A New Facile Route for The Preparation of Single-Source Precursors for Bulk, Thin-Film and Nanocrystallite I-III-VI Semiconductors.

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Crystal Data

DATA COLLECTION

A colorless plate of C40H42AgInP2S4 having approximate dimensions of 0.28 x 0.19 x 0.09 mm was mounted on a glass fiber in a random orientation. Preliminary examination and data collection were performed with Mo Kα radiation (λ = 0.71073 A) on a Nonius KappaCCD.

Cell constants and an orientation matrix for data collection were obtained from least squares refinement, using the setting angles of 32849 reflections in the range $2 < \theta < 27^o$. The monoclinic cell parameters and calculated volume are: a=15.6671(4), b =12.6092(4), c =21.6432(8) A, $\beta = 108.412(2)^o$, V =4056.7(4)A^3. For Z = 4 and F.W. = 935.67 the calculated density is 1.53 g/cm3. The refined mosaicity from DENZO/SCALEPACK was 0.37^o indicating good crystal quality. The space group was determined by the program ABSEN(ref 1). From the systematic presences of: h0l l=2n and from subsequent least squares refinement, the space group was determined to be P2/c(# 13).

The data were collected at a temperature of 150 ± 1. Data were collected to a maximum 2θ of 55.8^o.

DATA REDUCTION

A total of 32849 reflections were collected, of, which 9649 were unique.

Lorentz and polarization corrections were applied to the data. The linear absorption coefficient is 13.4 /cm for Mo K radiation. An empirical absorption correction using SCALEPACK (ref 2) was applied. Transmission coefficients ranged from 0.725 to 0.890 with an average value of 0.851. Intensities of equivalent reflections were averaged. The agreement factor for the averaging was 8.7% based on intensity.

STRUCTURE SOLUTION AND REFINEMENT

The structure was solved by direct methods using SIR97 (ref3). The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full matrix least squares where the function minimized was Σw(|Fo|2 |Fc|2)2 and the weight w is defined as 1/[σ2(Fo2)+(0.0299P)2+0.0000P] where P=(Fo2+2Fc2)/3

Scattering factors were taken from the "International Tables for Crystallography" (ref 4). 9646 reflections were used in

the refinements. However, only reflections with $Fo^2>2\sigma(Fo^2)$ were used in calculating R. The final cycle of refinement included 439 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of:

$$R1 = \Sigma \, |Fo - Fc| \, / \, \Sigma \, Fo = 0.039$$

$$R2 = SQRT \left(\Sigma \, w \left(Fo^2 - Fc^2 \right)^2 / \Sigma \, w \, (Fo^2)^2 \right) = 0.076$$

The standard deviation of an observation of unit weight was 0.86. The highest peak in the final difference Fourier had a height of 1.03 e/A^3. The minimum negative peak had a height of 0.97 e/A^3.

Refinement was performed on a AlphaServer 2100 using SHELXL97 (ref 5). Crystallographic drawings were done using programs ORTEP (ref 6) ,and PLUTON (ref 7).

(1) P. C. McArdle, J. Appl. Cryst., 29, 306 (1996).
(2) Z. Otwinowski and W. Minor, Methods Enzymol., 276, 307 (1997).
(3) A. Altomare, M. C. Burla, M. Camalli, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, G. Polidori, and R. Spagna. , J. Appl. Cryst., 32, 115 (1999)
(4) "International Tables for Crystallography", Vol. C, Kluwer Academic Publishers, Utrecht, The Netherlands, (199)2, Tables 4.2.6.8 and 6.1.1.4
(5) G. M. Sheldrick, SHELXL97. A Program for Crystal Structure Refinement. Univ. of Gottingen, Germany, (1997)
(6) C. K. Johnson, ORTEPII, Report ORNL 5138, Oak Ridge National Laboratory, Tennessee, USA (1976)
(7) A. L. Spek, PLUTON. Molecular Graphics Program. Univ. of Ultrecht, The Netherlands (1991)

1) Single crystal X-ray Data for $C_{40}H_{42}AgInP_2S_4$

Table of Bond Distances in Angstroms

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
In(1)	S(11)	2.4273(11)	C(115)	C(116)	1.391(5)
In(1)	S(11)	2.4273(11)	C(121)	C(122)	1.390(6)
In(1)	S(12)	2.4797(10)	C(121)	C(126)	1.407(5)
In(1)	S(12)	2.4797(10)	C(122)	C(123)	1.393(5)
In(2)	S(21)	2.4333(11)	C(123)	C(124)	1.380(6)
In(2)	S(21)	2.4334(11)	C(124)	C(125)	1.375(7)
In(2)	S(22)	2.4841(11)	C(125)	C(126)	1.384(5)
In(2)	S(22)	2.4841(11)	C(131)	C(132)	1.379(5)
Ag(1)	P(1)	2.4574(10)	C(131)	C(136)	1.390(5)
Ag(1)	P(1)	2.4574(10)	C(132)	C(133)	1.392(5)
Ag(1)	S(12)	2.6906(10)	C(133)	C(134)	1.355(6)
Ag(1)	S(12)	2.6907(10)	C(134)	C(135)	1.383(6)
Ag(2)	P(2)	2.4527(10)	C(135)	C(136)	1.376(5)
Ag(2)	P(2)	2.4527(10)	C(211)	C(216)	1.386(5)
Ag(2)	S(22)	2.6797(10)	C(211)	C(212)	1.387(5)

Ag(2)	S(22)	2.6797(10)	C(212)	C(213)	1.384(6)
S(11)	C(11)	1.824(4)	C(213)	C(214)	1.385(6)
S(12)	C(12)	1.830(5)	C(214)	C(215)	1.387(6)
S(21)	C(21)	1.816(4)	C(215)	C(216)	1.388(5)
S(22)	C(22)	1.834(4)	C(221)	C(226)	1.394(5)
P(1)	C(121)	1.819(4)	C(221)	C(222)	1.398(5)
P(1)	C(111)	1.824(4)	C(222)	C(223)	1.380(5)
P(1)	C(131)	1.827(4)	C(223)	C(224)	1.390(5)
P(2)	C(231)	1.822(4)	C(224)	C(225)	1.379(5)
P(2)	C(211)	1.823(4)	C(225)	C(226)	1.385(5)
P(2)	C(221)	1.824(4)	C(231)	C(232)	1.387(5)
C(114)	C(113)	1.374(6)	C(231)	C(236)	1.392(5)
C(114)	C(115)	1.378(5)	C(232)	C(233)	1.396(5)
C(112)	C(113)	1.375(6)	C(233)	C(234)	1.371(6)
C(112)	C(111)	1.392(5)	C(234)	C(235)	1.383(6)
C(111)	C(116)	1.392(5)	C(235)	C(236)	1.382(5)

Numbers in parentheses are estimated standard deviations in

the least significant digits.

CRYSTAL DATA AND DATA COLLECTION PARAMETERS for

$C_{40}H_{42}AgInP_2S_4$

formula	$C_{40}H_{42}AgInP_2S_4$
formula weight	935.67
space group	P2/c (No. 13)
a, A	15.6671(4)
b, A	12.6092(4)
c, A	21.6432(8)
β, deg	108.412(2)
V, A^3	4056.7(4)
Z	4
d_{calc},g cm^{-3}	1.532
crystal dimensions, mm	0.28x0.19x0.09
temperature, K	150.
radiation (wavelength)	MO K_α(0.71073A)
monochromator	graphite
linear abs coef, mm^{-1}	1.340
absorption correction applied	empirical[a]
transmission factors: min, max	0.72, 0.89
diffractometer	Nonius KappaCCD
h, k, l range	0 to 20 0 to 16 -28 to 27
2θ range, deg	4.24-55.79
mosaicity, deg	0.37
programs used	SHELXL-97
F_{000}	1888.0
weighting	$1/[\sigma^2(Fo^2)+(0.0299P)^2+0.0000P]$ where $P=(Fo^2+2Fc^2)/3$
data collected	32849
unique data	9649
R_{int}	0.087

data used in refinement	9646
cutoff used in R-factor calculations	$F_o^2>2.0\sigma(F_o^2)$
data with I>2.0σ(I)	5328
number of variables	439
largest shift/esd in final cycle	0.00
$R(F_o)$	0.039
$R_w(F_o^2)$	0.076
goodness of fit	0.857

[a] Otwinowski Z. & Minor, W. Methods Enzymol.,**1996**, 276, 307.

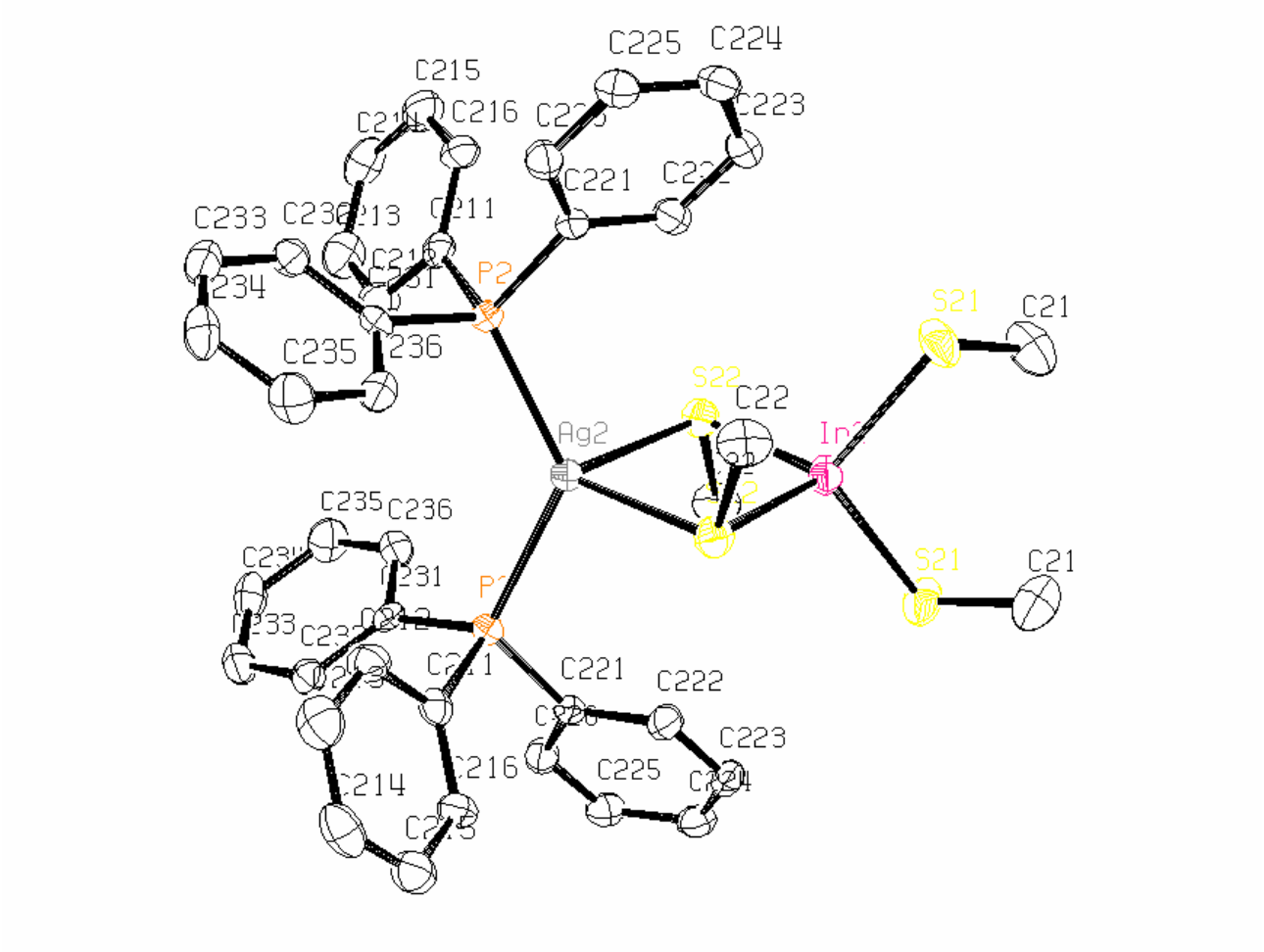


Table of Bond Angles in Degrees

for $C_{40}H_{42}AgInP_2S_4$

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
S(11)	In(1)	S(11)	111.83(6)	C(211)	P(2)	Ag(2)	113.79(11)
S(11)	In(1)	S(12)	107.26(3)	C(221)	P(2)	Ag(2)	113.86(12)
S(11)	In(1)	S(12)	115.13(4)	C(113)	C(114)	C(115)	119.9(4)
S(11)	In(1)	S(12)	115.13(4)	C(113)	C(112)	C(111)	119.8(4)
S(11)	In(1)	S(12)	107.26(3)	C(114)	C(113)	C(112)	121.1(4)
S(12)	In(1)	S(12)	99.87(5)	C(112)	C(111)	C(116)	119.1(4)
S(21)	In(2)	S(21)	108.91(5)	C(112)	C(111)	P(1)	119.1(3)
S(21)	In(2)	S(22)	108.80(3)	C(116)	C(111)	P(1)	121.8(3)
S(21)	In(2)	S(22)	114.84(4)	C(114)	C(115)	C(116)	119.7(4)
S(21)	In(2)	S(22)	114.85(4)	C(115)	C(116)	C(111)	120.4(3)
S(21)	In(2)	S(22)	108.80(3)	C(122)	C(121)	C(126)	118.5(4)
S(22)	In(2)	S(22)	100.64(5)	C(122)	C(121)	P(1)	125.3(3)
P(1)	Ag(1)	P(1)	127.63(5)	C(126)	C(121)	P(1)	116.1(3)
P(1)	Ag(1)	S(12)	105.85(3)	C(121)	C(122)	C(123)	120.5(4)
P(1)	Ag(1)	S(12)	110.64(3)	C(124)	C(123)	C(122)	120.1(4)
P(1)	Ag(1)	S(12)	110.64(3)	C(125)	C(124)	C(123)	120.0(4)
P(1)	Ag(1)	S(12)	105.85(3)	C(124)	C(125)	C(126)	120.6(4)
S(12)	Ag(1)	S(12)	89.71(4)	C(125)	C(126)	C(121)	120.1(4)
P(2)	Ag(2)	P(2)	128.40(5)	C(132)	C(131)	C(136)	118.6(4)
P(2)	Ag(2)	S(22)	112.32(3)	C(132)	C(131)	P(1)	124.4(3)
P(2)	Ag(2)	S(22)	103.31(3)	C(136)	C(131)	P(1)	117.0(3)
P(2)	Ag(2)	S(22)	103.30(3)	C(131)	C(132)	C(133)	119.9(4)
P(2)	Ag(2)	S(22)	112.32(3)	C(134)	C(133)	C(132)	120.7(4)
S(22)	Ag(2)	S(22)	91.03(5)	C(133)	C(134)	C(135)	120.4(4)
C(11)	S(11)	In(1)	101.02(14)	C(136)	C(135)	C(134)	119.1(4)
C(12)	S(12)	In(1)	102.06(15)	C(135)	C(136)	C(131)	121.4(4)
C(12)	S(12)	Ag(1)	107.93(14)	C(216)	C(211)	C(212)	118.9(4)
In(1)	S(12)	Ag(1)	85.21(3)	C(216)	C(211)	P(2)	122.8(3)
C(21)	S(21)	In(2)	99.95(14)	C(212)	C(211)	P(2)	118.4(3)
C(22)	S(22)	In(2)	101.74(14)	C(213)	C(212)	C(211)	120.9(4)
C(22)	S(22)	Ag(2)	113.59(15)	C(212)	C(213)	C(214)	120.3(4)
In(2)	S(22)	Ag(2)	84.16(3)	C(213)	C(214)	C(215)	119.0(4)
C(121)	P(1)	C(111)	106.40(19)	C(214)	C(215)	C(216)	120.7(4)
C(121)	P(1)	C(131)	104.77(17)	C(211)	C(216)	C(215)	120.3(4)
C(111)	P(1)	C(131)	102.62(17)	C(226)	C(221)	C(222)	118.8(3)
C(121)	P(1)	Ag(1)	111.49(12)	C(226)	C(221)	P(2)	122.9(3)
C(111)	P(1)	Ag(1)	116.19(12)	C(222)	C(221)	P(2)	118.3(3)
C(131)	P(1)	Ag(1)	114.30(13)	C(223)	C(222)	C(221)	120.2(4)
C(231)	P(2)	C(211)	103.73(17)	C(222)	C(223)	C(224)	120.6(4)
C(231)	P(2)	C(221)	102.71(16)	C(225)	C(224)	C(223)	119.5(4)
C(211)	P(2)	C(221)	104.26(18)	C(224)	C(225)	C(226)	120.4(4)
C(231)	P(2)	Ag(2)	116.98(13)	C(225)	C(226)	C(221)	120.5(3)

Bond Angles (cont.)

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
C(232)	C(231)	C(236)	119.1(3)	C(234)	C(233)	C(232)	120.5(4)
C(232)	C(231)	P(2)	122.4(3)	C(233)	C(234)	C(235)	119.9(4)
C(236)	C(231)	P(2)	118.5(3)	C(236)	C(235)	C(234)	120.2(4)
C(231)	C(232)	C(233)	119.9(4)	C(235)	C(236)	C(231)	120.4(4)

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

Synthetic procedure

A 500 ml 3 neck flask is charged with NaSEt in anhydrous methanol. $InCl_3$ (1.92 g, 10.9 mmol) is rapidly added, resulting in a clear solution (on some occasions small white flocculent ppt is also observed). The mixture is stirred and allowed react for 15-30minutes. A solution, or suspension of anhydrous CuCl (Aldrich) (3.11 g, 3.82 mmol), and PPh_3 (3.11 g, 3.82 mmol), in a mixture of anhydrous CH_3CN/CH_2Cl_2 (3:1 volume ratio), is rapidly added to $Na^+[In(SEt)_4]^-$ formed *in situ*. After 24 hours the reaction is concentrated and the product extracted with pentane (200 mL) and filtered through Celite. Evaporation of the pentane affords the pale yellow liquid-oil precursor. A similar preparative route is used for the preparation of the Ag analogues, but in the absence of light.

Selective NMR and Analysis data

For **1**[$\{PPh_3\}_2Cu(SEt)_2In(SEt)_2$]: ^{1}H NMR: 300 MHz; $CDCl_3$; δ 1.24 ppm (t); δ 2.67 ppm (q); δ 7.33 ppm (m):
Elemental Analysis by Galbraith Labs, Knoxville TN 37921. Calc. for **1** (%), C 55.78, H 5.32; Found (%) C 55.61, H 5.21

For **2** [$\{PPh_3\}_2Cu(SePh)_2In(SePh)_2$]: ^{1}H NMR: 300 MHz; $CDCl_3$; δ 6.89 ppm (s); δ 7.02 ppm (d); δ 7.26 ppm (br d), δ 7.37 ppm (m)
Elemental Analysis by Galbraith Labs, Knoxville TN 37921. Calc. for **3** (%), C 54.30, H 3.80; Found (%) C 54.57, H 3.73

For **3** [$\{PBu_3\}_2Cu(SEt)_2In(SEt)_2$]: ^{1}H NMR: 300 MHz; $CDCl_3$; δ 2.76 ppm (q); δ 1.56 ppm (br m); δ 1.43 ppm (br m) ; δ 1.33 ppm (t); δ 0.94 ppm (t)

For **4** [$\{PPh_3\}_2Cu(SMe)_2In(SMe)_2$]: ^{1}H NMR: 300 MHz; $CDCl_3$; δ 2.12 ppm (s); δ 7.31 ppm (br s);
Elemental Analysis by Galbraith Labs, Knoxville TN 37921. Calc. for **4** (%), C 53.90, H 4.75; Found (%) C 53.73, H 4.53

For **5** [$\{PBu_3\}_2Cu(SePh)_2In(SePh)_2$]: ^{1}H NMR: 300 MHz; $CDCl_3$; δ 0.86 ppm (t); δ 1.32 ppm (br s); δ 7.07 ppm (m), δ 7.50 ppm (br s)

For **6** [$\{PPh_3\}_2Ag(SMe)_2In(SMe)_2$]: ^{1}H NMR: 300 MHz; $CDCl_3$; δ 7.33 ppm (br m); δ 2.12 ppm (s)
Elemental Analysis by Galbraith Labs, Knoxville TN 37921. Elemental Analysis Calc. for **6** (%), C 51.35, H 4.52; Found (%) C 51.62, H 4.59

For **7** [$\{PBu_3\}_2Ag(SEt)_2In(SEt)_2$]: ^{1}H NMR: 300 MHz; $CDCl_3$; δ 0.90 ppm (t); δ 1.30 ppm (t); δ 1.41 ppm (br s); δ1.61 ppm (br s); δ2.74 ppm (q)

Selective EDAX Analysis DATA

EDAX data for SSP **3** to afford $CuInS_2$:

ELEMENT	Wt%	At%	K-Ratio	Z	A	F
S K	25.58	49.12	0.1879	1.1233	0.6447	1.0143
In K	49.06	26.30	0.3958	0.9092	0.8874	1.0000
Cu K	25.36	24.58	0.2404	1.0028	0.9451	1.0000
Total	100.00	100.00				
ELEMENT	**Net Inte.**	**Bkgd Inte.**	**Inte. Error**	**P/B**		
S K	103.78	5.70	0.87	18.20		
In K	69.72	4.56	1.07	15.28		
Cu K	34.65	2.38	1.52	14.58		
Total	100.00	100.00				

EDAX data for SSP **7** to afford $AgIn_5S_8$:

ELEMENT	Wt %	At %*	K-Ratio	Z	A	F
S K	25.60	54.79	0.2063	1.1393	0.6906	1.0245
Ag K	19.31	12.29	0.1558	0.9455	0.8532	1.0000
In K	55.09	32.93	0.4671	0.9264	0.9152	1.0000
Total	100.00	100.00				
ELEMENT	**Net Inte.**	**Bkgd Inte.**	**Inte. Error***	**P/B**		
S K	15.44	1.93	2.85	8		
In K	3.98	2.60	7.62	1.53		
Cu K	11.09	2.93	3.71	3.78		
Total	100.00	100.00				

*overlapping bands hinders exact deciphering At/Wt %.

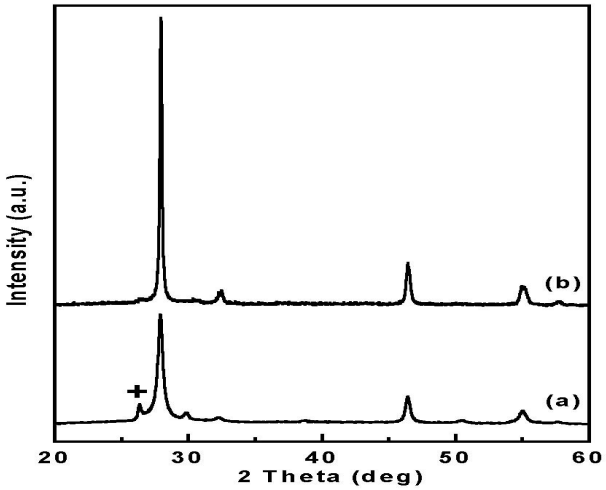
THERMAL DATA: TGA & DSC:

Single Source Precursors **[{L}$_2$Cu(ER)$_2$M(ER)$_2$]**	**TGA**		**DSC**		
	Onset °C	**MRW** ** **°C**	**Residue %**	**M.P. °C**	**Dec. °C**
1 [{PPh_3}$_2$Cu(SEt)$_2$In(SEt)$_2$]	236	269	25	122	266
2 [{PPh_3}$_2$Cu(SePh)$_2$In(SePh)$_2$]	223	253	22	53	219
3 [{$P(Bu^n)_3$}$_2$Cu(SEt)$_2$In(SEt)$_2$]	189	238	27	-	264
4 [{PPh_3}$_2$Cu(SMe)$_2$In(SMe)$_2$]	221	254	27	164	242
5 [{PBu_3}$_2$Cu(SePh)$_2$In(SePh)$_2$]	229	255	26	*	*
6 [{PPh_3}$_2$Ag(SMe)$_2$In(SMe)$_2$]	229	272	29	141	238
7 [{PBu_3}$_2$Ag(SEt)$_2$In(SEt)$_2$]	187	239	30	-	285

*not recorded; **if more then one MRW, then Max value listed

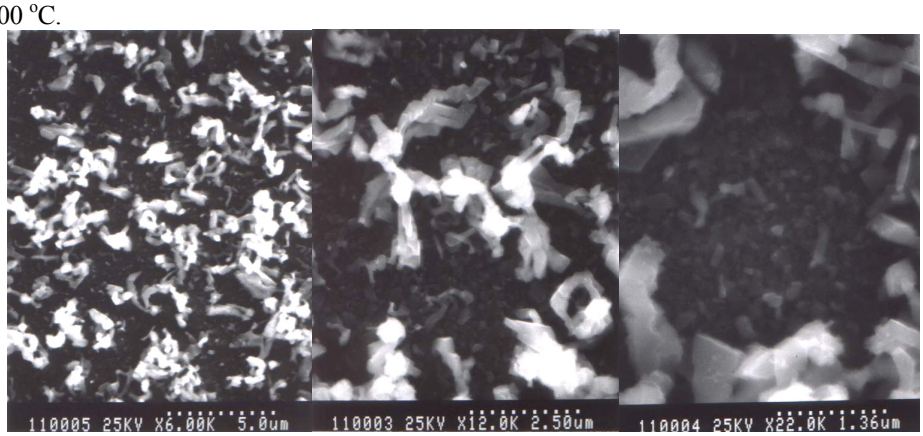
XRD Pattern DATA

XRD DATA of the CuInS2 film grown in the cold-wall reactor at 400 °C. (a) as-grown and (b) after annealing at 600 °C for 10 min under N_2 flow from SSP **3.**



SEM Images for deposited $AgIn_5S_8$ polycrystalline thin films using SSP 7.

Films grown at 400 ^oC.



Films grown at 450 ^oC.