

# Thermoanalytical study of precursors for In<sub>2</sub>S<sub>3</sub> thin films deposited by spray pyrolysis

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**Abstract** Thermal decomposition of precursors for In<sub>2</sub>S<sub>3</sub> thin films obtained by drying aqueous solutions of InCl<sub>3</sub> and SC(NH<sub>2</sub>)<sub>2</sub> at the In:S molar ratios of 1:3 (**1**) and 1:6 (**2**) was monitored by simultaneous TG/DTA/EGA-FTIR measurements in the dynamic 80%Ar + 20%O<sub>2</sub> atmosphere. XRD and FTIR were used to identify the dried precursors and products of the thermal decomposition. The precursors **1** and **2** are complex compounds, while in **2** free SC(NH<sub>2</sub>)<sub>2</sub> is also present. The thermal degradation of **1** and **2** in the temperature range of 30–900 °C consists of four mass loss steps, the total mass loss being 89.1 and 78.5%, respectively. According to XRD, In<sub>2</sub>S<sub>3</sub> is formed below 300 °C, crystalline In<sub>2.24</sub>(NCN)<sub>3</sub> is detected only in **1** above 520 °C and In<sub>2</sub>O<sub>3</sub> is the final decomposition product at 900 °C. The gaseous species evolved include CS<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>NCN, HNCS, which upon oxidation yield also COS, SO<sub>2</sub>, HCN and CO<sub>2</sub>.

**Keywords** TG/DTA · EGA-FTIR · Indium sulphide · Thiourea · Indium complex · Chemical spray pyrolysis · Ex situ FTIR and XRD

## Introduction

Indium sulphide (In<sub>2</sub>S<sub>3</sub>) thin films are often used as buffer layers instead of CdS in chalcopyrite absorber layer based solar cells [1, 2]. Recently it was suggested that a transition

metal substituted In<sub>2</sub>S<sub>3</sub> could be a promising absorber material for a new type of thin film solar cell exploiting two-photon processes [3]. In<sub>2</sub>S<sub>3</sub> thin films can be manufactured by different physical and chemical deposition methods. Chemical spray pyrolysis (CSP) has been often used because it is an economical, rapid, non-vacuum and simple method to prepare thin films. In the CSP process, aqueous or alcoholic solutions containing InCl<sub>3</sub> and SC(NH<sub>2</sub>)<sub>2</sub> (tu) as starting chemicals are pulverized in the form of fine droplets to the preheated substrate where In<sub>2</sub>S<sub>3</sub> film is formed. CSP has been used to deposit In<sub>2</sub>S<sub>3</sub> thin films with device quality properties, e.g., a buffer layer for solar cells [4, 5]. According to the literature, the main parameters influencing the properties of In<sub>2</sub>S<sub>3</sub> thin films are the molar ratio of In and S sources (In:S) in the spray solution and the deposition temperature [5–7]. For example, the deposition of a sulphur-rich precursor solution with the In:S molar ratio of 1:6 minimizes oxide formation in the sprayed thin film [7]. However, the formation of In<sub>2</sub>S<sub>3</sub> in the CSP process has not been studied in detail. Formation of In<sub>2</sub>S<sub>3</sub> in the spray process is described by one reaction only:  $2\text{InCl}_3 + 3\text{CS}(\text{NH}_2)_2 + 6\text{H}_2\text{O} \rightarrow \text{In}_2\text{S}_3 + 3\text{CO}_2 + 6\text{NH}_4\text{Cl}$  [8]. This general reaction seems to be too simple in the light of the studies performed on the formation of other metal sulphides, such as CdS, ZnS, SnS and Cu<sub>x</sub>S in the CSP process. It is known that several complexes with different stoichiometry and water content are formed in aqueous solutions containing metal halogenides and thiourea [9–14], which upon their thermal decomposition lead to the formation of metal sulphides. Moreover, the molar ratio of the precursors in the spray solution may have a strong effect on the phase composition of the CSP-deposited metal sulphide films. For example, ZnS films prepared by spray of aqueous solutions containing ZnCl<sub>2</sub> and thiourea in the molar ratio of 1:1 comprise a ZnO impurity phase already at low growth temperatures in addition to the main phase of ZnS

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[15]. Deposition of the solution with the Zn:S molar ratio of 1:2, which corresponds to the stoichiometry of dichlorobis(thiourea-S)-zinc(II) ( $[\text{Zn}(\text{tu})_2\text{Cl}_2]$ ), results in ZnS films with no ZnO phase at similar deposition temperatures [15].

Thermal decomposition of these metal halogenide thiourea complexes has been found to be a complicated multistep process [9–12, 16]. Generally, these complexes decompose at temperatures above 200 °C, leading to the formation of metal sulphides irrespective of the atmosphere. Metal sulphides are the final decomposition products in an inert atmosphere, however, in oxidative atmospheres metal oxides are the final products.

In(III) halides ( $\text{InX}_3$ ) are known to form numerous five-coordinate and six-coordinate compounds with  $\text{InX}_3\text{L}_2$  and  $\text{InX}_3\text{L}_3$ -type molecules (L represents a ligand) [17]. It is also known that neutral sulphur-based donors, such as thioether and thiourea, form adducts with indium ion [17]. The crystal structure is known for  $\text{InCl}_3\{\text{SC}(\text{NMe}_2)_2\}_2$  [18]. A probable interaction of the precursors in the spray solution is neglected [8].

The aim of this study was to obtain a better understanding of the formation of  $\text{In}_2\text{S}_3$  films in the spray pyrolysis process. In order to follow the spray process, we prepared aqueous solutions containing  $\text{InCl}_3$  and  $\text{SC}(\text{NH}_2)_2$  in the molar ratio of 1:3 and 1:6, let the solvent evaporate, and characterized the dried samples in terms of their structure and elemental composition. Thermal decomposition of dried samples was monitored by simultaneous TG/DTA and EGA-FTIR methods in  $\text{Ar} + \text{O}_2$ .

## Experimental

### Chemicals and synthesis of samples

$\text{SC}(\text{NH}_2)_2$  (tu) (p.a. > 98%, Merck-Schnhardt S32896) and  $\text{InCl}_3$  prepared from indium (p.a. 99.99%, Alfa Aesar) and concentrated HCl (Merck) were employed for the synthesis. All the chemicals were used as received without any further purification.

The precursor solutions were prepared by mixing 0.1 M  $\text{InCl}_3$  and 0.75 M  $\text{SC}(\text{NH}_2)_2$  aqueous solutions in the molar ratios ( $\text{InCl}_3:\text{SC}(\text{NH}_2)_2$ ) of 1:3 (**1**) and 1:6 (**2**) at room temperature. In both cases,  $[\text{In}^{3+}]$  was set to  $5 \times 10^{-2}$  mol/L. The solutions were let to slowly evaporate at 50 °C in a furnace for a week.

### Characterization of dried precursors and products of their thermal decomposition

Fourier transformed infrared (FTIR) spectroscopy and X-ray diffraction (XRD) were used to characterize the dried powders **1** and **2** and the products of their thermal

decomposition. FTIR transmission spectra were measured in the region of 4000–400  $\text{cm}^{-1}$  on a Perkin-Elmer GX1 spectrophotometer using the KBr pellet technique. XRD patterns were recorded by a Rigaku Ultima IV diffractometer with Cu  $K\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ , 40 kV at 40 mA) using the silicon strip detector D/teX Ultra. The elemental composition of the dried samples **1** and **2** was determined by an Elemental Analysensysteme GmbH Vario EL CHNOS Elemental Analyser for S, C, N, H. Chlorine content was determined in **1** by the amperometric titration. In addition, heat treatments of **1** and **2** were performed in a preparative scale in air using a Nabertherm furnace. Heat treatment temperatures were determined on the basis of the dynamic TG runs.

### Thermal analysis

TG/DTA measurements, coupled with the evolved gas analysis by FTIR (EGA-FTIR), were carried out on a SetSys-Evolution instrument connected to a Nicolet 380 FTIR spectrometer. The analyses were carried out in a dynamic 80%Ar + 20%O<sub>2</sub> (artificial air) atmosphere in the temperature range of 30–1000 °C using the heating rate of 10 °C  $\text{min}^{-1}$ , the gas flow rate of 60 mL/min and open Al<sub>2</sub>O<sub>3</sub> crucibles. The initial mass of sample **1** was 7.8 mg and that of **2** was 7.4 mg. The gases evolved were led through a heated tube into a FTIR gas cell. The FTIR gas cell and the connecting tube were kept at 220 °C. The absorption spectra were recorded in the region of 4000–400  $\text{cm}^{-1}$  with a resolution of 4  $\text{cm}^{-1}$  and 60 scans averaged.

The evolved gases were identified on the basis of their FTIR reference spectra available in the literature [19] and in the public domain spectral libraries of NIST [20].

## Results and discussion

### Characterization of dried samples **1** and **2**

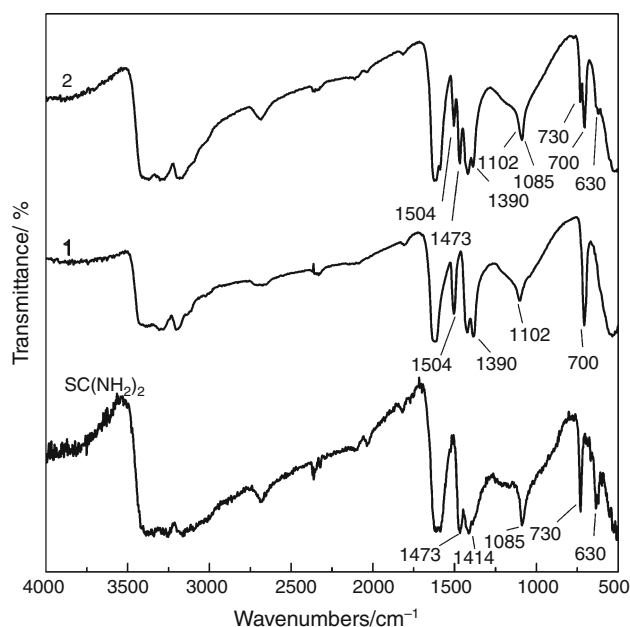
IR spectra of the dried samples **1** and **2** and that of free thiourea (tu) are compared in Fig. 1. The vibrations that peaked at 1473 and 1085  $\text{cm}^{-1}$  in the spectrum of thiourea are characteristic of CN group stretching vibrations,  $\nu(\text{CN})$  [9]. However, in **1** and **2**, the  $\nu(\text{CN})$  vibrations are shifted to higher frequencies of 1504 and 1102  $\text{cm}^{-1}$ , respectively. The increased wavenumbers of the CN group vibrations in **1** and **2** indicate the strengthening of the bond between carbon and nitrogen atoms [9, 21, 22]. IR spectrum of the free tu ligand exhibits strong and sharp vibrations at 1414, 730 and 630  $\text{cm}^{-1}$  characteristic of CS group stretching vibrations,  $\nu(\text{CS})$  [9, 23]. In **1** and **2**, these vibrations are shifted to lower frequencies, to 1390 and 700  $\text{cm}^{-1}$ ,

respectively. The shift of CS group stretching vibrations towards lower wavenumbers in **1** and **2** than that in free tu is due to the reduced double bond character between carbon and sulphur atoms [13, 21, 23]. Moreover, for dried sample **2** additional peaks at 1473, 1085, 730 and 630 cm<sup>-1</sup> can be observed, which are characteristic of  $\nu(\text{CN})$  and  $\nu(\text{CS})$  in thiourea. According to the IR study, sample **1** is a complex compound where tu is coordinated to the In ion through the sulphur atom. Similar behaviour is reported for the Cd, Cu and Zn chloride complexes with thiourea [9, 13, 14]. Sample **2** is composed of a thiourea complex compound and free thiourea.

According to XRD (XRD patterns not presented), powders **1** and **2** are crystalline materials. XRD patterns of **1** and **2** remained unidentified. Both **1** and **2** contain no InCl<sub>3</sub> as a starting material, replica characteristic of SC(NH<sub>2</sub>)<sub>2</sub> phase (JCPDS Card No. 00-031-1934) [24] were present in the XRD pattern of **2**.

According to the elemental analysis, the composition of **1** (found, in mass%) is: S 20.1%, C 7.7%, N 18.8%, H 2.3%, Cl 23.4% and the composition of **2** (found, in mass%) is: S 27.4%, C 10.3%, N 24.5%, H 3.5%. The composition of **1** is close to that calculated for a compound with a hypothetical formula InCl<sub>3</sub>·3(SCN<sub>2</sub>H<sub>4</sub>): In 25.5%, Cl 23.7%, S 21.4%, C 8.0%, N 18.7%, H 2.7%. The composition of **2** is close to that calculated for a mixture of (InCl<sub>3</sub>·3(SCN<sub>2</sub>H<sub>4</sub>) + 3(SCN<sub>2</sub>H<sub>4</sub>)): In 17.0%, S 28.4%, C 10.6%, N 24.8%, H 3.5%.

According to the results of the FTIR spectroscopy and chemical analyses, powder **1** is a complex compound



**Fig. 1** FTIR spectra of dried samples **1**, **2** and thiourea (SC(NH<sub>2</sub>)<sub>2</sub>) recorded at room temperature

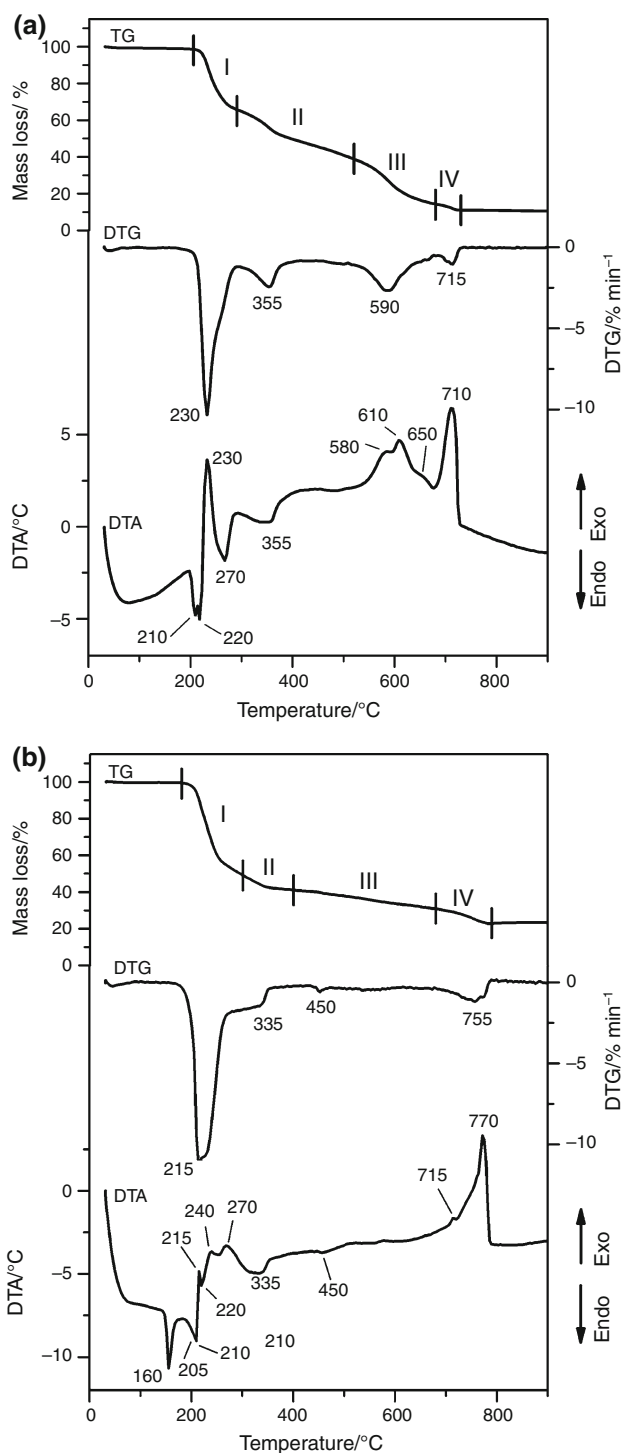
where three SC(NH<sub>2</sub>)<sub>2</sub> molecules are coordinated to one In<sup>3+</sup> cation of the InCl<sub>3</sub> molecule with a general formula InCl<sub>3</sub>·3(SC(NH<sub>2</sub>)<sub>2</sub>). A similar compound has been precipitated from aqueous solutions containing InCl<sub>3</sub> and SC(NH<sub>2</sub>)<sub>2</sub> in the molar ratios of 1:1 and 1:3 [25]. Powder **2** is a mixture of **1** and SC(NH<sub>2</sub>)<sub>2</sub>.

### Thermal analysis

Figures 2a and b show the TG, DTG, DTA curves of samples **1** and **2**, respectively. According to DTG, the thermal degradation of both **1** and **2** in the temperature interval of 30–900 °C in air (80%Ar + 20%O<sub>2</sub>) consists of four mass loss steps (Fig. 2a, b; Table 1).

The thermal decomposition of **1** takes place in the interval of 205–730 °C with a total mass loss of 89.1% (Fig. 2a). The first mass loss step occurs in the temperature range of 205–300 °C with a DTG maximum at 230 °C and a mass loss of ca., 34%. The DTA curve shows two sequential endothermic processes with maxima at 210 and 220 °C undergoing a strong exothermic effect with a maximum at 230 °C, and followed by an endothermic effect at 270 °C. The first endothermic effect that peaked at 210 °C obviously corresponds to the melting of **1**. Thermal decomposition of **1** takes place instantly after melting, indicated by the endothermic effect at 220 °C. Exothermic effect with a maximum at 230 °C is obviously due to the sudden oxidation of the evolved CS<sub>2</sub> vapour (see section Study of gaseous and solid products of thermal decomposition). The second decomposition step (300–520 °C) with the DTG maximum at 355 °C and a mass loss of 26.4% is an endothermic process with the DTA maximum at 355 °C. The third decomposition step (520–680 °C) with the DTG maximum at 590 °C involves exothermic reactions with maxima at 580, 610 and 650 °C. The fourth decomposition step in the temperature region of 680–730 °C contains an exothermic process that peaked at 710 °C with the DTG maximum at 715 °C. The characteristic mass losses of the third and fourth decomposition steps are 24.6 and 3.3%, respectively.

The thermal decomposition of **2** takes place in the temperature interval of 180–790 °C in four steps, with a total mass loss of 78.5% (Fig. 2b). Thermal behaviour of **2** is more complex than that of **1**. The endothermic effects detected at 160 and 205 °C obviously belong to the melting and the decomposition of thiourea, respectively [19], as in addition to the complex compound, **2** contains free, non-coordinated thiourea. Endothermic effects at 210 and 220 °C, characteristic of melting and decomposition of the complex compound, are less pronounced than in the case of **1** (Fig. 2b) due to the exothermic processes placed at 215 and 240 °C. The second mass loss step in the temperature interval of 300–400 °C is an endothermic reaction with the



**Fig. 2** Simultaneous TG, DTG and DTA curves of **1** (a) and **2** (b). Flowing 80%Ar + 20%O<sub>2</sub>: 60 mL min<sup>-1</sup>, heating rate: 10 °C min<sup>-1</sup>, initial sample mass for **1** –7.8 mg and **2** –7.4 mg

DTG maximum at 335 °C. The third mass loss step between 400–680 °C is an endothermic reaction with the DTG maximum at 450 °C. The mass losses in the second and third decomposition steps are 9.6 and 10.2%, respectively. The last, fourth, decomposition step (680–790 °C)

involves three exothermic processes with maxima at 715 and 770 °C.

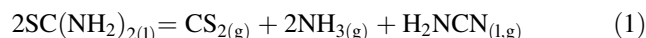
According to XRD, the final decomposition product of **1** and **2** at 900 °C in 80%Ar + 20%O<sub>2</sub> is In<sub>2</sub>O<sub>3</sub> (PDF 01-073-6440) [24]. For **1**, the yield of 10.9% is much lower than the calculated 30.9%, which refers to the release of some volatile In species (e.g. InCl<sub>3</sub>). For **2**, the yield of 21.5% is close to the theoretical value 20.4%, indicating that the excess of thiourea in the precursor hinders the release of volatile indium species from the system.

The first decomposition step for both **1** and **2** consists of the decomposition of thiourea. The thermal degradation of **1** (Fig. 2a) starts at 205 °C, while in the case of **2** the decomposition begins at a lower temperature, at 180 °C, due to free non-coordinated tu present in the sample (Table 1). The decomposition of **2** is more complex, particularly in the first decomposition step, due to several overlapping endo and exo effects. The main difference in the decomposition behaviour of **1** and **2** is observed in the temperature range of 300–680 °C, showing different mass losses of 51 and 19.8%, respectively. The exothermic effects observed for **1** at 580 and 610 °C do not occur in the case of **2**. The last exo effect of **1** at 710 °C is shifted towards higher temperatures for **2**, and is observed at 770 °C. The decompositions of **1** and **2** are completed at 730 and 790 °C, respectively.

#### Study of gaseous and solid products of thermal decomposition

FTIR spectra of the evolved gases obtained by a TG/DTG analysis coupled with simultaneous EGA-FTIR measurements were used to study gaseous species evolved over the thermal degradation of **1** and **2**. Figure 3 depicts the FTIR spectrum of gases evolved from **1** at 240 °C in 80%Ar + 20%O<sub>2</sub>. The evolution profiles of gaseous species from **1** and **2** are compared in Fig. 4.

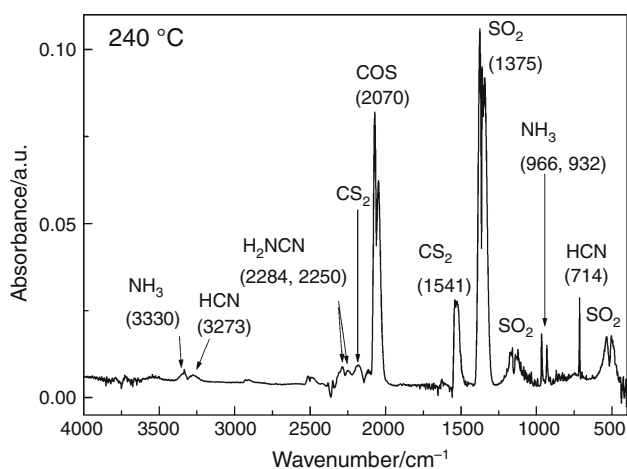
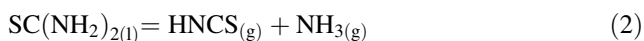
The evolution of carbon disulphide (CS<sub>2</sub>) starts at 210 °C from **1** and at 200 °C from **2**, accompanied by the release of ammonia (NH<sub>3</sub>) and a small amount of cyanamide (H<sub>2</sub>NCN), which are the decomposition products of adjacent thiourea ligands in the melt (Eq.1) [9, 19].



Evolution of CS<sub>2</sub> from **2** occurs in two steps, as shown in Fig. 4. The first evolution step issues from the decomposition of free thiourea, the second step from the decomposition of the complex compound. Isothiocyanic acid (HNCS) also evolves in the early stage of decomposition, but in a very small amount. Evolution of HNCS could occur according to the reaction (2), as reported previously [9].

**Table 1** Decomposition steps, mass losses and temperatures of DTA and DTG peaks of dried powders of **1** and **2**, recorded using the heating rate of 10 °C min<sup>-1</sup> in 80%Ar + 20%O<sub>2</sub> atmosphere on the SetSys-Evolution instrument

Sample	Step	TG temp. range/°C	DTG <sub>max</sub> /°C	DTA peak (±)/°C	Mass loss/%
<b>1</b>	1	205–300	230	210 (–)	34.8
				220 (–)	
				230 (+)	
				270 (–)	
				270 (–)	
2	300–520	355	355 (–)	26.4	
			590	580 (+)	24.6
3	520–680	715	610 (+)	3.3	
			650 (+)		
4	680–730	715	710 (+)	89.1	
			715 (+)		
Total mass loss					89.1
<b>2</b>	1	180–300	215	160 (–)	50.7
				205 (–)	
				210 (–)	
				215 (+)	
				220 (–)	
2	300–400	335	270 (+)	9.6	
			240 (+)		
3	400–680	450	335 (–)	10.2	
			450 (–)		
4	680–790	755	715 (+)	8.0	
			760 (+)		
Total mass loss					78.5

**Fig. 3** EGA-FTIR spectra of evolved gases of **1** at 240 °C. Flowing 80%Ar + 20%O<sub>2</sub>: 60 mL min<sup>-1</sup>, heating rate: 10 °C min<sup>-1</sup>, initial sample mass: 7.8 mg

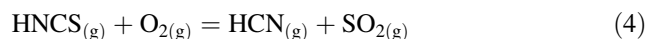
The FTIR spectra of the solid residues (Fig. 5a, b) obtained by heating of **1** up to 225 °C and of **2** up to 180 °C reveal an absorption peak at 2070 cm<sup>-1</sup>, which can be assigned to the stretching vibration of both thiocyanate

(SCN) and hydrogen bonded RNH<sub>3</sub><sup>+</sup> groups, and indicate isomerization of thiourea into ammonium thiocyanate [9]. The decomposition of the latter compound could be responsible for gaseous species, such as HNCS and NH<sub>3</sub>.

A sudden evolution of carbonyl sulphide (COS) and sulphur dioxide (SO<sub>2</sub>) occurs at slightly higher temperatures after the release of CS<sub>2</sub> (Fig. 4). Both COS and SO<sub>2</sub> are the products of the exothermic oxidation of the CS<sub>2</sub> vapour (3) [16, 19]. The maximum evolution of COS and SO<sub>2</sub> takes place close to 240 °C. Hence, the exothermic peaks on the DTA curves of **1** at 230 °C, and of **2** at 215 and 240 °C could be assigned as belonging to the oxidation of the CS<sub>2</sub> vapour.

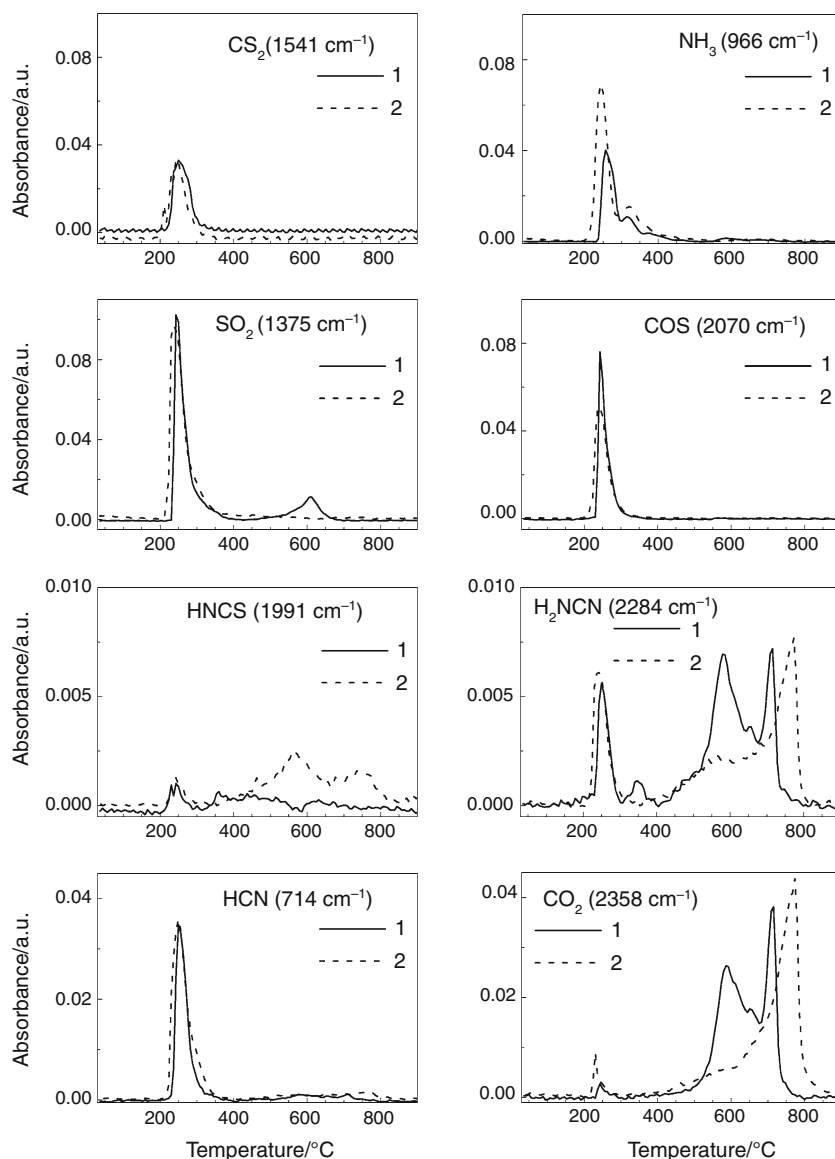


Additionally, the release of hydrogen cyanide (HCN) from **1** and **2** occurs at temperatures higher than 210 °C, reaching the maximum evolution at 250 °C. The release of HCN could be considered as the oxidation product of HNCS according to the reaction (4) [9].



FTIR spectra (Fig. 5a, b) indicate that the solid residues obtained by heating of **1** and **2** up to 300 °C (the end

**Fig. 4** Evolution profiles of gases, as determined by TG/EGA-FTIR of **1** (1:3) and **2** (1:6). Flowing 80%Ar + 20%O<sub>2</sub>: 60 mL min<sup>-1</sup>, heating rate: 10 °C min<sup>-1</sup>, initial sample mass for **1** –7.8 mg and **2** –7.4 mg



temperature of the first decomposition step) still contain organic residues. According to XRD the main solid product at 300 °C is In<sub>2</sub>S<sub>3</sub>, while traces of InCl<sub>3</sub> are present in **1** (Table 2).

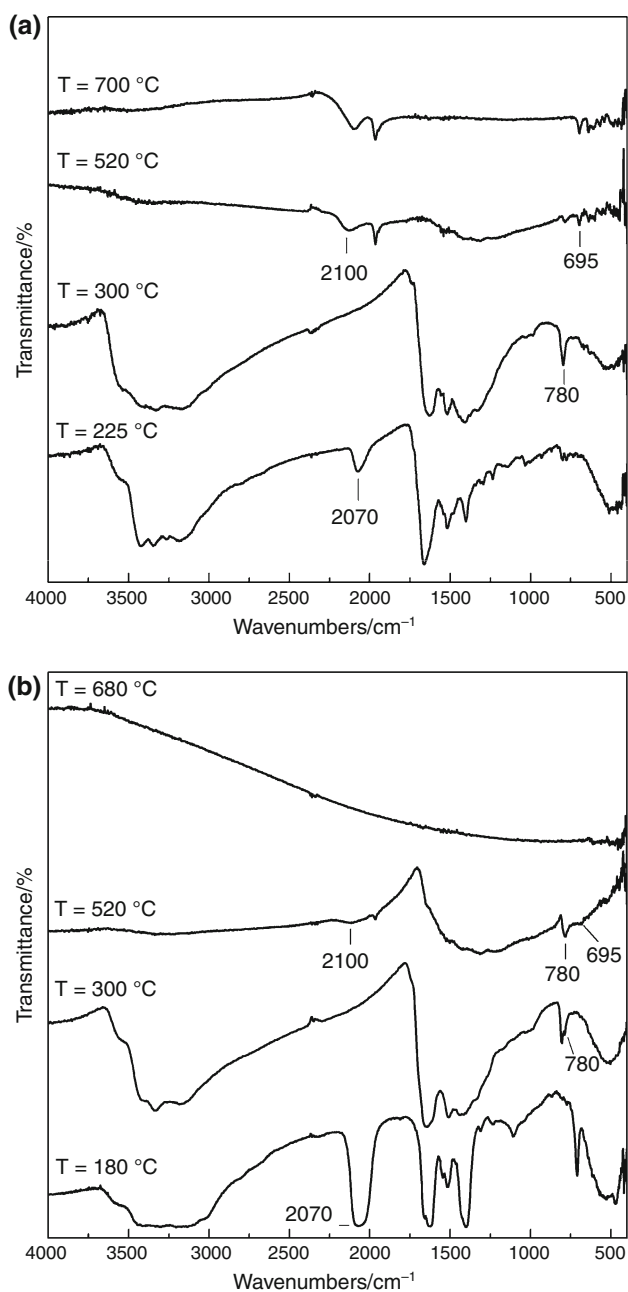
In the temperature interval of 300–400 °C, both **1** and **2** show endothermic decomposition reactions and evolution of NH<sub>3</sub>, while H<sub>2</sub>NCN and HNCS are released only from **1** (Fig. 4). In the case of **2**, evolution of H<sub>2</sub>NCN and HNCS takes place at temperatures above 400 °C, with a delay compared to **1**. The re-occurrence of the evolution of H<sub>2</sub>NCN could suggest the formation of indium cyanamide.

Indeed, the FTIR spectra of the solid residues of **1** and **2** prepared by heating up to 520 °C (Fig. 5 a, b) show absorptions around 2100 and 695 cm<sup>-1</sup> characteristic of the cyanamide group [12, 26]. In addition, the spectrum of **2** shows weak absorptions in the wavenumber range of 1650–1200 cm<sup>-1</sup> and at 780 cm<sup>-1</sup>, which could belong to a

polymerized product of cyanamide [27]. This speculation is supported by the fact that a strong evolution of H<sub>2</sub>NCN occurs above 500 °C (Fig. 4).

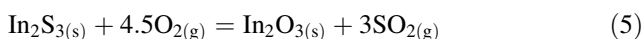
According to XRD, the solid product of **1** at the end of the second decomposition step (520 °C) contains crystalline phases of In<sub>2</sub>S<sub>3</sub>, In<sub>2.24</sub>(NCN)<sub>3</sub> and In<sub>2</sub>O<sub>3</sub> (Table 2). Thus, the formation of In<sub>2.24</sub>(NCN)<sub>3</sub> supposed according to FTIR (Fig. 5a) is confirmed by XRD. The formation of In<sub>2.24</sub>(NCN)<sub>3</sub> could take place similarly to that observed for ZnCN<sub>2</sub> [12]. In the present case, indium cyanamide is formed probably by the reaction of InCl<sub>3</sub> and H<sub>2</sub>NCN, the latter evolving from the decomposition of the complex in the first decomposition step. The solid product of **2** obtained by heating up to 520 °C contains crystalline In<sub>2</sub>O<sub>3</sub> and traces of In<sub>2</sub>S<sub>3</sub> (Table 2).

In the third decomposition step of **1** (520–680 °C) the exothermic effects at 580 and 650 °C (Fig. 2a) are



**Fig. 5** FTIR spectra of solid residues of **1** (a) and **2** (b) at the end of the decomposition steps

accompanied by an intensive evolution of CO<sub>2</sub> and H<sub>2</sub>NCN with strikingly similar evolution profiles (Fig. 4), indicating to the decomposition and combustion of organic pieces. The exothermic effect that peaked at 610 °C (Fig. 2a) is accompanied by the evolution of SO<sub>2</sub> with maxima also at 610 °C (Fig. 4). The evolution of SO<sub>2</sub> is probably due to the oxidation of In<sub>2</sub>S<sub>3</sub> according to Eq. (5).



The FTIR spectrum of the solid product of **1** at 700 °C (Fig. 5a) still shows vibrations at the 2100 and 700 cm<sup>-1</sup>

characteristic of In-cyanamide [26]. This result is in accordance with the XRD study, showing the presence of the crystalline In<sub>2.24</sub>(NCN)<sub>3</sub> phase in addition to the In<sub>2</sub>O<sub>3</sub> and traces of In<sub>2</sub>S<sub>3</sub> in the solid product obtained by heating of **1** up to 700 °C in 80%Ar + 20%O<sub>2</sub> (Table 2).

Thermal behaviour of **2** in the temperature interval of 400–680 °C differs significantly from that of **1**. Evolution profiles of H<sub>2</sub>NCN and CO<sub>2</sub> show a monotonous increase in this temperature interval without any distinct maxima, while a continuous evolution of HNCS is observed in this temperature range (Fig. 4). The evolution of SO<sub>2</sub> from **2** was observed up to 400 °C, and the evolution of a relatively small amount of SO<sub>2</sub> takes place also in this temperature range, and continues up to 780 °C (Fig. 4).

According to FTIR, the solid residue of **2** at 520 °C indicates relatively weak absorptions at 2100 and 695 cm<sup>-1</sup> (Fig. 5b) characteristic of C≡N [26] in In-cyanamide, while absorption bands in the region of 1600–1000 cm<sup>-1</sup> indicate the presence of organic residues. The solid residue at 680 °C (Fig. 5b) shows no vibrations at 2100 and 690 cm<sup>-1</sup> characteristic of C≡N in In-cyanamide. According to XRD, the main solid product of **2** at 520 °C is In<sub>2</sub>O<sub>3</sub> with traces of In<sub>2</sub>S<sub>3</sub> (Table 2). The solid product at 680 °C consists of the crystalline In<sub>2</sub>O<sub>3</sub> phase.

At temperatures above 700 °C, strong exothermic effects occur at 710 and 770 °C for **1** and **2**, respectively (Fig. 2a, b). The evolution of CO<sub>2</sub> and H<sub>2</sub>NCN with strikingly similar profiles was recorded for both samples in this final decomposition step (Fig. 4). In addition, the continuous release of HNCS recorded from **2** in the temperature interval of 700–800 °C confirms further decomposition of an organic matter [12].

Probably the decomposition of In<sub>2.4</sub>(NCN)<sub>3</sub> accompanied by the evolution of H<sub>2</sub>NCN and the combustion of organic pieces that leads to the evolution of CO<sub>2</sub> are characteristic reactions for **1** in this step, resulting in In<sub>2</sub>O<sub>3</sub> as the final product. The release of H<sub>2</sub>NCN from **2** (Fig. 4), where no In<sub>2.4</sub>(NCN)<sub>3</sub> phase was observed in the solid residue at 680 °C (Table 2), could originate from the decomposition of polymerization products formed at lower temperatures [9]. According to the literature, H<sub>2</sub>NCN evolved in the first decomposition step (200–300 °C) is highly reactive and it may react with other decomposition products or polymerize [9]. It could be speculated that the presence of polymerization products affects the decomposition of **2**, shifting the formation of the pure In<sub>2</sub>O<sub>3</sub> phase towards higher temperatures. This assumption is supported by the TG data (Table 1) showing that the characteristic mass loss of the final decomposition step (680–730 °C) of **1** (3.3%) is significantly lower than that observed for **2** (8.0%) in the temperature interval of 680–790 °C. This indicates that the content of organic matter in **2** is significantly larger than in **1** at the beginning of the last decomposition step.

**Table 2** Crystalline decomposition products of **1** and **2**, as detected by XRD. Heat treatments were performed in a preparative scale in air in laboratory oven

<b>1</b> (In:S = 1:3)		<b>2</b> (In:S = 1:6)	
<i>T</i> /°C	Main crystalline phases and JCPDS reference files	<i>T</i> /°C	Main crystalline phases and JCPDS reference files
300	$\alpha$ -In <sub>2</sub> S <sub>3</sub> (01-084-1385) (InCl <sub>3</sub> (00-034-1145))	300	$\alpha$ -In <sub>2</sub> S <sub>3</sub> (01-084-1385)
410	$\beta$ -In <sub>2</sub> S <sub>3</sub> (01-074-7284) In <sub>2</sub> O <sub>3</sub> (01-073-6440)	410	$\beta$ -In <sub>2</sub> S <sub>3</sub> (01-074-7284)
520	In <sub>2</sub> O <sub>3</sub> (01-073-6440) In <sub>2.24</sub> (NCN) <sub>3</sub> (00-051-0853) ( $\beta$ -In <sub>2</sub> S <sub>3</sub> (01-074-7284))	520	In <sub>2</sub> O <sub>3</sub> (01-073-6440) ( $\beta$ -In <sub>2</sub> S <sub>3</sub> (01-074-7284))
700	In <sub>2</sub> O <sub>3</sub> (01-073-6440) In <sub>2.24</sub> (NCN) <sub>3</sub> (00-051-0853)	680	In <sub>2</sub> O <sub>3</sub> (01-073-6440)
900	In <sub>2</sub> O <sub>3</sub> (01-073-6440)	820	In <sub>2</sub> O <sub>3</sub> (01-073-6440)

## Conclusions

According to FTIR and XRD, samples **1** and **2** obtained by drying aqueous solutions of InCl<sub>3</sub> and SC(NH<sub>2</sub>)<sub>2</sub> at the molar ratios of In:S = 1:3 (**1**) and 1:6 (**2**) contain a complex compound, where SC(NH<sub>2</sub>)<sub>2</sub> is coordinated to In atom via S atom. **1** does not contain free SC(NH<sub>2</sub>)<sub>2</sub>, while in **2** free SC(NH<sub>2</sub>)<sub>2</sub> is also present. According to the elemental analyses, the composition of the dried sample **1** is close to a compound with the hypothetical formula InCl<sub>3</sub>·3(SCN<sub>2</sub>H<sub>4</sub>), and **2** is a mixture of phases InCl<sub>3</sub>·3(SCN<sub>2</sub>H<sub>4</sub>) + 3 SCN<sub>2</sub>H<sub>4</sub>.

The thermal decomposition of **1** in the temperature range of 205–730 °C and that of **2** in the temperature interval of 180–790 °C in 80%Ar + 20%O<sub>2</sub> consists of four mass loss steps with a total mass loss of 89.1 and 78.5%, respectively. Thermal degradation of **2** starts at a lower temperature due to the decomposition of non-coordinated SC(NH<sub>2</sub>)<sub>2</sub> present in **2**, followed by the decomposition of the complex compound, as recorded for **1**. In the case of both samples, In<sub>2</sub>S<sub>3</sub> is formed in the first decomposition step and In<sub>2</sub>O<sub>3</sub> is the final product. In the first decomposition step, CS<sub>2</sub>, NH<sub>3</sub> and H<sub>2</sub>NCN evolved as the decomposition products of thiourea, which upon oxidation yield to the evolution of COS, SO<sub>2</sub>, HCN and CO<sub>2</sub>. Thermal degradation of **1** and **2** are similar in the first decomposition step, differences appear at higher temperatures. Above 400 °C, the decomposition steps of **2** are shifted towards higher temperatures than those of **1**. Nevertheless, intensive evolution of H<sub>2</sub>NCN and CO<sub>2</sub> with strikingly similar profiles is characteristic of both. It should be noticed that the release of volatile indium species and the formation of In<sub>2.24</sub>(NCN)<sub>3</sub> as an intermediate decomposition product is hindered in the case of **2**.

This study shows for the first time that the formation of In<sub>2</sub>S<sub>3</sub> in the spray pyrolysis process occurs through an indium chloride thiourea complex compound, supposedly of InCl<sub>3</sub>·3(SCN<sub>2</sub>H<sub>4</sub>) formed in an aqueous spray solution containing an appropriate molar ratio of InCl<sub>3</sub> and SC(NH<sub>2</sub>)<sub>2</sub>. Thermal decomposition of the complex compound is a complicated process, where metal sulphide is formed in the first decomposition step at temperatures below 300 °C, which is similar to that previously reported for cadmium, zinc and copper sulphide formation in the spray process [9, 10, 12].

The thermal decomposition of the precursors for In<sub>2</sub>S<sub>3</sub> thin films by the CSP method depends on the In:S molar ratio in the solution. Results of the current study show that an aqueous spray solution with the In:S molar ratio of 1:6 and deposition temperatures up to 400 °C are preferred to deposit In<sub>2</sub>S<sub>3</sub> thin films by the spray pyrolysis method in 80%Ar + 20%O<sub>2</sub> to minimize the formation of the In<sub>2</sub>O<sub>3</sub> phase. At the same time the deposition of solutions with the In:S molar ratio of 1:6 may result in a high amount of organic residues in the film.

In order to determine the composition and structure of the complex, it should be prepared as a single crystal. To identify the thermal decomposition reactions more precisely, additional studies are needed. Therefore, the TG/DTA studies of the complex should be complemented by the EGA-MS investigations in air and in an inert atmosphere, and then compared to the results of the EGA-FTIR reported in this communication.

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