

**Table S(1a):** Lattice and Refinement Parameter of Sb<sub>2</sub>S<sub>3</sub> from Sb(xanthate)<sub>3</sub> precursors

Precursor	Method	Time/temp. (°C)	<i>a</i>	<i>b</i>	<i>c</i>	Vol (nm <sup>3</sup> )	Av. cryst. size (nm)
Sb(S <sub>2</sub> COPr <sup>n</sup> ) <sub>3</sub>	solvothermal treatment	5 min / 197	11.3083 (16)	3.8429 (5)	11.2314 (17)	487.4 (1)	269
		30 min / 197	11.3077 (11)	3.8361 (3)	11.2270 (11)	487.0 (1)	625
		2 h / 197	11.3090 (11)	3.8370 (3)	11.2273 (11)	487.2 (1)	435
	hydrothermal treatment	2 h / 160	11.3271 (180)	3.8429 (42)	11.2459 (169)	489.5 (12)	27
		2 h / 200	11.3064 (17)	3.8369 (4)	11.2312 (16)	487.2 (1)	128
		36 h / 200	11.3093 (26)	3.8395 (7)	11.2364 (26)	487.9 (2)	85
Sb(S <sub>2</sub> COBu <sup>i</sup> ) <sub>3</sub>	solvothermal treatment	5 min / 197	11.3083 (18)	3.8391 (5)	11.2295 (18)	487.5 (1)	192
		30 min / 197	11.3084 (10)	3.8379 (3)	11.2302 (11)	487.4 (1)	448
		2 h / 197	11.3084 (15)	3.8379 (4)	11.2294 (15)	487.4 (1)	197
	hydrothermal treatment	2 h / 160 <sup>b</sup>	-	-	-	-	-
		2 h / 200	11.3089 (23)	3.8364 (6)	11.2314 (24)	487.3 (2)	113
		36 h / 200	11.3078 (19)	3.8364 (5)	11.2298 (19)	487.2 (1)	141

**Table S(1b):** Lattice and Refinement Parameter of Sb<sub>2</sub>S<sub>3</sub> from Sb(dithiocarbamate)<sub>3</sub> precursors

Precursor	Method	Time/temp. (°C)	<i>a</i>	<i>b</i>	<i>c</i>	Vol (nm <sup>3</sup> )	Av. cryst. size (nm)
Sb(S <sub>2</sub> CNEt <sub>2</sub> ) <sub>3</sub>	solvothermal treatment	5 min / 197	11.3071 (14)	3.8373 (4)	11.2266 (15)	487.1 (1)	410
		30 min / 197	11.3088 (14)	3.8370 (4)	11.2277 (15)	487.2 (1)	275
		2 h / 197	11.3050 (21)	3.8357 (6)	11.2197 (21)	486.5 (1)	226
	hydrothermal treatment	2 h / 160 <sup>a</sup>	11.30 (1)	3.835 (3)	11.227 (12)	486 (1)	27
		2 h / 200	11.3195 (30)	3.8386 (8)	11.2363 (29)	488.2 (2)	58
		36 h / 200	11.3198 (38)	3.8411 (10)	11.2422 (40)	488.8 (3)	55
Sb[S <sub>2</sub> CN(CH <sub>2</sub> ) <sub>5</sub> ] <sub>3</sub>	solvothermal treatment	5 min / 197	11.3150 (42)	3.8380 (10)	11.2347 (41)	487.9 (3)	51
		30 min / 197	11.3076 (23)	3.8367 (6)	11.2270 (24)	487.1 (2)	62
		2 h / 197	11.3096 (15)	3.8371 (4)	11.2283 (15)	487.2 (1)	108
	hydrothermal treatment	2 h / 160	11.3055 (52)	3.8318 (14)	11.2128 (55)	487.7 (4)	49
		2 h / 200	11.3098 (24)	3.8372 (6)	11.2286 (24)	487.3 (4)	68
		36 h / 200	11.3135 (22)	3.8378 (6)	11.2302 (22)	487.6 (1)	83
Sb(S <sub>2</sub> CNMeCy) <sub>3</sub>	solvothermal treatment	5 min / 197	11.3139 (19)	3.8386 (5)	11.2317 (20)	487.8 (1)	100
		30 min / 197	11.3153 (20)	3.8390 (7)	11.2321 (3)	487.9 (1)	104
		2 h / 197	11.3086 (27)	3.8377 (7)	11.2274 (28)	487.3 (2)	123
	hydrothermal treatment	2 h / 160 <sup>b</sup>	-	-	-	-	-
		2 h / 200	11.3102 (22)	3.8372 (6)	11.2303 (23)	487.4 (2)	76
		36 h / 200	11.3126 (20)	3.8379 (5)	11.2290 (19)	487.5 (1)	94

**Table S(1c):** Lattice and Refinement Parameter of Sb<sub>2</sub>S<sub>3</sub> from Sb(dithiophosphate)<sub>3</sub> precursors

Precursor	Method	Time/temp. (°C)	<i>a</i>	<i>b</i>	<i>c</i>	Vol (nm <sup>3</sup> )	Av. cryst. size (nm)
Sb[S <sub>2</sub> P(OEt) <sub>2</sub> ] <sub>3</sub>	solvothermal treatment	5 min / 197	11.3039 (22)	3.8370 (6)	11.2295 (23)	487.1 (2)	169
		30 min / 197	11.3117 (12)	3.8385 (3)	11.2314 (11)	487.6 (1)	405
		2 h / 197	11.3104 (17)	3.8403 (5)	11.2409 (17)	488.3 (1)	179
	hydrothermal treatment	2 h / 160 <sup>b</sup>	-	-	-	-	-
		2 h / 200	11.3104 (23)	3.8400 (6)	11.2352 (23)	488.0 (2)	98
		36 h / 200	11.3054 (19)	3.8378 (5)	11.2271 (20)	487.1 (1)	132
Sb[S <sub>2</sub> P(O <sup>i</sup> Bu) <sub>2</sub> ] <sub>3</sub>	solvothermal treatment	5 min / 197	11.3068 (18)	3.8379 (5)	11.2341 (18)	487.5 (1)	250
		30 min / 197	11.3073 (12)	3.8368 (3)	11.2292 (12)	487.2 (1)	634
		2 h / 197	11.3047 (15)	3.8370 (4)	11.2279 (15)	487.0 (1)	335
	hydrothermal treatment	2 h / 160 <sup>b</sup>	-	-	-	-	-
		2 h / 200	11.3157 (32)	3.8384 (8)	11.2403 (32)	488.2 (2)	94
		36 h / 200	11.3104 (21)	3.8379 (6)	11.2336 (22)	487.6 (2)	101

<sup>a</sup> Peak broadening lead to large errors and the average crystal size is not certain; <sup>b</sup> No peaks were found in the diffractogram

Figure S(1a) TGA of  $\text{Sb}(\text{S}_2\text{COEt})_3$

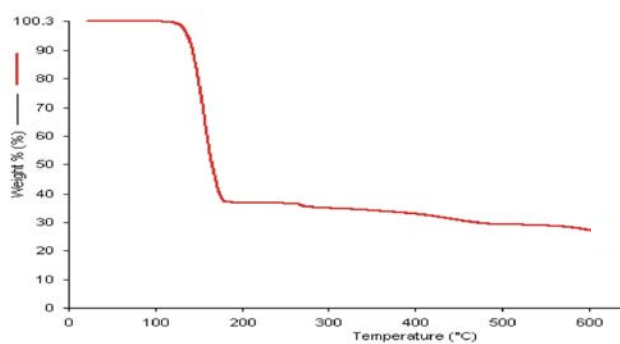


Figure S(1b) TGA of  $\text{Sb}(\text{S}_2\text{COPr}^i)_3$

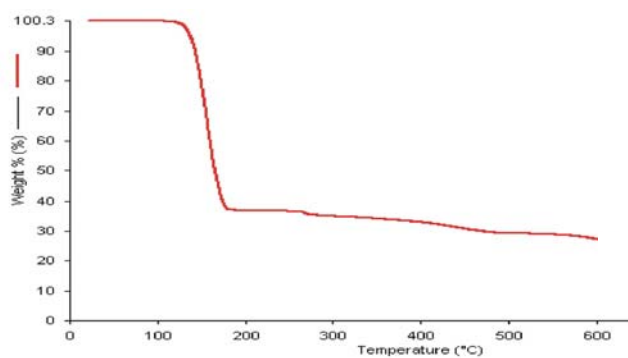


Figure S(2a) EDAX qualitative analysis of film grown from (2) at 200 °C.

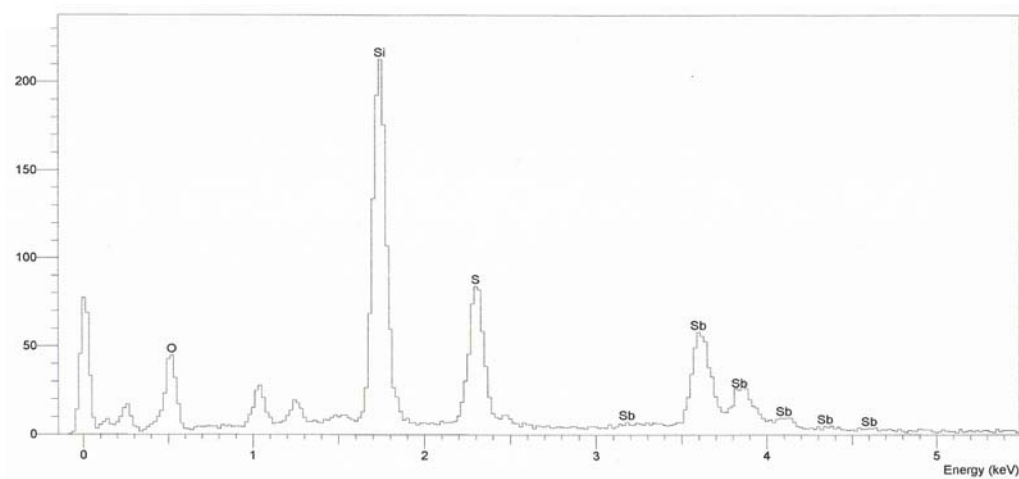


Figure S(2b) EDAX qualitative analysis of film grown from (3) at 240 °C on glass slides.

