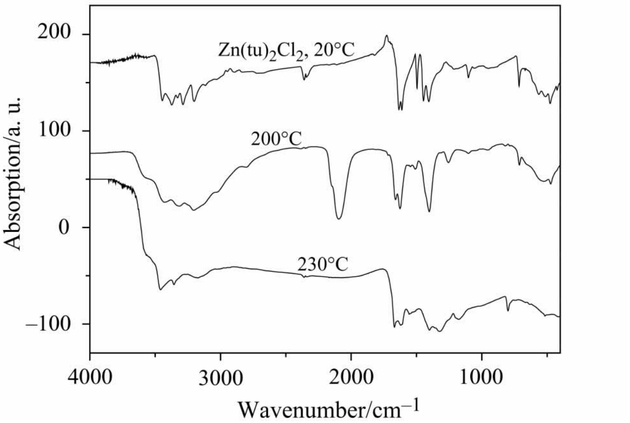

Fig. 3 FTIR spectra of $Zn(tu)_2Cl_2$ and its decomposition product at 200 and 230°C in air

The results of OEA show a continuous decrease in the C and N contents when increasing the thermal treatment temperature in the range of 400–520°C. For example, the N contents were 11.26 and 5.51 mass%, while those for C were 7.21 and 3.50 mass% when the samples were heated at 430 and 520°C, respectively. The atomic ratio of N/C=1.34 remains constant, however, and is characteristic for the samples prepared in this temperature region, indicating together with the IR spectra similar type of organic residues.

The intermediates prepared at 760°C in flowing nitrogen atmosphere and at 700°C in air show quite similar IR spectra with strong absorptions at 673, 695 and at 2046 cm^{-1} (Fig. 4). In addition, two strong absorptions at 834 and 895 cm^{-1} were detected if the sample was heated in air. In the case of Cd complex the vibrations at 2000–2200 and 650 cm^{-1} were identified as belonging to $CdCN_2$ [1]. The extra phases in both residues of **1** will be discussed below on the basis of powder XRD.

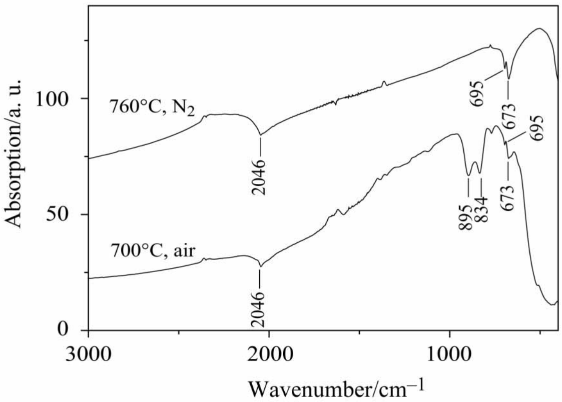

Fig. 4 FTIR spectra of $Zn(tu)_2Cl_2$ decomposition products prepared at 760°C in flowing nitrogen and at 700°C in air

X-ray diffraction study

The results on crystalline decomposition products of **1** are presented in Table 2. According to XRD, complete decomposition of **1** occurs already during the first decomposition step and as a result ZnS (sphalerite) forms at below 300°C in both atmospheres. Well-crystallised sphalerite phase, detected in the residue heated up to 760°C, transforms to the wurtzite polymorph if heating is continued up to 980°C in an inert atmosphere. This temperature is slightly lower than reported earlier (1020°C) [15]. Also Balek *et al.* have by high-sensitivity DSC measurements observed the sphalerite-wurtzite polymorphic transition to occur at a much lower temperature, viz. around 450°C [16].

In air, the sphalerite is detected up to 550°C while at higher temperatures the oxidation of ZnS occurs. The appearance of ZnO already at 490°C is earlier than expected by the oxidation route of ZnS. Zinc chloride-containing phases, viz. simonkolleite ($ZnCl_2{\cdot}4Zn(OH)_2{\cdot}H_2O$) and zinc oxide chloride hydrate ($ZnO{\cdot}ZnCl_2{\cdot}2H_2O$), have been found in the residues heated up to 490 and 520°C, respectively, and cooled back to room temperature. The heating of **1** up to 550°C results in crystalline phases of ZnS and ZnO. The additional formation of ZnO could be possible along the following path:

$$ZnCl_2{\cdot}4Zn(OH)_2{\cdot}H_2O \rightarrow ZnO{\cdot}ZnCl_2{\cdot}2H_2O \rightarrow ZnO+ZnCl_2 \qquad (1)$$

Part of the released $ZnCl_2$ probably volatilises as discussed above. The remaining part can react with the evolved gases. An unidentified phase, showing cyanamide vibrations according to FTIR (Fig. 4), was observed by XRD as a product of the decomposition step 4 for **1** in both atmospheres. Taking into account an intensive H_2NCN evolution at temperatures higher than 500°C (Table 3), the formation of zinc cyanamide appears probable:

$$ZnCl_2+H_2NCN \rightarrow ZnCN_2+2HCl \qquad (2)$$

The XRD patterns of the products in the decomposition step 4 (760 in inert and 700°C in air) contain well-resolved diffraction peaks at *d*= 4.62, 3.31, 3.19, 2.312, 2.228, 2.198, 1.988, 1.774, 1.726 and 1.677 Å, in addition to those of the final products (ZnS or ZnO). However, the diffraction peaks do not belong to the $ZnCN_2$ phase (orthorhombic), JCPDS file (01-0788) presented in the ICDD database. Our crystallographic calculations, applied to the powder diffraction pattern of the proposed $ZnCN_2$ phase, give the best fit in the case of hexagonal symmetry being the same as reported for $SrCN_2$, also prepared at high temperatures (500–1000°C) [17].

In air, $ZnCN_2$ may oxidize according to (3),

$$ZnCN_2+3/2O_2 \rightarrow ZnO+CO_2+N_2 \tag{3}$$

which is a plausible reaction for the decomposition step 5, leading to pure final product of ZnO.

In an inert atmosphere, the sublimation or decomposition of $ZnCN_2$ and the phase transition sphalerite to wurtzite could be the main reactions in the final decomposition step (No. 5) resulting in pure ZnS at 980°C.

In addition to the phases presented in the Table 2, the condensation of NH_4Cl (JCPDS 7-7) was confirmed by XRD to take place in the cold zone of the quartz tube close to the gas output under Ar flow when performing heat treatment under isothermal conditions in the temperature range of 390–760°C.

Evolved gas analysis

EGA analysis was performed to get a better understanding of the thermal decomposition steps of **1**. The EGA-FTIR analysis in air shows the same type of complexity which was observed in the case of $Cd(tu)_2Cl_2$ [1]. In Table 3 the gaseous species have been grouped according to four temperature intervals between 200 and 660°C. The first decomposition products between 200 and 240°C are carbon disulfide (CS_2) and ammonia (NH_3). By 240°C exothermic oxidation of CS_2 occurs as judged from a sudden decrease in the CS_2 contents and increases in those of sulfur dioxide (SO_2) and carbonyl sulfide (COS):

$$CS_2+1.5O_2 = SO_2+COS \tag{4}$$

The heat evolved in this reaction may contribute to the intense evolution of hydrogen cyanide (HCN) as well, observed at 240°C. Release of isothiocyanic acid (HNCS) and cyanamide (H_2NCN) is also observed above 240°C. All these gases are among the decomposition products of thiourea as shown in our earlier EGA studies [1, 6] and thus the first decomposition step in the TG curves could be explained by decomposition of the ligand in **1** which leads to the formation of zinc sulfide.

Between 330 and 500°C the evolution of HNCS becomes dominant together with that of NH_3 and COS. The reoccurrence of H_2NCN and evolving of CO_2 at temperatures higher than 500°C together with continuous release of HNCS confirm the decomposition of organic matter. The evolution of SO_2, originating from the oxidation of zinc sulfide in air, becomes considerable above 650°C. No definite concentration of HCl could be observed by the measuring system which is the only difference to $Cd(tu)_2Cl_2$ [1], otherwise the evolution curves of the gaseous species are found quite similar to those of the analogous Cd compound [1].

Table 3 Gaseous species observed in various temperature ranges in air up to 660°C (the newly evolved ones are underlined, the dominating ones are in bold). For explanations, see the text

Temperature interval/°C	Gaseous species evolved
200–240	**CS_2, NH_3**
240–330	**HCN, SO_2, COS, CS_2, NH_3**, HNCS, H_2NCN
330–500	**HNCS, COS, SO_2, HCN, NH_3**, CS_2, H_2NCN
500–660	**SO_2, CO_2, H_2NCN**, COS, HNCS, HCN, NH_3

Conclusions

Dichlorobis(thiourea)zinc(II) $Zn(tu)_2Cl_2$ (**1**) can be crystallized at room temperature from an aqueous solution containing zinc chloride and thiourea (*tu*) in the appropriate molar ratio. Heating of **1** in air or nitrogen leads first to the appearance of ZnS (sphalerite, zinc-blende) which is formed below 300ºC. In air, the oxidation products of ZnS occur above 600ºC indicated by the formation of ZnO and release of SO_2 gas. In an inert atmosphere DTA and XRD studies revealed that for ZnS only a polymorphic transformation of the cubic sphalerite takes place above 780ºC whereupon the hexagonal wurtzite phase is formed.

The mechanism of thermal degradation of **1** is quite complex as also found in the case of the corresponding cadmium complex [1]. It involves the formation of $ZnCl_2$-containing phases, viz. simonkolleite ($ZnCl_2{\cdot}4Zn(OH)_2{\cdot}H_2O$) and zinc oxide chloride hydrate which upon decomposition above 500ºC yield $ZnCl_2$ and ZnO. The observed zinc losses are due to volatilization of $ZnCl_2$. The remaining part of $ZnCl_2$ reacts with cyanamide H_2NCN which is evolving from the thiocarbamide ligand or its polymerised decomposition products. This reaction produces $ZnCN_2$ which in air oxidizes to ZnO. Finally, above 1000ºC zinc losses in an inert atmosphere occur through the sublimation of ZnS.

Thermoanalytical studies of the precursor (**1**) including EGA as well as characterization of the solid decomposition products by IR and XRD indicate that, in spite of the complexity of the process, $Zn(tu)_2Cl_2$ can be used as a precursor for the deposition of ZnS thin films by spray pyrolysis. However, at higher temperatures the vapour pressure of ZnS is considerable and consequently its losses by sublimation may be significant. On the other hand, major part of chloride impurities, including NH_4Cl and $ZnCl_2$ formed, could be effectively expelled by the high processing temperature. In practice therefore a compromise between the deposition temperature leading to ZnO formation and impurity level of the films must be sought after. Indeed, our recent studies indicate that phase-pure ZnS can be obtained by spray pyrolysis of **1** in air already at 450ºC thus making the present process technically feasible. This is an-other example of a chemical process to produce thin films and it shows how thermoanalytical techniques can be exploited in developing such processes [18].

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