Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supporting Information

Solid solutions of $M_{2-2x}In_{2x}S_3$ (M = Bi or Sb) by Solventless Thermolysis

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Table S1: Composition used for the synthesis of Bi-In-S system.

Composition (x) [In]/[In]+[Bi]	**$In[S_2COEt]_3$ (mmol)**	**$Bi[S_2COEt]_3$ (mmol)**
0	0	0.35
0.2	0.42	1.67
0.4	0.42	0.62
0.6	0.42	0.20
0.8	0.42	0.10
1	0.42	0

Table S2: Composition used for the synthesis of Sb-In-S system.

Composition (x) [In]/[In]+[Sb]	**$In[S_2COEt]_3$ (mmol)**	**$Sb[S_2COEt]_3$ (mmol)**
0	0	0.41
0.2	0.42	1.67
0.4	0.42	0.61
0.6	0.42	0.20
0.8	0.42	0.10
1	0.42	0

Table S3: Yield, melting point and elemental analysis for antimony, bismuth and indium ethylxanthates.

	Precursor	**Colour**	**Yield (%)**	**M.p. (°C)**	**Elemental analysis**			
					Carbon found(cal.)%	**Hydrogen found(cal.)%**	**Sulfur found(cal.)%**	**Metal found(cal.)%**
1	$Sb[S_2COEt]_3$	Yellow	79	90.3	22.6 (22.3)	3.1 (3.1)	39.7 (39.6)	24.2 (25.1)
2	$Bi[S_2COEt]_3$	Dark-yellow	80	110	19.1 (18.9)	2.7 (2.6)	33.5 (33.5)	36.5 (36.5)
3	$In[S_2COEt]_3$	White	92	135[a]	23.1 (22.6)	3.2 (3.2)	40.3 (40.2)	23.2 (23.9)

[a] with decomposition.

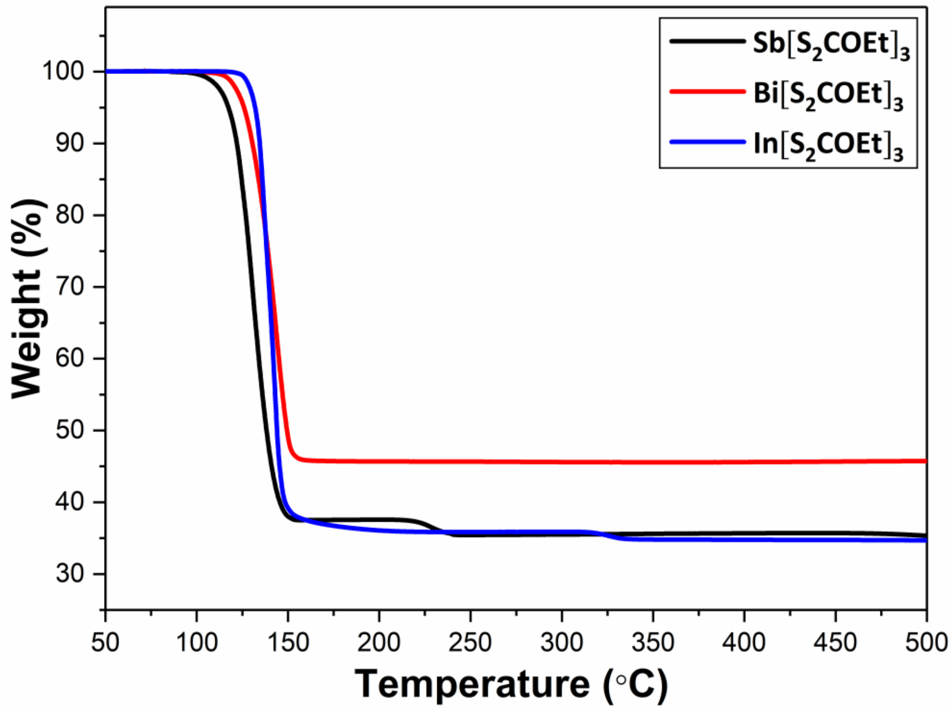

Figure S1: TGA curves of antimony, bismuth and indium ethylxanthates

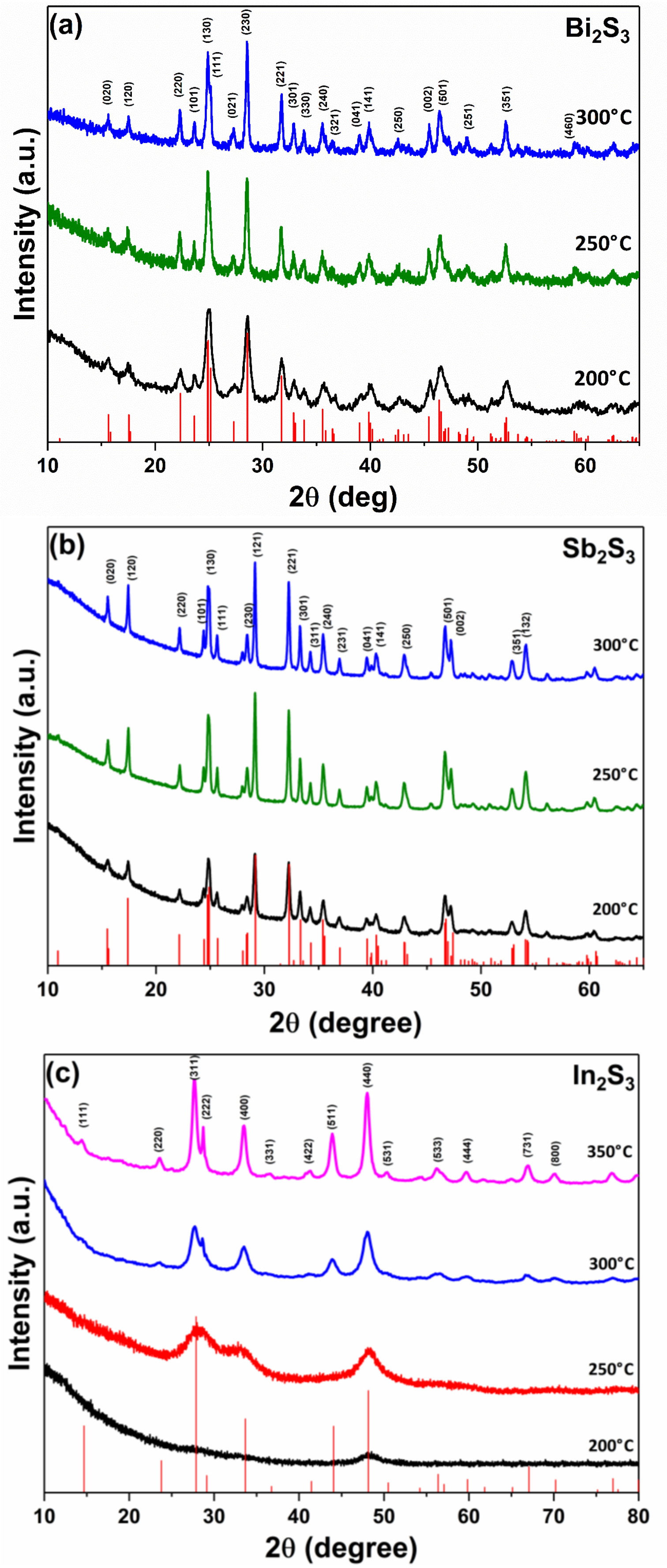

Figure S2: XRD patterns of (a) Sb_2S_3 from $Sb[S_2COEt]_3$, (b) Bi_2S_3 from $Bi[S_2COEt]_3$ and (c) In_2S_3 from $In[S_2COEt]_3$ at different temperatures for one hour.

Table S4: The Rietveld analysis of the XRD patterns for the $Bi_{2(1-x)}In_{2x}S_3$ ($0 \le x \le 1$) samples.

$Bi_{2(1-x)}In_{2x}S_3$	Phase	SG	weight (%)	a (Å)	b (Å)	c (Å)
x = 0.2	Orthorhombic Bi_2S_3	Pbnm	78(2)	11.08±0.005	11.27±0.004	3.95±0.001
	Cubic In_2S_3	Fd-3m:2	22(2)	10.79±0.003		
x = 0.4	Orthorhombic Bi_2S_3	Pbnm	69(5)	11.09±0.008	11.30±0.007	3.95±0.002
	Cubic In_2S_3	Fd-3m:2	31(5)	10.78±0.014		
x = 0.6	Orthorhombic Bi_2S_3	Pbnm	36(4)	11.02±0.017	11.28±0.015	3.99±0.006
	Cubic In_2S_3	Fd-3m:2	64(4)	10.72±0.006		
x = 0.8	Orthorhombic Bi_2S_3	Pbnm	11(2)	11.07±0.016	11.32±0.016	3.99±0.005
	Cubic In_2S_3	Fd-3m:2	89(2)	10.73±0.006		

Table S5: The Rietveld analysis of the XRD patterns for the $Sb_{2(1-x)}In_{2x}S_3$ ($0 \le x \le 1$) samples.

$Sb_{2(1-x)}In_{2x}S_3$	Phase	SG	weight (%)	a (Å)	b (Å)	c (Å)
x = 0.2	Orthorhombic Sb_2S_3	Pbnm	84(2)	11.28±0.002	11.17±0.002	3.82±0.001
	Cubic In_2S_3	Fd-3m:2	16(2)	10.69±0.014		
x = 0.4	Orthorhombic Sb_2S_3	Pbnm	60(5)	11.32±0.003	11.19±0.003	3.83±0.001
	Cubic In_2S_3	Fd-3m:2	40(5)	10.75±0.006		
x = 0.6	Orthorhombic Sb_2S_3	Pbnm	27(7)	11.21±0.010	11.34±0.013	4.02±0.003
	Cubic In_2S_3	Fd-3m:2	73(7)	10.81±0.006		
x = 0.8	Orthorhombic Sb_2S_3	Pbnm	22(4)	11.19±0.012	11.37±0.012	3.97±0.003
	Cubic In_2S_3	Fd-3m:2	78(4)	10.74±0.006		

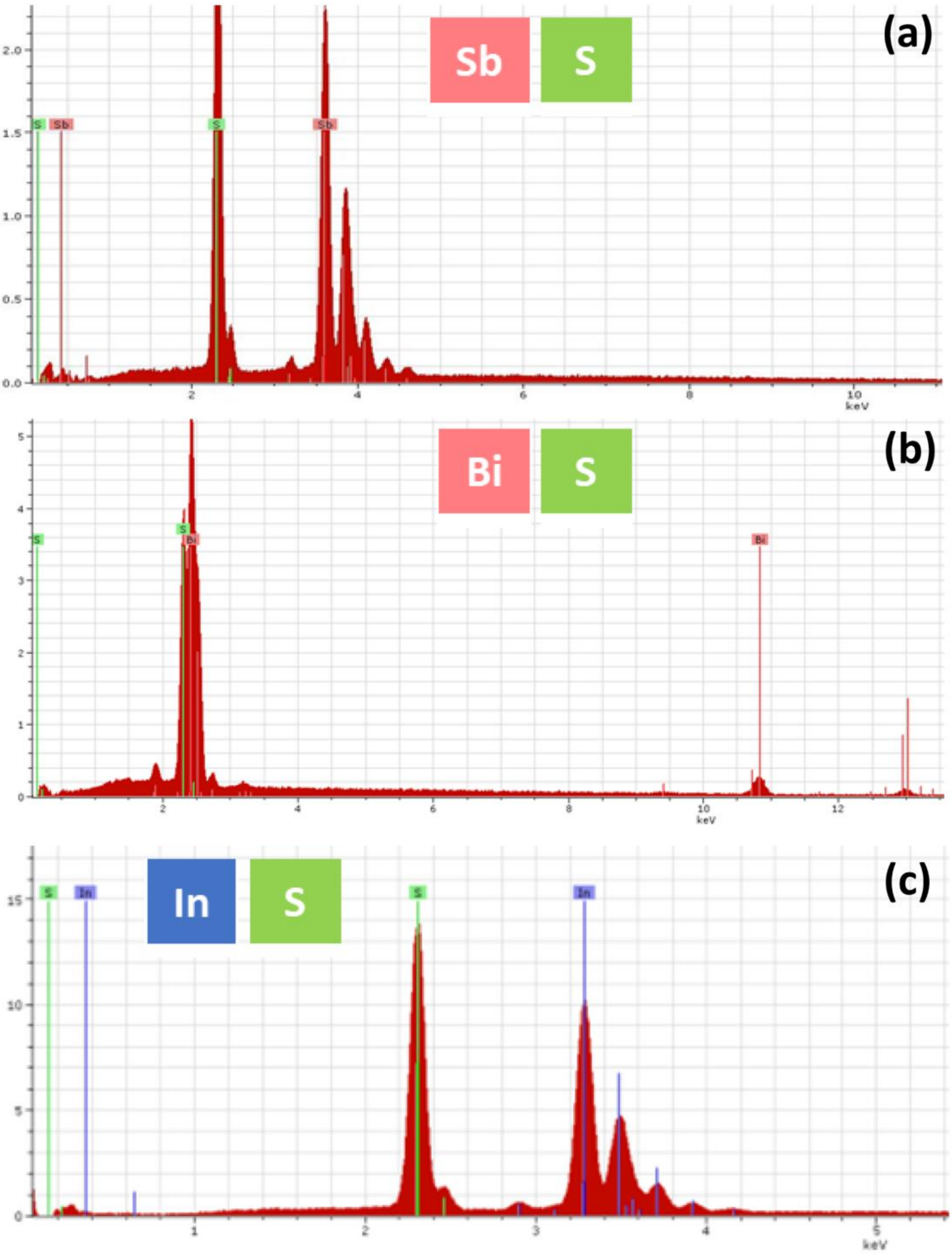

Figure S3: EDX spectra of (a) Sb_2S_3, (b) Bi_2S_3 and (c) In_2S_3.

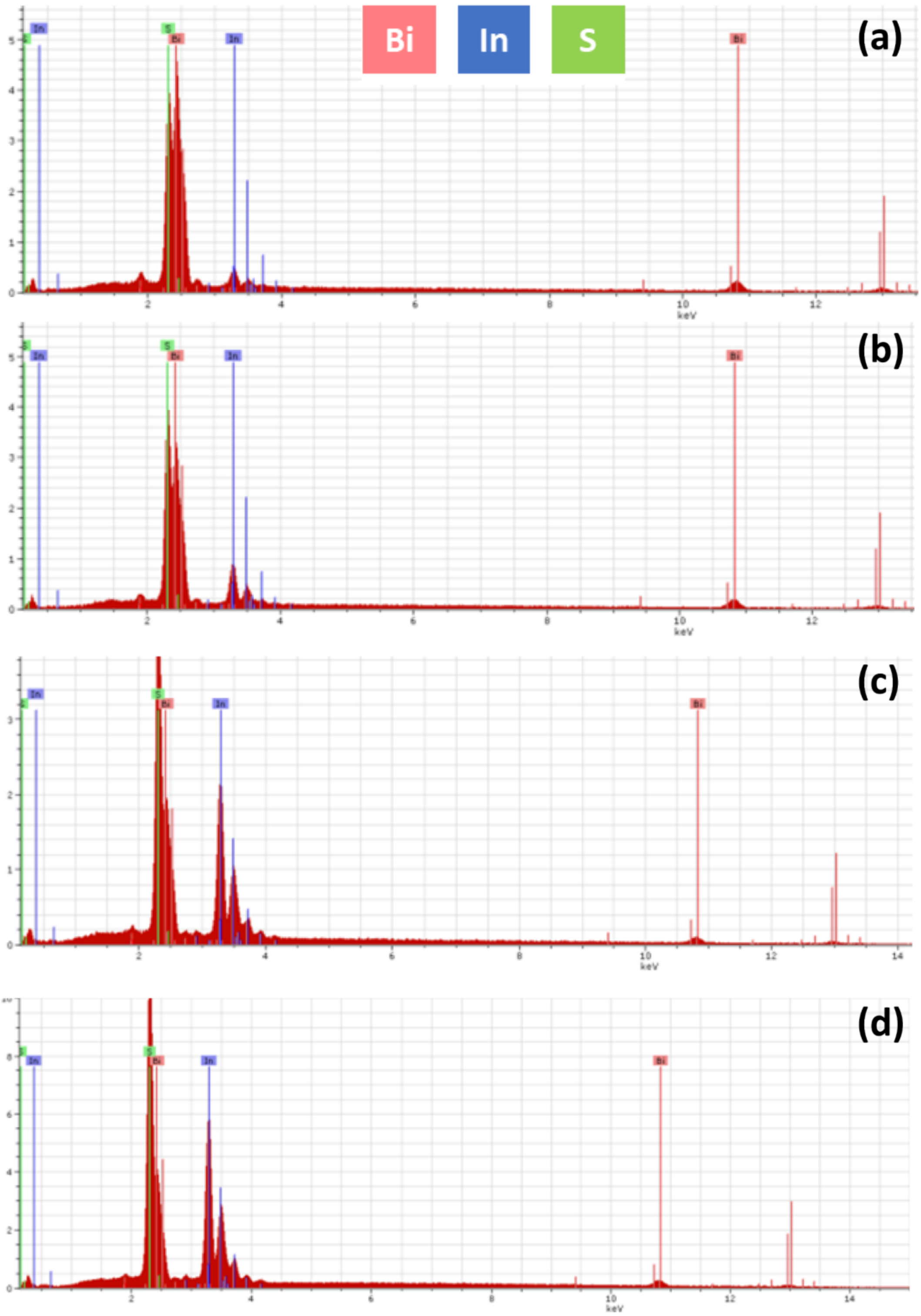

Figure S4: EDX spectra of $Bi_{2(1-x)}In_{2x}S_3$ samples at various indium mole fraction: (a) x = 0.2, (b) x = 0.4, (c) x = 0.6 and (d) x = 0.8.

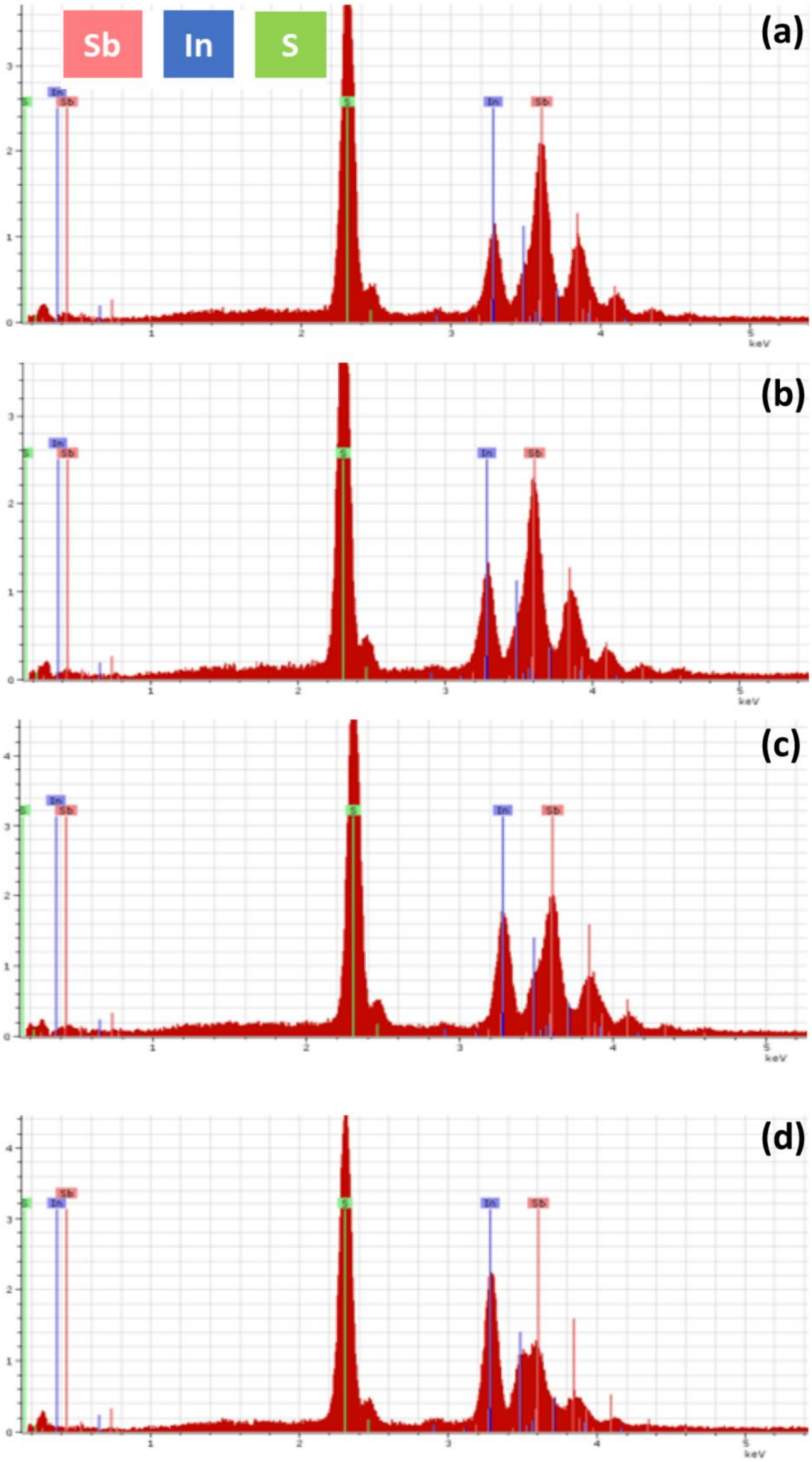

Figure S5: EDX spectra of $Sb_{2(1-x)}In_{2x}S_3$ samples at various indium mole fraction: (a) x = 0.2, (b) x = 0.4, (c) x = 0.6 and (d) x = 0.8.

Table S6: Composition of $Bi_{2(1-x)}In_{2x}S_3$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1 mole fraction of indium) calculated from the elements in the feed and analysis of final products by EDX spectroscopy.

x	Elemental composition required (atomic%)			Stoichiometry required	Elemental composition by EDX (atomic%)			Stoichiometry by EDX
	Bi	**In**	**S**		**Bi**	**In**	**S**	
0	40	0	60	Bi_2S_3	40.7±2.0	0	59.3±2.96	$Bi_{2.03}S_{2.96}$
0.2	32	8	60	$Bi_{1.6}In_{0.4}S_3$	33.6±1.7	8.3±0.4	58.1±2.90	$Bi_{1.6}In_{0.4}S_{2.9}$
0.4	24	16	60	$Bi_{1.2}In_{0.8}S_3$	25.6±1.3	17.1±0.8	57.3±2.86	$Bi_{1.2}In_{0.8}S_{2.9}$
0.6	16	24	60	$Bi_{0.8}In_{1.2}S_3$	16.4±0.8	26.8±1.3	56.8±2.84	$Bi_{0.8}In_{1.3}S_{2.8}$
0.8	8	32	60	$Bi_{0.4}In_{1.6}S_3$	9.6±0.5	32.4±1.6	58.1±2.90	$Bi_{0.4}In_{1.6}S_{2.9}$
1	0	40	60	In_2S_3	0	40.3±2.0	59.7±2.98	$In_{2.02}S_{2.98}$

Table S7: The content of Sb, In and S in $Sb_{2(1-x)}In_{2x}S_3$ (x = 0, 0.2, 0.4, 0.6, 0.8, 1 mole fraction of indium) calculated from the elements in the feed and analysis of final products by EDX spectroscopy.

x	Elemental composition required (atomic%)			Stoichiometry required	Elemental composition by EDX (atomic%)			Stoichiometry by EDX
	Sb	**In**	**S**		**Sb**	**In**	**S**	
0	40	0	60	Sb_2S_3	40.6±2.0	0	59.4±2.97	$Sb_{2.03}S_{2.97}$
0.2	32	8	60	$Sb_{1.6}In_{0.4}S_3$	33±1.6	8±0.4	59±2.95	$Sb_{1.6}In_{0.4}S_{2.98}$
0.4	24	16	60	$Sb_{1.2}In_{0.8}S_3$	24.1±1.2	16.2±0.8	59.7±2.98	$Sb_{1.2}In_{0.8}S_{2.98}$
0.6	16	24	60	$Sb_{0.8}In_{1.2}S_3$	15.9+0.8	23.8±1.2	60.3±3.01	$Sb_{0.8}In_{1.2}S_3$
0.8	8	32	60	$Sb_{0.4}In_{1.6}S_3$	8.5±0.4	31.9±1.6	59.6±2.98	$Sb_{0.4}In_{1.6}S_{2.98}$
1	0	40	60	In_2S_3	0	40.3±2.0	59.7	$In_{2.02}S_{2.98}$

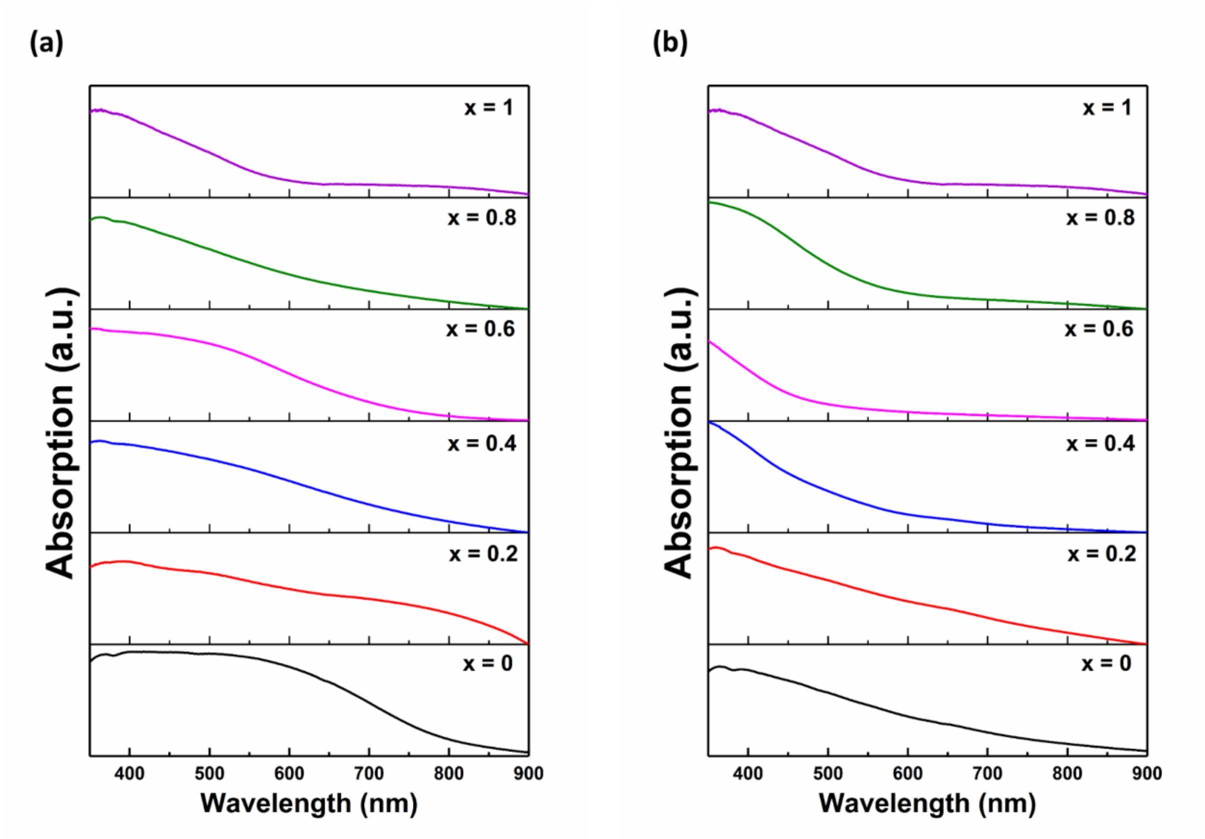

Figure S6: Absorption spectra of (a) $Bi_{2-2x}In_{2x}S_3$ ($0 \leq x \leq 1$) and (b) $Sb_{2-2x}In_{2x}S_3$ ($0 \leq x \leq 1$).

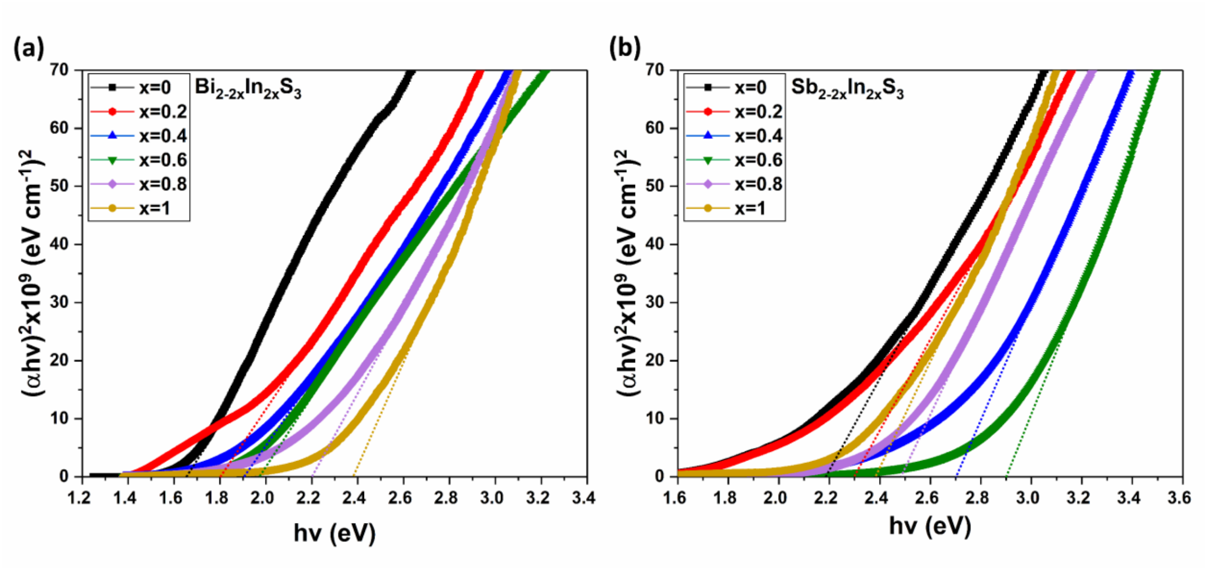

Figure S7: Tauc plots for (a) $Bi_{2-2x}In_{2x}S_3$ and (b) $Sb_{2-2x}In_{2x}S_3$ ($0 \leq x \leq 1$).