SYNTHESIS, CHARACTERIZATION, AND PROCESSING OF COPPER, INDIUM, AND GALLIUM DITHIOCARBAMATES FOR ENERGY CONVERSION APPLICATIONS

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Ten dithiocarbamate complexes of indium(III) and gallium(III) have been prepared and characterized by elemental analysis, infrared spectra and melting point. Each complex was decomposed thermally and its decomposition products separated and identified with the combination of gas chromatography/mass spectrometry. Their potential utility as photovoltaic materials precursors was assessed. Bis(dibenzyldithiocarbamato)- and bis(diethyldithiocarbamato)copper(II), $Cu(S_2CN(CH_2C_6H_5)_2)_2$ and $Cu(S_2CN(C_2H_5)_2)_2$ respectively, have also been examined for their suitability as precursors for copper sulfides for the fabrication of photovoltaic materials. Each complex was decomposed thermally and the products analyzed by GC/MS, TGA and FTIR. The dibenzyl derivative complex decomposed at a lower temperature (225-320°C) to yield CuS as the product. The diethyl derivative complex decomposed at a higher temperature (260-325°C) to yield Cu_2S. No Cu containing fragments were noted in the mass spectra. Unusual recombination fragments were observed in the mass spectra of the diethyl derivative. Tris(bis(phenylmethyl)carbamodithioato-*S*,*S*'), commonly referred to as tris(*N*,*N*-dibenzyldithiocarbamato)indium(III), $In(S_2CNBz_2)_3$, was synthesized and characterized by single crystal X-ray crystallography. The compound crystallizes in the triclinic space group *P*1(bar) with two molecules per unit cell. The material was further characterized using a novel analytical system employing the combined powers of thermogravimetric analysis, gas chromatography/mass spectrometry, and Fourier transform infrared (FT-IR) spectroscopy to investigate its potential use as a precursor for the chemical vapor deposition (CVD) of thin film materials for photovoltaic applications. Upon heating, the material thermally decomposes to release CS_2 and benzyl moieties in to the gas phase, resulting in bulk In_2S_3. Preliminary spray CVD experiments indicate that $In(S_2CNBz_2)_3$ decomposed on a Cu substrate reacts to produce stoichiometric $CuInS_2$ films.

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Synthesis, Characterization, and Processing of Copper, Indium, and Gallium Dithiocarbamates for Energy Conversion Applications

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Why Thin Film Materials for Aerospace Power?

Depictions of thin-film solar cell applications (clockwise from upper left): lunar surface power, Mars surface power, Solar Electric Propulsion for planetary exploration, and terrestrial high-altitude airship. Key is the high mass-specific power offered by thin-film technologies.

Solid-state Material and Processing Apparatus

$CuInQ_2$ MOLECULAR STRUCTURE

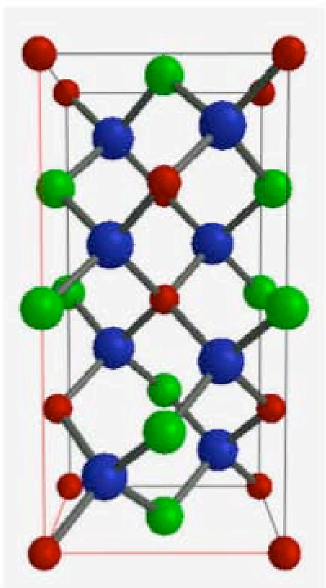
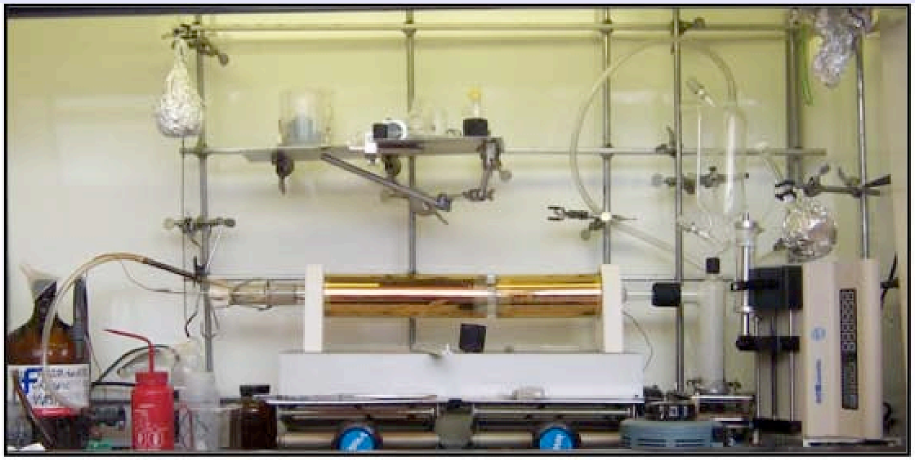


Diagram of $CuInQ_2$ unit cell.

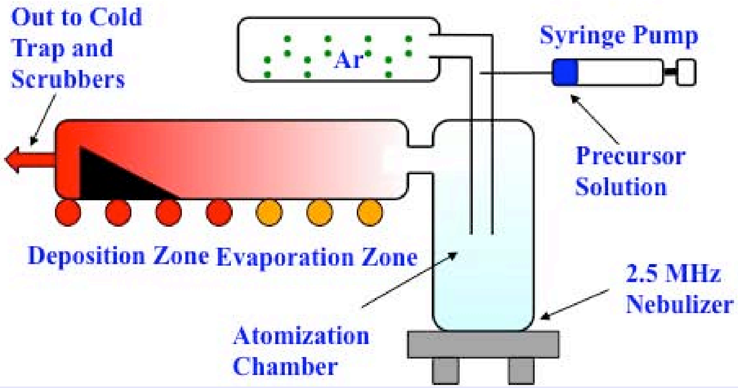
Copper

Indium

Selenium or Sulfur



Picture (top) and diagram (bottom) of a horizontal atmospheric hot-wall reactor.

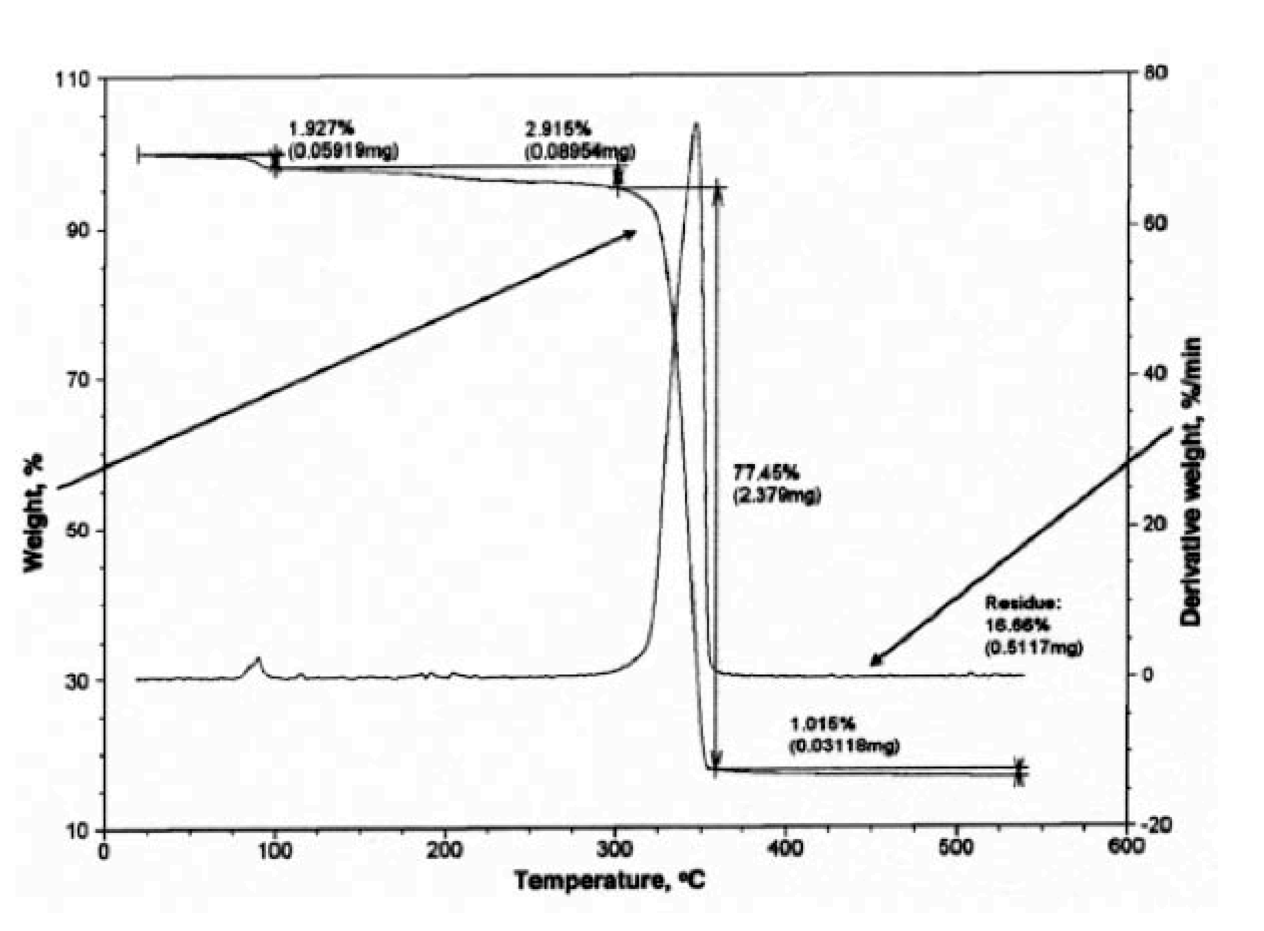


Indium and Gallium Dithiocarbamate Complexes

Table 1. Thermogravimetric Analysis of Indium(III) and Gallium(III) Dithiocarbamate Complexes

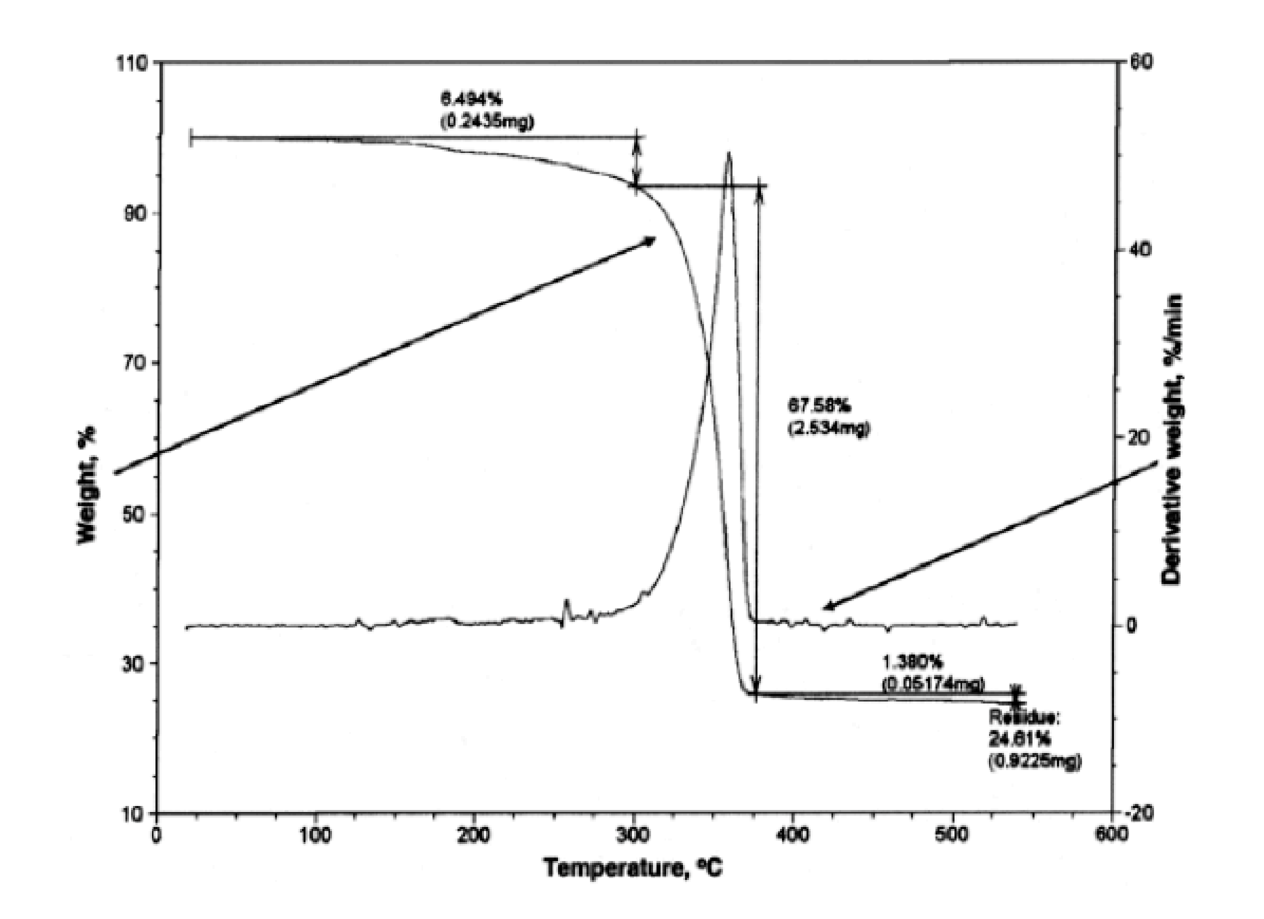
Complex	Theoretical Residue (M_2S_3)	Theoretical Residue (MS)	Theoretical Residue (M_2S)	Residue Percentage
$In(S_2CN(CH_2C_6H_5)_2)_3$	17.49 %	15.77 %	14.05 %	16.81 ± 2.92 %
$In(S_2CN(C_2H_5)_2)_3$	29.13 %	26.27 %	23.41 %	26.26 ± 1.27 %
$In(S_2CN(CH_2)_4O)_3$	27.10 %	24.43 %	21.77 %	28.18 ± 1.05 %
$In(S_2CN(CH_2)_4)_3$	29.45 %	26.56 %	23.66 %	25.67 ± 0.21 %
$Ga(S_2CN(CH_2C_6H_5)_2)_3$	13.29 %	11.48 %	9.68 %	26.95 ± 3.00 %
$Ga(S_2CN(CH_2)_4O)_3$	21.18 %	18.30 %	15.43 %	51.39 %
$Ga(S_2CH(CH_2)_4)_3$	23.19 %	20.03 %	16.88 %	27.32 %

Thermogravimetric Analysis of Compound 1



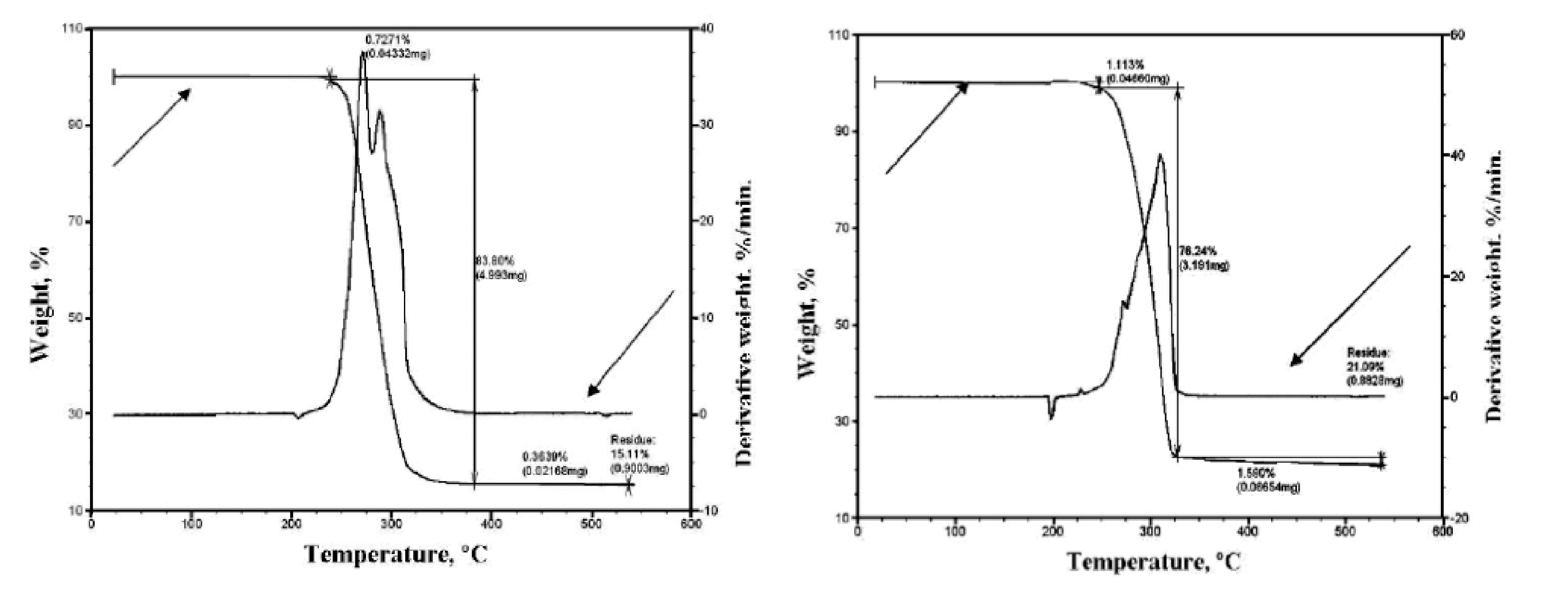
Data for compound (1) $In(S_2CN(CH_2C_6H_5)_2)_3$ is best fit to In_2S_3

Thermogravimetric Analysis of Compound 2



Data for compound (2) $In(S_2CN(C_2H_5)_2)_3$ is best fit to InS

Thermogravimetric Analysis of Copper Compounds

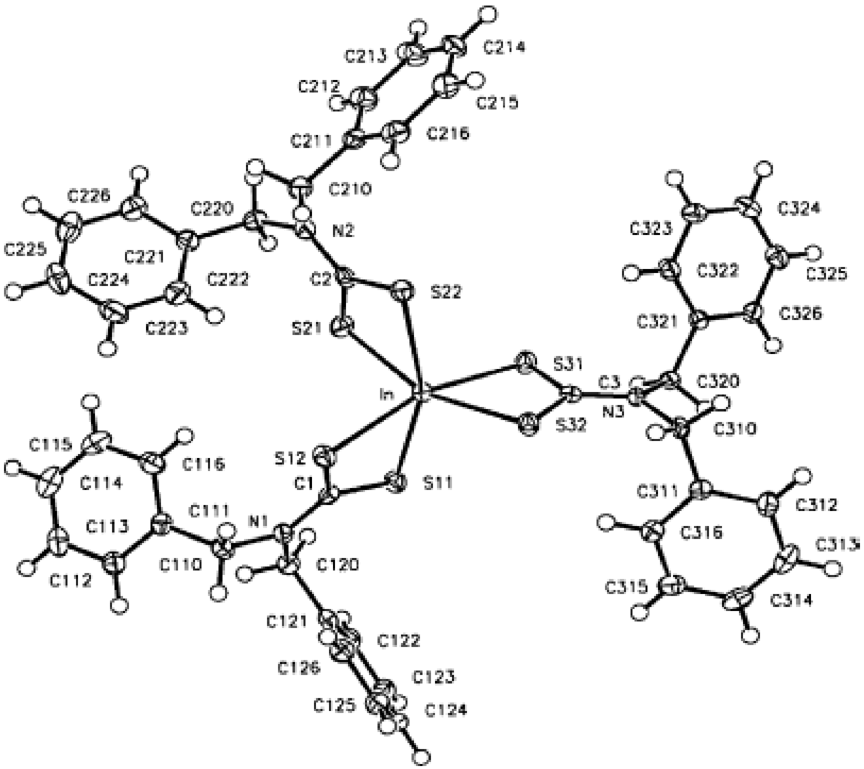


Thermogravimetric analysis plots for $Cu(S_2CN(CH_2C_6H_5)_2)_2$ left (best fit is CuS) and $Cu(S_2CN(C_2H_5)_2)_2$ right (best fit is Cu_2S).

Structural Characterization of Compound 1

Crystallographic data for Tris(bis(phenylmethyl)carbamodithioato-S,S')indium (III)

Molecular formula	$C_{45}H_{42}InN_3S_6$
Formula weight	932.06
Temperature (K)	150
Radiation (wavelength)	Mo K_α(0.71073Å)
Space group	$P\bar{1}$ (No. 2)
a (Å)	9.9396(2)
b (Å)	12.9719(3)
c (Å)	16.7988(4)
α (°)	91.9439(8)
β (°)	97.6047(8)
γ (°)	103.2196(13)
V, (Å^3)	2085.39(8)
Z	2
D_{calc} (g cm^{-3})	1.484
Crystal size, mm	0.44x0.40x0.25
μ (mm^{-1})	0.881
h, k, l range	0 to 12, -16 to 16, -21 to 21
2θ range (°)	2.45 - 54.95
Data collected	19459
Unique data	9255
Data used in refinement	9220
Cutoff used in R-factor calculations	$F_o^2 > 2.0\sigma(F_o^2)$
Data with I>2.0σ(I)	7423
Parameters	496
R(F_o)	0.033
$R_w(F_o^2)$	0.072
Goodness-of-fit	1.042



Data Table for Compound 1

ORTEP of $In(S_2CNBz_2)_3$ - key atoms labeled. The thermal ellipsoids enclose 50% of electron density.

Selected Bond distances and angles for Compound 1, $In(S_2CNBz_2)_3$

In–S(11)	2.5887(6)	S(11)–In–S(12)	69.465(18)
In–S(12)	2.6189(6)	S(21)–In–S(22)	69.654(17)
In–S(21)	2.5750(6)	S(32)–In–S(31)	70.412(17)
In–S(22)	2.6170(6)	S(11)–In–S(21)	92.718(18)
In–S(31)	2.5941(6)	S(11)–In–S(31)	94.76(2)
In–S(32)	2.5669(6)	S(11)–In–S(32)	104.272(19)
S(11)–C(1)	1.723(2)	S(22)–In–S(12)	97.593(19)
S(12)–C(1)	1.732(2)	S(22)–In–S(31)	100.03(2)
S(21)–C(2)	1.726(2)	S(22)–In–S(32)	95.804(18)
S(22)–C(2)	1.722(2)	S(21)–In–S(31)	97.289(19)
S(31)–C(3)	1.721(2)	S(21)–In–S(12)	92.236(19)
S(32)–C(3)	1.736(2)	S(12)–In–S(32)	104.221(18)
N(1)–C(1)	1.328(3)	S(11)–In–S(22)	158.18(2)
N(1)–C(120)	1.470(3)	S(21)–In–S(32)	159.56(2)
N(1)–C(110)	1.475(3)	S(12)–In–S(31)	162.00(2)
N(2)–C(2)	1.332(3)	S(11)–C(1)–S(12)	118.38(13)
N(2)–C(210)	1.477(3)	S(21)–C(2)–S(22)	118.64(13)
N(2)–C(220)	1.480(3)	S(31)–C(3)–S(32)	118.78(13)
N(3)–C(3)	1.328(3)		
N(3)–C(320)	1.473(3)		
N(3)–C(310)	1.486(2)		

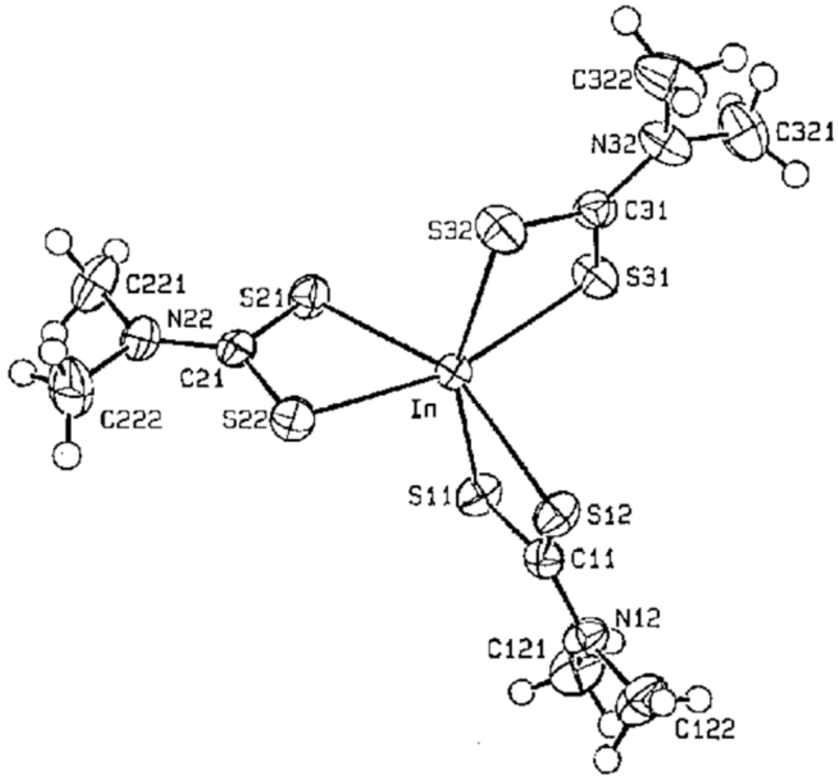
Numbers in parentheses are estimated standard deviations in the least significant digits.

Structural Characterization of Compound 2

Table I. Crystallographic Data for $In[S_2CN(CH_3)_2]_3$

Molecular formula	$InS_6N_{3.5}C_{12}H_{21.5}$
Formula weight	522.03
Crystal size (mm)	0.50 x 0.38 x 0.34
Space group (No.)	$P\bar{1}$ (No. 2)
a (Å)	9.282(1)
b (Å)	10.081(1)
c (Å)	12.502(2)
α (˚)	73.91(1)
β (˚)	70.21(1)
γ (˚)	85.84(1)
V ($Å^3$)	1057.3(3)
Z	2
d_{calc} (g cm^{-3})	1.64
μ (cm^{-1})	16.52
Transmission coefficient	1.000 - 0.811
2θ Range (˚)	4.00 - 45.00
Scan method	ω-2θ
No. unique data	2757
No. observed data ($1>3\sigma(I)$)	2373
R^a	0.046
R_w^b	0.061
GOF	2.191
Largest shift/e. s. d. final cycle	0.09

Data Table for Compound 2



ORTEP of $In(S_2CNEt_2)_3$ - key atoms labeled. The thermal ellipsoids enclose 50% of electron density.

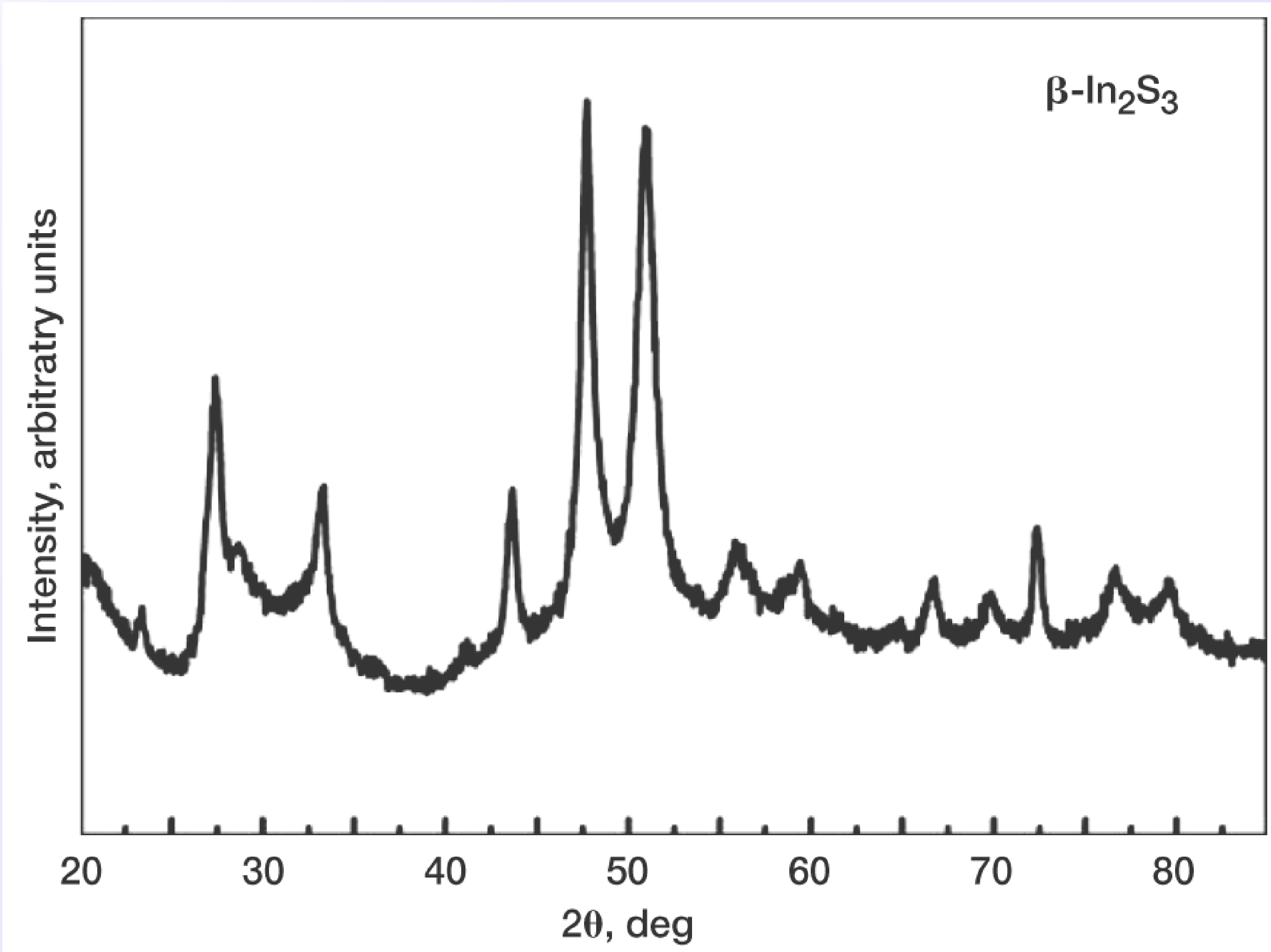
Selected Bond distances and angles for Compound 2, $In(S_2CNEt_2)_3$

Table II. Selected bond distances (Å) and angles (°) for $In[S_2CN(CH_3)_2]_3$.

Bond	Distance	Atoms	Angle
In-S11	2.602(2)	S11-In-S12	69.62(6)
In-S12	2.583(2)	S11-In-S21	96.15(6)
In-S21	2.582(2)	S11-In-S22	105.88(7)
In-S22	2.590(2)	S11-In-S31	91.83(6)
In-S31	2.600(2)	S11-In-S32	157.88(7)
In-S32	2.608(2)	In-S11-C11	85.6(2)
N12-C11	1.319(9)	In-S12-C11	86.4(2)
N22-C21	1.308(9)	S11-C11-N12	120.7(6)
S11-C11	1.727(7)	S11-C11-S12	118.4(4)
S12-C11	1.720(7)	C11-N12-C121	121.8(7)
S21-C21	1.724(7)		
S22-C21	1.723(7)		
S31-C31	1.725(8)		
S32-C31	1.713(8)		

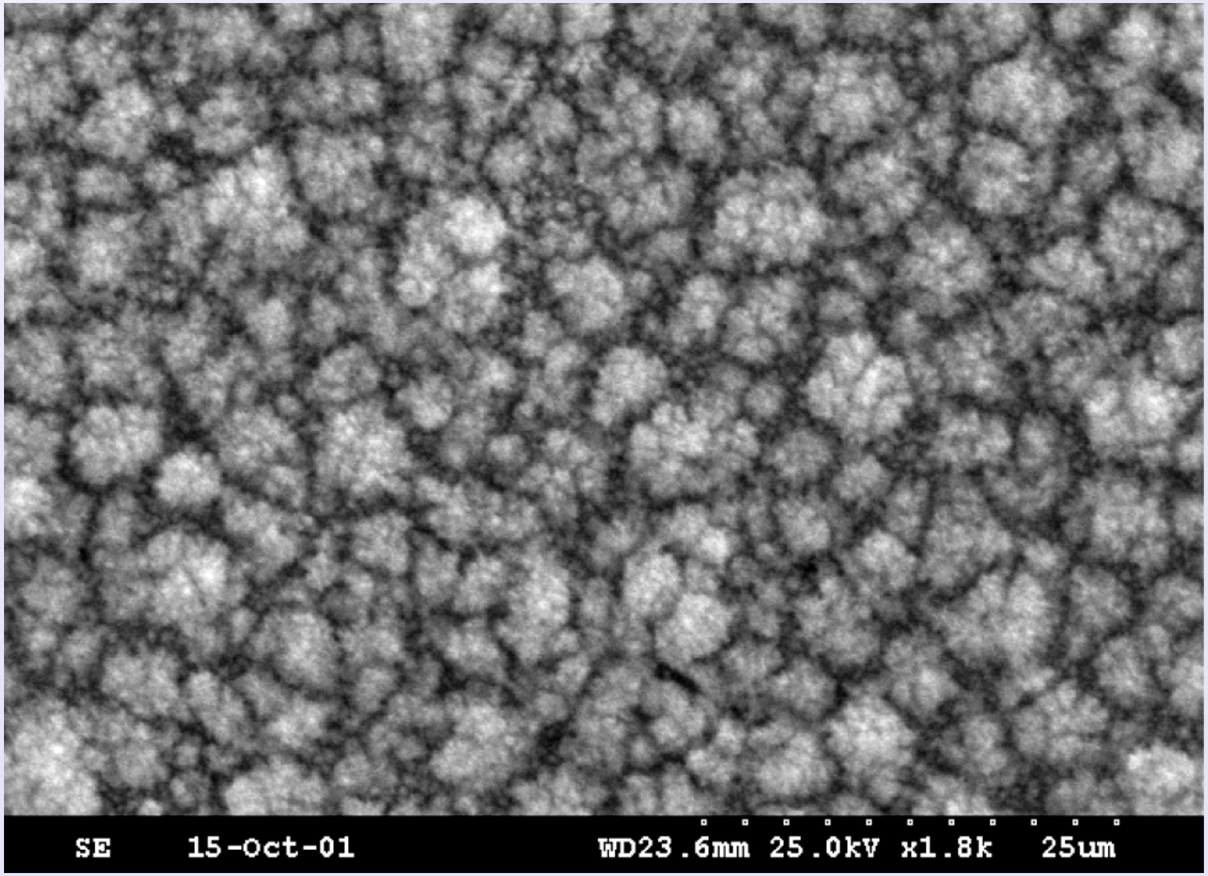
Numbers in parentheses are estimated standard deviations in the least significant digits.

Product of Thermal Decomposition of Compound 1



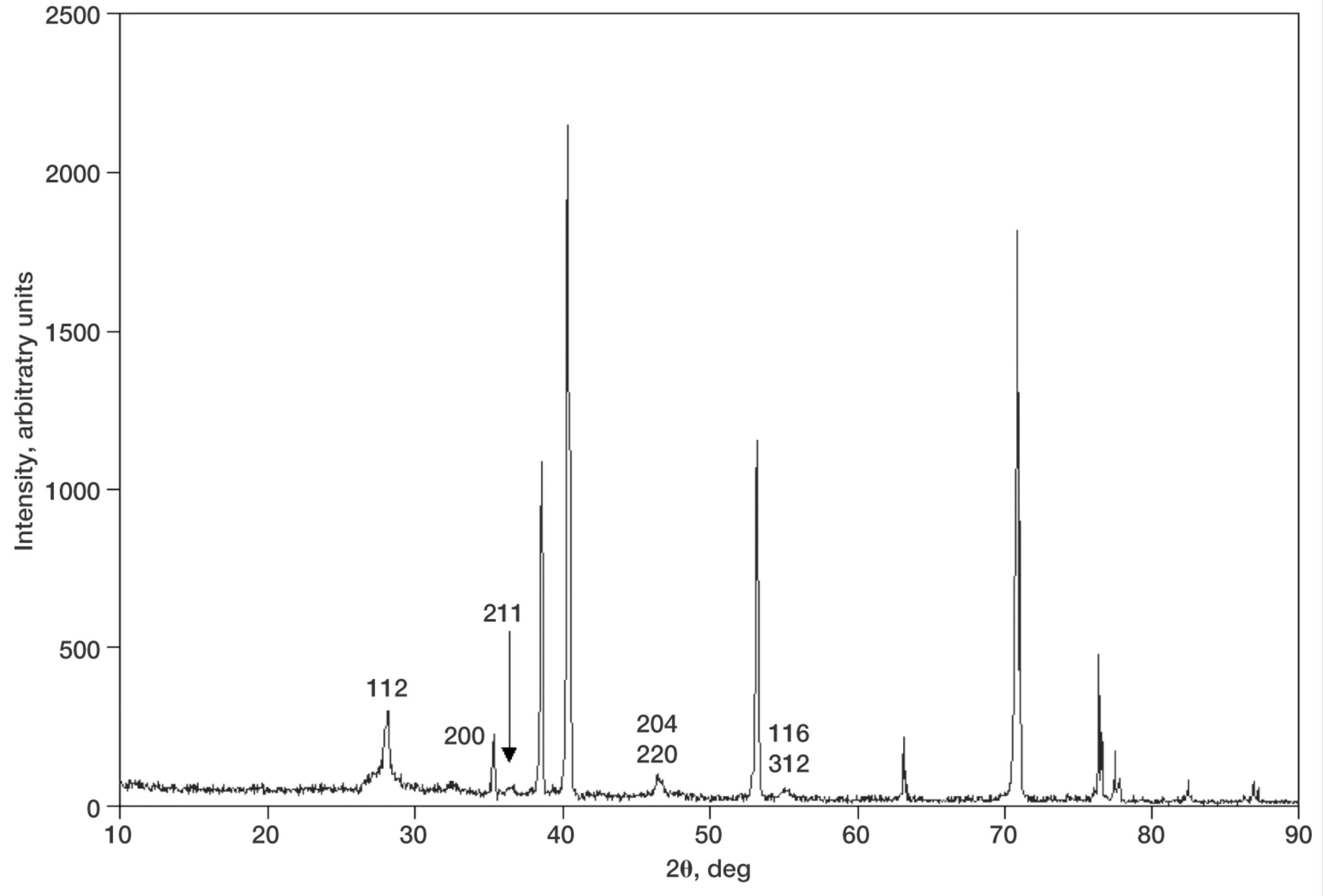
XRD powder pattern of solid residue from decomposition of (I), fits In_2S_3.

Spray Pyrolysis of Compound 1 on a Cu/Ti Substrate



XRD pattern of a $CuInS_2$ film deposited from (I) at 425°C from a 0.005 M solution with 2 slpm flow rate of Ar carrier gas on Cu/Ti substrate. EDS showed film to be near stoichiometric; magnification 1800X; scale is 25 μm.

Spray Pyrolysis of Compound 1 on a Cu/Ti Substrate



XRD pattern of a $CuInS_2$ film deposited from (I) at 425°C from a 0.005 M solution using 2 slpm flow rate of Ar carrier gas. Unlabelled peaks are attributed to the Ti substrate.

Conclusions

- $In(S_2CN(CH_2C_6H_5)_2)_3$ (**1**) appears to be a superior compound for spray deposition for photovoltaic applications. It decomposes in a narrower, lower temperature range than $In(S_2CN(CH_2CH_3)_2)_3$ and yields a product which is nearly pure In_2S_3.
- The techniques of GC/MS and TGA continues to yield results that enable precursor metal dithiocarbamates to be evaluated for photovoltaic applications.
- Compounds **1** and **2** were characterized by single crystal X-ray diffraction; their thermal properties were probed using a specialized tool employing the combined analytical techniques of thermogravimetric analysis, gas chromatography/mass spectrometry and Fourier-transform infrared spectroscopy.
- Examination of the gas phase species produced during heating, and evaluation of the composition and structure of the resulting solids confirm that compound **1** can be used to deposit pure indium sulfide.
- Implementation of $In(S_2CNBz_2)_3$ in a spray CVD apparatus indicates that it is possible to produce $CuInS_2$ films on a copper-coated substrate. Further investigations are warranted to determine the feasibility of achieving device quality $CuInS_2$ films.