A facile synthesis of MInSe_2 ($\text{M} = \text{Cu}, \text{Ag}$) via low temperature pyrolysis of single source molecular precursors, $[(\text{R}_3\text{P})_2\text{MIn}(\text{SeCOAr})_4]$

SHAMIK GHOSHAL, LILADHAR B KUMBHARE, VIMAL K JAIN* and GAUTAM K DEY†

Chemistry Division, †Materials Science Division, Bhabha Atomic Research Centre, Mumbai 400 085, India

MS received 27 September 2006; revised 15 February 2007

Abstract. The reaction of KSeCOAr with InCl_3 and $[\text{MCl}(\text{PR}_3)_2]$ in benzene afforded bimetallic complexes, $[(\text{R}_3\text{P})_2\text{MIn}(\text{SeCOAr})_4]$ ($\text{PR}_3 = \text{PEt}_3$ or PPh_3 ; $\text{M} = \text{Cu}$ or Ag ; $\text{Ar} = -\text{C}_6\text{H}_5$ (phenyl) or $4\text{-MeC}_6\text{H}_4$ (tolyl)). The triethylphosphine complexes decomposed rapidly when $\text{M} = \text{Ag}$ while slowly when $\text{M} = \text{Cu}$. All these complexes were characterized by elemental analysis, IR, UV-VIS, NMR (^1H , ^{31}P) spectral data. Pyrolysis in a furnace at 300°C gave tetragonal MInSe_2 ($\text{M} = \text{Cu}, \text{Ag}$) structure. Solvothermal decomposition of $[(\text{PPh}_3)_2\text{CuIn}(\text{SeCOAr})_4]$ in boiling ethylene glycol gave nanorods of CuInSe_2 which were characterized by XRD, EDAX, SEM and TEM.

Keywords. Chalcopyrite; selenocarboxylates; nanoparticles; indium; copper; silver.

1. Introduction

The family of I–III–VI chalcopyrite semiconductor materials is of considerable current interest due to their suitability for photovoltaic and opto-electronic device applications (Fonash 1981; Lofferski 1996; Rao *et al* 2002). Among them, copper indium diselenide, (CuInSe_2 , CIS), a direct band gap semiconductor with optical band gap of 1.04 eV, is extensively used in solar cells. An efficiency of $\sim 19\%$ under test conditions of CIS has been claimed recently (Rau and Schock 1993; Hengel *et al* 1996). The CIS is prepared in several ways which include elemental deposition, selenization, electrodeposition, etc.

Metalloorganic route has emerged as a versatile strategy in materials synthesis as it offers control over shape, size and morphology of the product (Murray *et al* 2000; Schubert and Husing 2000; Ng *et al* 2006). Copper indium selenolates, $[(\text{PR}_3)_2\text{CuIn}(\text{SeR}')_4]$ ($\text{R} = \text{Bu}, \text{Ph}$; $\text{R}' = \text{Et}, \text{Bu}^i, \text{Ph}$), (Hirpo *et al* 1993; Banger *et al* 2003; Castro *et al* 2003) and copper indium thiolates, $[(\text{PPh}_3)_2\text{CuIn}(\text{SR}')_4]$ ($\text{R} = \text{Et}, \text{Bu}^i$), (Hirpo *et al* 1993; Banger *et al* 2003; Castro *et al* 2003, 2004), have been employed to prepare thin films of CuInE_2 ($\text{E} = \text{S}$ or Se). Thermolysis of $[(\text{PPh}_3)_2\text{CuIn}(\text{SePh})_4]$ in dioctyl phthalate at 300°C yields CIS nanoparticles (Castro *et al* 2003). The latter are generally obtained by the reaction of CuCl_2 (or CuCl), InCl_3 and Se metal under different conditions (Malik *et al* 1999; Jiang *et al* 2000; Xiao *et al* 2001; Grisaru *et al* 2003). Recently, binuclear copper-/silver-indium thiocarboxylate complexes, $[(\text{PPh}_3)$

$\text{CuIn}(\text{SCOR})_4]$ and $[(\text{PPh}_3)_2\text{AgIn}(\text{SCOR})_4]$, have been reported which on pyrolysis gave corresponding ternary metal sulfides (Deivaraj *et al* 2001, 2003). We have reported a facile cleavage of C–Se bond in metal selenocarboxylates (Kumbhare *et al* 2006). This has led us to prepare low decomposition temperature single source molecular precursors for metal selenides (Kedarnath *et al* 2006). In the above perspective, it was considered worthwhile to explore the chemistry of bimetallic copper-/silver-indium selenocarboxylates with the hope that these complexes would serve as single source molecular precursors for MInSe_2 . The results of this work are reported herein.

2. Materials and methods

All preparations were carried out in freshly distilled dried solvents under nitrogen atmosphere. The compounds, KSeCOAr ($\text{Ar} = -\text{C}_6\text{H}_5$ or $4\text{-MeC}_6\text{H}_4$) (Kumbhare *et al* 2006), $[\text{CuCl}(\text{PR}_3)_2]$ ($\text{PR}_3 = \text{PEt}_3, \text{PPh}_3$) (Chi *et al* 1992) and $\text{AgCl}(\text{PR}_3)_2$ (Sanghani *et al* 1982), were prepared according to the literature methods. IR spectra were recorded as Nujol mull between CsI plates on a Bomen MB-102 FT–IR spectrometer. NMR spectra (^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$) were recorded in CDCl_3 (deuterated chloroform) on a Bruker DPX 300 NMR spectrometer operating at 300, 75.5 and 121.5 MHz, respectively. Chemical shifts were referenced to internal chloroform peak (for ^1H and ^{13}C) and 85% H_3PO_4 for $^{31}\text{P}\{^1\text{H}\}$. Electronic spectra were recorded in benzene on a Chemito spectrascan UV–VIS double beam spectrophotometer. Powder X-ray diffraction patterns were recorded on a Phillips PW-1820 in-

*Author for correspondence (jainvk@barc.gov.in)

Table 1. Analytical and spectroscopic data for copper/silver–indium selenocarboxylates.

Compound	% Yield colour	M.P. (°C)	% Analysis found (calcd)			IR (cm ⁻¹) $\nu_{\text{C=O}}$	UV-VIS λ_{max} (nm)	NMR in CDCl ₃ (δ in ppm) ^a
			C	H	In			
[(PPh ₃) ₂ CuIn(SeCOPh) ₄]	81 Yellow	105	54.3 (53.4)	3.7 (3.5)	7.5 (8.0)	1659 1624 1577	282, 309	¹ H: 7.22–7.46 (m), 7.82 (d, 7Hz) (Ph) ³¹ P{ ¹ H}: -1.0 ¹³ C{ ¹ H}: 127.8 (C-2/6 or C-3/5); 129.0 (C-3/5 or C-2/6); 131.5 (C-4); 141.4 (C-1); 200.1 (C=O) (PhCOSe); 128.5 (d, 8 Hz, C-3/5); 129.6 (s, C-4); 134.9 (d, 15 Hz, C-2/6); 132.6 (d, 31 Hz, C-1) (Ph ₃ P)
[(PPh ₃) ₂ CuIn(SeCOTol) ₄]	76 Yellow	147	55.1 (54.6)	4.1 (3.9)	7.2 (7.7)	1669 1647 1601	282, 310	¹ H: 2.32 (s, tol-Me); 6.96 (d, 7.8 Hz), 7.70 (d, 7.8 Hz) (C ₆ H ₄); 7.08–7.37 (m, PPh ₃) ³¹ P{ ¹ H}: -0.8 ¹³ C{ ¹ H}: 21.4 (s, tol-4), 128.5 (s, C-2/6 or C-3/5); 129.2 (C-3/5 or C-2/6); 139.0 (s, C-4); 143.0 (s, C-1), 199.8 (s, C=O) (tolCOSe); 128.4 (d, 4 Hz, C-3/5); 129.5 (s, C-4); 134.0 (d, 15 Hz, C-2/6), 133.2 (d, 24 Hz, C-1) (PPh ₃)
[(PEt ₃) ₂ CuIn(SeCOPh) ₄]	70 Sticky-solid	—	—	—	—	1637 1577	284, 310	¹ H: 1.13 (br), 1.58 (br) (PEt ₃); 7.36 (t, 7.7 Hz); 7.47 (d, 7 Hz); 8.08 (d, 7.5 Hz) (Ph) ³¹ P{ ¹ H}: -7.8
[(PEt ₃) ₂ CuIn(SeCOTol) ₄]	61 Yellow	112	43.6 (43.8)	4.4 (4.8)	9.0 (9.5)	1623 1597	284, 305	¹ H: 1.15 (br), 1.62 (br) (PEt ₃); 2.36 (s, tol, Me); 7.15 (d, 7.9 Hz), 7.97 (d, 7.9 Hz) (C ₆ H ₄) ³¹ P{ ¹ H}: -7.9
[(PPh ₃) ₂ AgIn(SeCOPh) ₄]	78 Off white	93–96	52.4 (51.8)	3.8 (3.4)	7.3 (7.7)	1654 1622	296, 335, 346 (sh)	¹ H: 7.16–7.83 (m) Ph ³¹ P{ ¹ H}: 3.9
[(PPh ₃) ₂ AgIn(SeCOTol) ₄]	88 Off white	122	52.1 (53.0)	3.3 (3.8)	7.2 (7.4)	1669 1644 1601	283, 335, 347 (sh)	¹ H: 2.28 (s, tol-Me); 6.93 (d, 7.5 Hz), 7.69 (d, 7.4 Hz) (C ₆ H ₄); 7.23–7.36 (m) (PPh ₃) ³¹ P{ ¹ H}: 4.7

^aPh = C₆H₅ (phenyl); tol = 4-MeC₆H₄ (*p*-tolyl).

strument. SEM and EDAX were carried out on a Tescan Vega 2300T/40 instrument. A JEOL-2000FX transmission electron microscope operating at 160 kV accelerating voltage was used for TEM studies. The samples for TEM were prepared by placing a drop of the sample dispersed in absolute ethanol on a carbon coated copper grid.

2.1 Preparation of [(PPh₃)₂CuIn(SeCOPh)₄]

To a benzene suspension of InCl₃ (121 mg, 0.55 mmol), a solid [CuCl(PPh₃)₂] (339 mg, 0.54 mmol) was added with stirring which continued for 30 min. To this reaction mixture, KSeCOPh (486 mg, 2.18 mol) was added. The reactants

were further stirred for an additional 1 h and the contents were filtered through a G-3 filtration unit. The filtrate was stripped off under a reduced pressure to give a yellow solid (641 mg, 81%). Similarly, all other complexes were prepared. Pertinent data are given in table 1.

2.2 Thermal studies

2.2a Pyrolysis in a furnace: A weighed quantity (~350 mg) of the complex, [(PPh₃)₂MIn(SeCOAr)₄] (Ar = Ph or tol; M = Cu or Ag), in a quartz boat was heated in a furnace at 300°C under a flowing nitrogen atmosphere for 2 h. After cooling the furnace to room temperature, the

Table 2. XRD and EDAX data for $M\text{InSe}_2$ obtained from pyrolysis of $[(\text{PPh}_3)_2\text{MIn}(\text{SeCOAr})_4]^\dagger$.

Compound	Furnace heating		in refluxing ethylene glycol	
	XRD d (Å)	EDAX % found (calcd)	XRD d (Å)	EDAX % found (calcd)
$[(\text{PPh}_3)_2\text{CuIn}(\text{SeCOPh})_4]$	3.35	Cu = 19.7 (18.9)	3.35	Cu = 17.1 (18.9)
	2.05	In = 34.9 (34.1)	2.04	In = 36.8 (34.1)
	1.74	Se = 45.4 (47.0)	1.74	Se = 46.1 (47.0)
$[(\text{PPh}_3)_2\text{CuIn}(\text{SeCOtol})_4]$	3.34	Cu = 17.2 (18.9)	3.34	Cu = 19.4 (18.9)
	2.04	In = 37.6 (34.1)	2.04	In = 32.0 (34.1)
	1.74	Se = 45.2 (47.0)	1.74	Se = 48.6 (47.0)
$[(\text{PPh}_3)_2\text{AgIn}(\text{SeCOPh})_4]$	3.52	Ag = 28.9 (28.3)		
	2.19	In = 31.0 (30.2)		
	2.13	Se = 40.1 (41.5)		
	1.84			
	1.79			
$[(\text{PPh}_3)_2\text{AgIn}(\text{SeCOtol})_4]$	3.47	Ag = 31.2 (28.3)		
	2.16	In = 28.1 (30.2)		
	2.11	Se = 40.7 (41.5)		
	1.83			

[†]XRD patterns are in conformity with the reference patterns: CuInSe_2 – JCPDS file No: 40-1487; AgInSe_2 – JCPDS file No: 35-1099.

Figure 1. XRD pattern of CuInSe_2 obtained from pyrolysis of $[(\text{PPh}_3)_2\text{CuIn}(\text{SeCOtol})_4]$: a. furnace heating (300°C) and b. in ethylene glycol (196°C). **Figure 2.** XRD pattern of AgInSe_2 obtained from $[(\text{PPh}_3)_2\text{AgIn}(\text{SeCOPh})_4]$, furnace heating (300°C).

residue in quartz boat was again weighed and was characterized by XRD and EDAX.

2.2b Solvothermal decomposition: Pyrolysis of the complexes was also carried out in ethylene glycol under similar conditions, which were optimized from several repeat experiments. A typical experiment is described below.

Ethylene glycol (25 cm³) in a three necked 100 ml flask was refluxed under nitrogen atmosphere for 30 min. To this boiling ethylene glycol, powdered $[(\text{PPh}_3)_2\text{CuIn}(\text{SeCOtol})_4]$ (172 mg, 0.11 mmol) was added with vigorous stirring. Refluxing and stirring continued for an additional 1 h, whereupon a black precipitate formed. The solution was cooled to 40°C, followed by addition of methanol (5 cm³),

and then it was centrifuged. The supernatant was decanted and the black residue was washed with methanol and dried under vacuum. The black powder was analysed by XRD, EDAX, SEM and/or TEM.

3. Results and discussion

The reaction of KSeCOAr with a premixed 1 : 1 mixture of InCl_3 and $[\text{MCl}(\text{PR}_3)_2]$ in benzene afforded bimetallic complexes of composition $[(\text{R}_3\text{P})_2\text{MIn}(\text{SeCOAr})_4]$ [$\text{M} = \text{Cu}$, Ag ; $\text{PR}_3 = \text{PEt}_3$, PPh_3 ; $\text{Ar} = \text{Ph}$ or $4\text{-MeC}_6\text{H}_4$ (tol)] as yellow ($\text{M} = \text{Cu}$) and off-white ($\text{M} = \text{Ag}$) complexes (1). The reaction involving $[\text{AgCl}(\text{PEt}_3)_2]$ leads to excessive decomposition with concomitant formation of a black powder, which was identified as AgInSe_2 from XRD pattern. However, the corresponding triethylphosphine copper complexes, $[(\text{Et}_3\text{P})_2\text{CuIn}(\text{SeCOAr})_4]$, could be isolated in the solid state but slowly decomposed at room temperature within a few days.

The IR spectra of $[(\text{R}_3\text{P})_2\text{MIn}(\text{SeCOAr})_4]$ displayed $\nu_{\text{C=O}}$ absorptions in the region $1580\text{--}1670\text{ cm}^{-1}$. These absorptions appeared at higher wavenumbers than the corresponding potassium salts (1538 cm^{-1}), indicating that these complexes have unidentate ArCOSe ligands. The electronic spectra were characterized by two intense bands which may be assigned to $n \rightarrow \sigma^*$ ($\sim 285\text{ nm}$) and $n \rightarrow \pi^*$ ($\sim 310\text{ nm}$) transitions of the selenocarboxylate group. A shoulder at $\sim 345\text{ nm}$ in silver complexes may be attributed to $\pi \rightarrow \pi^*$ transition (table 1).

Figure 3. SEM picture of CuInSe_2 obtained from pyrolysis of $[(\text{PPh}_3)_2\text{CuIn}(\text{SeCOAr})_4]$ in ethylene glycol (196°C).

^1H NMR spectra showed expected resonances. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of these complexes exhibited a singlet indicating the formation of single molecular species. The $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of $[(\text{PPh}_3)_2\text{CuIn}(\text{SeCOAr})_4]$ displayed single set of resonances for selenocarboxylate ligands as well as for PPh_3 (table 1). The carbonyl carbon resonance appeared in the region ($\sim 200\text{ ppm}$) reported for metal selenocarboxylates (Kedarnath *et al* 2006). The $^{31}\text{P}\{^1\text{H}\}$ resonances in copper complexes were deshielded from the corresponding signal for $[\text{CuCl}(\text{PR}_3)_2]$ (^{31}P δ : -3.9 (for $\text{R} = \text{Ph}$); -10.1 (for $\text{R} = \text{Et}$) ppm). However, for silver complexes, $[(\text{PPh}_3)_2\text{AgIn}(\text{SeCOAr})_4]$, ^{31}P signal is deshielded relative to $[\text{AgCl}(\text{PPh}_3)_2]$ (^{31}P δ = 6.9 ppm).

The TG data of $[(\text{PPh}_3)_2\text{CuIn}(\text{SeCOAr})_4]$ ($\text{Ar} = \text{Ph}$ or tol) and $[(\text{PPh}_3)_2\text{AgIn}(\text{SeCOAr})_4]$ showed decomposition in the region $237\text{--}267^\circ\text{C}$ with a weight loss of 75% (calcd. wt loss for CuInSe_2 , 77.5%), 74.4% (calcd. wt loss for CuInSe_2 , 76.6%) and 72% (calcd. wt loss for AgInSe_2 , 74.3%), respectively indicating formation of MInSe_2 ($\text{M} = \text{Cu}$ or Ag). Pyrolysis of $[(\text{PPh}_3)_2\text{MIn}(\text{SeCOAr})_4]$ in a furnace at 300°C under a flowing nitrogen atmosphere gave a black residue, which from weight loss, XRD pattern, and EDAX analysis (table 2) has been identified as MInSe_2 ($\text{M} = \text{Cu}$ or Ag). The XRD patterns (figures 1 and 2) revealed the formation of tetragonal phases of the corresponding ternary selenides and are in conformity with the appropriate reference patterns (JCPDS file no 40-1487 for CuInSe_2 ; JCPDS file No 35-1099 for AgInSe_2).

Pyrolysis of $[(\text{PPh}_3)_2\text{CuIn}(\text{SeCOAr})_4]$ was carried out in boiling (196°C) ethylene glycol to assess whether these complexes can be used for the preparation of CuInSe_2 nanoparticles. Thus pyrolysis of $[(\text{PPh}_3)_2\text{CuIn}(\text{SeCOAr})_4]$ in boiling ethylene glycol gave black CuInSe_2 nanoparticles, which were isolated in tetragonal phases (from XRD). The broadening in XRD pattern reflects their formation in nanometric regime. The particle size estimated from the Scherrer's formula (Cullity 1978) for CuInSe_2 is 12 nm. The SEM picture of CuInSe_2 showed large spherical aggregates (figure 3). The TEM images of CuInSe_2 are shown in figure 4. The micrograph of CuInSe_2 shows the formation of nanorods with size of length, 17–29 and width, 10 nm. The selective area electron diffraction (SAED) pattern of CuInSe_2 (figure 4) is well in agreement with the tetragonal phase [CuInSe_2 ; d values in nm: 0.335, 0.206, 0.172 (JCPDS file no: 40-1487)].

4. Conclusions

Ternary chalcopyrite semiconductor materials, MInSe_2 ($\text{M} = \text{Cu}$, Ag), have been successfully synthesized through a facile solvothermal route employing single source molecular precursors, $[(\text{PPh}_3)_2\text{MIn}(\text{SeCOAr})_4]$. The convenient synthesis of molecular precursors may be extended to the preparation of precursors for other useful ternary materials. The phase purity and narrow size distribution of the nanorods

Figure 4. TEM pictures (a) bright field, (b) dark field and (c) SAED pattern of CuInSe_2 nanoparticles obtained from $[(\text{PPh}_3)_2\text{CuIn}(\text{SeCOTol})_4]$ in ethylene glycol.

obtained by this method may provide an edge over other routes.

Acknowledgements

One of the authors (SG) is grateful for the award of a Senior Research Fellowship by the Department of Atomic Energy. Authors thank Drs T Mukherjee and S K Kul-

shreshtha for encouragement. We are grateful to Head, Radio Chemistry Division, Bhabha Atomic Research Centre, Mumbai, for providing microanalyses.

References

- Banger K K, Jin M H C, Harris J D, Fanwick P E and Hepp A F
2003 *Inorg. Chem.* **42** 7713

- Castro S L, Bailey S G, Raffaele R P, Banger K K and Hepp A F 2003 *Chem. Mater.* **15** 3142
- Castro S L, Bailey S G, Raffaele R P, Banger K K and Hepp A F 2004 *J. Phys. Chem.* **B108** 12429
- Chi K M, Farkas J, Hampden-Smith M J, Kodas T T and Duesler E N 1992 *J. Chem. Soc. Dalton Trans.* 3111
- Cullity B D 1978 *Elements of X-ray diffraction* (London: Addison-Wesley Inc.)
- Deivaraj T C, Park J H, Afzaal M, O'Brien P and Vittal J J 2001 *Chem. Commun.* 2304
- Deivaraj T C, Park J H, Afzaal M, O'Brien P and Vittal J J 2003 *Chem. Mater.* **15** 2383
- Fonash S J 1981 *Solar cell device physics* (New York: Academic Press)
- Grisaru H, Palchik O, Gedanken A, Palchik V, Slifkin M A and Weiss A M 2003 *Inorg. Chem.* **42** 7148
- Hengel I, Klenk R, Garcia Villora E and LuxSteiner M-Ch 1996 *Proc. 2nd world conf. exh. photovol. sol. energy conv., Vienna.* p. 545
- Hirpo W, Dhingra S, Sutorik A C and Kanatzidis M G 1993 *J. Am. Chem. Soc.* **115** 1597
- Jiang Y, Wu Y, Mo X, Yu W, Xie Y and Qian Y 2000 *Inorg. Chem.* **39** 2964
- Kedarnath G, Kumbhare L B, Jain V K, Phadnis P P and Nethaji M 2006 *Dalton Trans.* 2714
- Kumbhare L B, Jain V K and Varghese B 2006a *Inorg. Chim. Acta* **359** 409
- Kumbhare L B, Jain V K and Butcher R J 2006b *Polyhedron* **25** 3159
- Lofferski J J 1996 *Cryst. Res. Technol.* **S31** 419
- Malik M A, O'Brien P and Revaprasadu N 1999 *Adv. Mater.* **11** 1441
- Murray C B, Kagan C R and Bawendi M G 2000 *Ann. Rev. Mater. Sci.* **30** 545
- Ng M T, Boothroyd C B and Vittal J J 2006 *J. Am. Chem. Soc.* **128** 7118
- Rao G V, Chandra G H, Reddy P S, Hussain O M, Reddy K T R and Uthanna S 2002 *J. Optoelect. Adv. Mater.* **4** 387
- Rau U and Schock H W 1993 *Appl. Phys.* **A69** 131
- Sanghani D V, Smith P J, Allen D W and Taylor B F 1982 *Inorg. Chim. Acta* **59** 203
- Schubert U and Husing N 2000 *Synthesis of inorganic materials* (Weinheim: Wiley-VCH)
- Xiao J, Xie Y, Xiong Y, Tang R and Qian Y 2001 *J. Mater. Chem.* **11** 1417