Bis(triphenyltin) Chalcogenides as Convenient Precursors to Phase-Pure Binary Semiconductors[1]

Philip Boudjouk,* Dean J. Seidler, Steven R. Bahr, and Gregory J. McCarthy

Department of Chemistry, North Dakota State University, Fargo, North Dakota 58105

Received May 19, 1994. Revised Manuscript Received August 12, 1994[⊗]

Bis(triphenyltin) chalcogenides, $(Ph_3Sn)_2X$ (X = S, Se, and Te), were synthesized in good yield from Ph_3SnCl and anhydrous Na_2X made from elemental Na and X with a catalytic amount of naphthalene in THF. When heated to relatively modest temperatures (above 300 °C) under an inert atmosphere, it is observed that these compounds undergo a series of phenyl migrations in the condensed (liquid) state. This pyrolysis results in the loss of tetraphenyltin and diphenylchalcogen as "volatile" byproducts while leaving behind an inorganic powder. These powders are characterized by X-ray diffraction and found to be phase pure and highly crystalline SnS, SnSe, or SnTe. Combustion analysis detects less than 1% carbon contamination after rinsing with common solvents. Scanning electron micrographs show the powders to be polycrystalline agglomerates having platy (SnS and SnSe) or cubooctahedral (SnTe) habits.

Introduction

The orthorhombic group 14–16 compounds tin sulfide (SnS) and tin selenide (SnSe) are classified as narrow-bandgap (1.3 and 1 eV, respectively)[2] semiconductors and therefore have the potential to serve as efficient materials in photovoltaic applications.[3] SnS is especially favorable due to its high conversion efficiency in photovoltaic devices (~25%).[4] It also possesses favorable properties with respect to cost, availability, toxicity, and stability. SnTe is also a narrow-bandgap semiconductor (0.33 eV) and has received attention for use in infrared detectors.[5] The most common method used for the bulk preparation of group 14–16 semiconductor materials is by repeated mixing and heating of the elements in appropriate amounts in an evacuated and sealed quartz ampule, graphite crucible, or porcelain tube.[6] Typically, the temperatures for these reactions are in the region 900–1000 °C.[7] At such high temperatures the inside surfaces of the reaction vessel can serve as a source of water and oxygen contamination. In the synthesis of sulfides, explosions of the ampules have been observed in the 800–1000 °C region caused by the formation of volatile compounds such as elemental sulfur, SO_2, SO_3, and H_2S.[8]

An alternate route to these materials involves organometallic chemical vapor deposition (OMCVD) which has been used extensively for many types of semiconductor materials.[9] However, we found only one report describing the preparation of tin and lead chalcogenides using OMCVD in which tetraalkyl group 14 compounds and H_2S, H_2Se, or Me_2Te were combined in a OMCVD reactor at 625 °C producing tin and lead chalcogenide thin films.[10] The disadvantages of using this technique include the high volatility and toxicity associated with the starting materials and a tedious purification process. Effective mixing of the compounds in the gas phase is also difficult to ensure.

An approach to alleviating these disadvantages involves the use of single-source precursors in which elements desired in the semiconductor are incorporated in one molecule. Typically this tact leads to molecules with higher molecular weights and lower vapor pressures resulting in safer handling. Liquids and solids are the desired forms of these materials allowing conventional manipulation procedures of fairly large quantities in a drybox or glovebag. The ease with which these compounds can be weighed, transferred, and mixed eliminates the need for elaborate vacuum line setups and sophisticated valving systems.

Recently we reported that group 14–16 six-membered ring systems of the general formula $(Ph_2SnX)_3$ (X = S and Se) serve as convenient single-source precursors to microcrystalline powders of SnS and SnSe under very mild conditions.[11] These powders exhibit excellent crystallinity and very low carbon content. The aryl containing byproducts from the pyrolysis have relatively low vapor pressures and are solids and liquids at ambient conditions resulting in relatively easy handling.

Here we report on our continuing investigation of organometallic compounds containing aryl groups to

---

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1994.

[1] Seidler, D. J.; Boudjouk, P.; Bahr, S. R.; McCarthy, G. J. *206th National Meeting of the American Chemical Society,* Chicago, IL, Aug 22–27, 1993; Abstract, INOR 166.

[2] Bube, R. H. *Photoconductivity of Solids;* Wiley & Sons: New York, 1960.

[3] (a) Singh, J. P.; Bedi, R. K. *Thin Solid Films* **1991,** *199,* 9. (b) Nair, M. T. S.; Nair, P. K. *Semicond. Sci. Technol.* **1991,** *6,* 132. (c) Rodot, M. *Acta Electron* **1975,** *18,* 345. (d) Rodot, M. *Rev. Phys. Appl.* **1977,** *12,* 411.

[4] (a) Prince, M. B. *J. Appl. Phys.* **1955,** *26,* 534. (b) Loferski, J. J. *Appl. Phys.* **1956,** *27,* 777.

[5] (a) George, J.; Palson, T. I. *Thin Solid Films,* **1985,** *127,* 233 and references therein.

[6] Blitz, W., Mecklenburg, W. *Z. Anorg. Allg. Chem.* **1909,** *64,* 226.

[7] Abrikosov, N. K.; Bankina, V. F.; Poretskaya, L. V.; Shelimova, L. E. *Semiconducting II-VI, IV-VI, and V-VI Compounds;* Plenum: New York, 1969.

[8] Kazenkov, B. A. *Growth of Crystals;* Consultants Bureau: New York, 1966; Vol. 4.

[9] Ghandhi, S. K.; Bhat, I. B. *MRS Bull.* **1988,** *13,* 37.

[10] Manasevit, H. M.; Simpson, W. I. *J. Electrochem. Soc.* **1975,** *122,* 444.

[11] Boudjouk, P.; Bahr, S. R.; McCarthy, G. J. *Chem. Mater.* **1992,** *4,* 383.

0897-4756/94/2806-2108$04.50/0

produce semiconducting binary compounds via condensed-phase pyrolysis. We present the results of our study of the pyrolyses of linear analogues to the cyclics mentioned above, $(Ph_3Sn)_2X$, where X = S, Sn, and Te. A mechanism for the rearrangement of these acyclic compounds involving species containing tin–chalcogen double bonds, $Ph_2Sn{=}X$, leading to cyclic species en route to the binary compounds, SnS, SnSe, and SnTe, is proposed. We also describe new anhydrous routes to bis(triphenyltin) sulfide, bis(triphenyltin) selenide, and bis(triphenyltin) telluride. The ease of synthesis and high yields of bis(triphenyltin) telluride make this linear compound a very convenient precursor to polycrystalline SnTe.

Experimental Section

General Procedures. Triphenyltin chloride was purchased from Gelest, Inc. All other reagents were purchased from Aldrich and used without further purification. Selenium and organotin compounds are highly toxic. Tellurium and its compounds are poisonous. These substances may be harmful by inhalation, ingestion, or skin absorption. Thus protective clothing and gloves should be worn when handling them. All reactions and manipulations were carried out in a fume hood or drybox. The sodium chalcogenides were prepared from the elemental chalcogen powders, sodium chips cut from spheres, and a catalytic amount of naphthalene.[12,13] All reactions were run under a dry nitrogen atmosphere in THF that was freshly distilled from sodium/benzophenone ketyl under a dry nitrogen atmosphere just prior to its use. Bis(triphenyltin) sulfide and selenide are air and moisture stable. They can be worked up in water and handled in the open air after the reaction with triphenyltin chloride is complete. Bis(triphenyltin) telluride must be kept free of moisture and oxygen. Tellurium powder was transferred in an argon-filled glovebox. Benzene was stirred over concentrated H_2SO_4 and distilled from CaH_2. The first 10% fraction was discarded. The remainder was collected and stored over 3 Å molecular sieves. When preparing slurries of tellurium, the benzene was deoxygenated by bubbling with dry nitrogen for 15 min prior to use. In the preparation of samples that contained tellurium for NMR studies, oxygen was removed from the $CDCl_3$ in a similar fashion. Hexane was stirred over concentrated H_2SO_4 for at least 10 h and stored over molecular sieves after distillation under a dry nitrogen atmosphere.

High temperature pyrolyses were carried out using a Lindberg Model 55035 programmable tube furnace, 36 cm long and 3 cm in diameter with a 55 × 2.5 cm Vycor silica glass tube placed inside. One end of the tube was fitted with a one-holed rubber stopper connected to a dry nitrogen or helium source. The exit of the furnace was fitted with a single-holed Teflon stopper that led into a liquid nitrogen trap and then into a mineral oil bubbler to monitor the flow of nitrogen through the system. The flow was set to approximately 50 mL/min, and the tube was purged at this rate for at least 15 min prior to the introduction of the sample. The sample to be pyrolyzed was placed in a Coors porcelain boat which had been dried in an oven at 110 °C and cooled to room temperature in a desiccator. The filled crucible was placed in the tube at the center of the furnace. For all samples, the oven was programmed to ramp at a rate of 10 °C/min to 125 °C and hold this temperature for 15 min to remove any moisture that may be in the system. Following this delay, the temperature was then ramped at a rate of 4 °C/min to 450 °C and held for 2 h before allowing the oven to cool to room temperature. In all cases decomposition of the organometallic species began around 330 °C, as indicated by the condensation of volatile byproducts at the exit side of the tube. Due to their hazardous nature, the volatile byproducts were handled in a fume hood while wearing protective clothing.

Low-temperature pyrolysis experiments were carried out in glass tubes (0.75 cm × 20 cm) which were sealed at one end and flame dried under a constant flow of nitrogen. The tube was charged with 800 mg of the bis(triphenyltin) chalcogen and sealed with a septum. The end of the tube was then placed in a 340 °C oil bath until a black precipitate began to form. The tube was cooled and the contents dissolved in $CDCl_3$ for NMR analysis.

All NMR spectra were obtained on a JEOL GSX400 spectrometer at the following frequencies: ^{119}Sn (148.99 MHz) and ^{125}Te (125.89 MHz). A 5-mm broad-band probe equipped with a variable-temperature accessory maintained the temperature at 25 ± 0.5 °C. Samples were prepared in $CDCl_3$ in concentrations ranging from 0.05 to 0.25 M. ^{119}Sn shifts are relative to Me_4Sn in $CDCl_3$ (0 ppm). All ^{125}Te shifts are relative to Me_2Te in $CDCl_3$ (0 ppm). The ^{125}Te spectra were obtained using a pulse width of 15 μs, a pulse delay of 0.01 s and an acquisition time of 0.786 s. To obtain acceptable signal to noise, $(5-90) \times 10^3$ transients were required, depending upon sample concentration. Gas chromatographic analyses were carried out on a Hewlett-Packard 5880A Series GC equipped with a cross-linked methylsilicone capillary column and a FID detector. Melting points were taken on a Thomas-Hoover capillary melting point apparatus and are uncorrected. Combustion analyses to determine the amount of residual carbon remaining in the samples were performed by Galbraith Laboratories, Knoxville, TN.

Scanning electron microscopy (SEM) was performed on a JEOL JSM 35 instrument. The SEM samples were sputtered with Au to reduce charging effects. X-ray powder diffraction (XRD) patterns were recorded from ethanol slurry mounted samples on quartz zero background slides using a Philips automated diffractometer with Cu Kα radiation and data reduction software from MDI, Inc. Unit cell parameters were determined by a least-squares procedure. NIST SRM 640b silicon internal standard was used to ensure the accuracy of the cell parameters.

Synthesis of $(Ph_3Sn)_2S$ (1). A 250 mL three-neck round bottom flask, fitted with a condenser, a nitrogen inlet, and a 125 mL addition funnel, was charged with sodium chips (1.8 g, 78 mmol), sulfur powder (1.2 g, 37 mmol), naphthalene (1.0 g, 7.8 mmol), and 50 mL of THF. The reaction mixture was stirred and heated for 10 h producing a light yellow suspension of Na_2S. No sodium chips remained in the flask. The suspension was allowed to cool to room temperature. A THF solution of Ph_3SnCl (30.0 g, 77.9 mmol in 60 mL of THF) was added over 30 min. The light yellow suspension turned brown after several hours of stirring at room temperature. After an additional 10 h of stirring, this suspension was poured into 100 mL of water followed by extraction with five 50 mL portions of ether. The ether fractions were combined and dried over $MgSO_4$, and the solvent was removed on a rotary evaporator to give a waxy yellow solid. The solid was rinsed with hexane, dissolved in benzene, and filtered to yield a clear yellow solution. Recrystallization from benzene/hexane gave 25 g (88% yield) of white crystals of $(Ph_3Sn)_2S$ (**1**): mp 143–145 °C (lit.[14] 144.0–144.5 °C). ^{119}Sn NMR ($CDCl_3$): −52.1 ppm (lit.[15] −53.7 ppm).

Synthesis of $(Ph_3Sn)_2Se$ (2). A 250 mL three-neck flask, fitted with a condenser, a nitrogen inlet, and a 125 mL addition funnel, was charged with sodium chips (1.2 g, 52 mmol), selenium powder (2.1 g, 27 mmol), naphthalene (0.66 g, 5.1 mmol), and 50 mL of THF. The reaction mixture was stirred and heated for 10 h after which time there was observed a white suspension of Na_2Se. No remaining sodium was detected. The suspension was allowed to cool to room temperature. A solution of Ph_3SnCl (20.0 g, 51.9 mmol in 40 mL THF) was added at room temperature over 30 min. The white suspension turned to a light brown after several hours of

---

[12] So, J. H.; Boudjouk, P. In *Inorganic Syntheses*; Grimes, R. N., Ed.; Wiley-Interscience: New York, 1992; Vol. 29, p 30.

[13] Thompson, D. P.; Boudjouk, P. *J. Org. Chem.* **1988**, *53*, 2109.

[14] Davies, A. G.; Smith, P. J. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, England, 1982; Vol. 2, Chapter 11.

[15] Wrackmeyer, B. *Annu. Rep. NMR Spectrosc.* **1985**, *16*, 73.

stirring at room temperature. The suspension darkened as the reaction was allowed to stir for an additional 10 h. The product was worked-up in the same fashion as in the synthesis of compound **1** to give 15 g (74% yield) of $(Ph_3Sn)_2Se$ (**2**): mp 147–149 °C (lit.[14] 148.5 °C). ^{119}Sn NMR ($CDCl_3$): −77.2 ppm (lit.[15] −78.5 ppm).

Synthesis of $(Ph_3Sn)_2Te$ (3). A dry 100 mL three-neck round-bottom flask, fitted with a condenser, a nitrogen inlet, and a 125 mL addition funnel, was purged with nitrogen and charged with sodium chips (0.668 g, 29.0 mmol), tellurium powder (1.86 g, 14.6 mmol), naphthalene (0.37 g, 2.9 mmol), and 30 mL of THF. To ensure complete consumption of sodium metal, the mixture was refluxed for at least 10 h producing a light gray suspension of Na_2Te. (If the reaction mixture remains black after this time, a small amount of additional sodium may be added until the endpoint is obtained. If a dark green color persists, small amounts of tellurium added at 1 h intervals will eventually yield the desired light gray color.) A solution of Ph_3SnCl (11.2 g, 29.1 mmol) in 60 mL of THF was transferred by syringe to the addition funnel and added dropwise to the Na_2Te suspension over 30 min at room temperature. After stirring for an additional 2 h, the contents were refluxed for 12 h producing a light brown mixture. The THF was removed under reduced pressure using a vacuum pump. Pressure was equalized with nitrogen to avoid oxidation and 50 mL of benzene was added to the solid that remained. After stirring for 2 h, the slurry was transferred by syringe to a fritted separatory funnel fitted with a nitrogen outlet and a 250 mL collection flask. The entire apparatus had been dried and purged with nitrogen. An additional 50 mL of benzene was added to the reaction flask to aid the transfer. A positive nitrogen pressure was used to push the solution through the fritted funnel. A yellow transparent solution was collected. Crystallization from benzene/hexane gave 7.5 g (62% yield) of large silver-white crystals of $(Ph_3Sn)_2Te$ (**3**): mp 148–149 °C (lit.[16] 149–150 °C). ^{119}Sn NMR ($CDCl_3$): −142.4 ppm (lit.[17] −143.2 ppm). ^{125}Te NMR ($CDCl_3$): −1309.9 ppm (lit.[17] −1310 ppm).

Results and Discussion

Synthesis and Characterization of Bis(triphenyltin) Chalcogenides. Recently we reported a simple method for making anhydrous sodium sulfide and sodium selenide by combining sodium, the chalcogen, and a catalytic amount of naphthalene in THF under an inert atmosphere.[11,12] This procedure is also applicable to the synthesis of pure sodium telluride. Combining the sodium chalcogenide with Ph_3SnCl in the appropriate ratio produced the expected bis(triphenyltin) chalcogenide in excellent yields. The three derivatives can be easily crystallized from benzene/hexane solutions. In the sulfur and selenium cases the products are white crystalline solids which are air and moisture stable. Bis(triphenyltin) telluride forms silvery-white crystals and is sensitive to oxygen. When sealed under an inert atmosphere and refrigerated, samples were stable for extended periods of time.

Pyrolysis of Bis(triphenyltin) Chalcogenides. Pyrolyses were carried out in a tube furnace under a continuous flow of dry nitrogen at atmospheric pressure. The flow system was equipped with a liquid nitrogen trap for recovery of volatile byproducts. In all cases the pyrolysis produced a dark gray or brown powder that remained in the crucible. These powders were identified and found to be phase pure by comparison of their X-ray diffraction patterns to the reference patterns found in the ICDD Powder Diffraction File. Combustion analyses were carried out to determine the amount of residual carbon in the powder. Analysis of the powder taken directly from the crucible often showed carbon in the region of 1–5%. The absence of C–H bands in the IR spectra suggested that the carbon is present in one of its elemental forms. A similar observation was made for tin sulfide and tin selenide prepared from cyclic precursors.[11] The carbon could be reduced to <1% by rinsing the powders once with benzene or toluene and once with hexane.

Table 1. Product Distribution from the Pyrolysis of $(Ph_3Sn)_2X$

$$(Ph_3Sn)_2X \xrightarrow[450\ ^\circ C]{N_2,\ 1\ atm} \underset{\mathbf{A}}{2SnX} + \underset{\mathbf{B}}{4Ph_4Sn} + \underset{\mathbf{C}}{Ph_2X}$$

compound pyrolyzed	**A**	**B**[b]	**C**[b]	total mass recovery, %	% carbon in SnX[c]
$(Ph_3Sn)_2S$	16 (14)	75 (78)	3 (8)	93	0.53
$(Ph_3Sn)_2Se$	16 (17)	68 (73)	6 (10)	94	0.35
$(Ph_3Sn)_2Te$	19 (20)	65 (69)	X (11)	92	0.85

[a] Theoretical yield is in parentheses assuming the production of only **A**, **B**, and **C**. [b] Yield determined by GC. [c] Carbon content after rinsing the sample with solvent and drying.

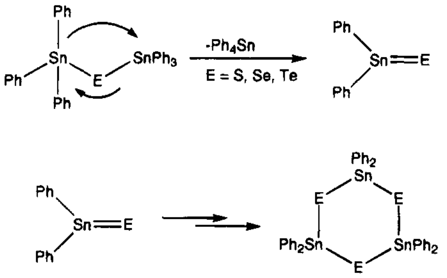

Figure 1. Proposed mechanism for the formation of cyclic intermediates.

Following the pyrolysis, generally 92–94% of the total mass was recovered. In each case, predominantly two volatile byproducts were observed: tetraphenyltin and the diphenyl chalcogenide. The yields were determined by GC relative to an internal standard of dodecane (Table 1).

This product distribution is consistent with the mechanism in Figure 1 which shows a series of simple phenyl migrations resulting in the loss of Ph_4Sn and the formation of $[Ph_2Sn{=}X]$ as a possible cofragment. Lighter element analogs of this reactive intermediate are well documented. They include thioformaldehyde,[18] selenoacetaldehyde,[19] dimethylsilathione,[20] diethylgermathione,[21] and several silaneselones.[22] These tin–chalcogen double-bonded intermediates may trimerize. We have already demonstrated that the pyrolysis of the cyclic trimers composed of tin–sulfur and tin–selenium produce tetraphenyltin and diphenyl chalcogen while leaving behind 2 mol of the tin chalcogenide.[11]

This mechanism is supported in the S and Se cases by ^{119}Sn NMR data obtained after low-temperature pyrolysis of the bis(triphenyltin) chalcogenides. The

---

(16) Schumann, H.; Thom, K. F.; Schmidt, M. *J. Organomet. Chem.* **1964**, *2*, 361.

(17) Jones, C. H. W.; Sharma, R. D.; Taneja, S. P. *Can. J. Chem.* **1986**, *64*, 980.

(18) Block, H.; Hirabayashi, T.; Mohmand, S.; Solouke, B. *J. Am. Chem. Soc.* **1982**, *104*, 3119.

(19) Hutchinson, M.; Kroto, H. W. *J. Mol. Spectrosc.* **1978**, *70*, 347.

(20) Moedritzer, K. *J. Organomet. Chem.* **1970**, *21*, 315.

(21) Lavayssiere, H.; Dousse, G.; Barrau, J.; Satge, J. Bouchalt, M. *J. Organomet. Chem.* **1978**, *161*, C59.

(22) Boudjouk, P. *Polyhedron* **1991**, *10*, 1231.

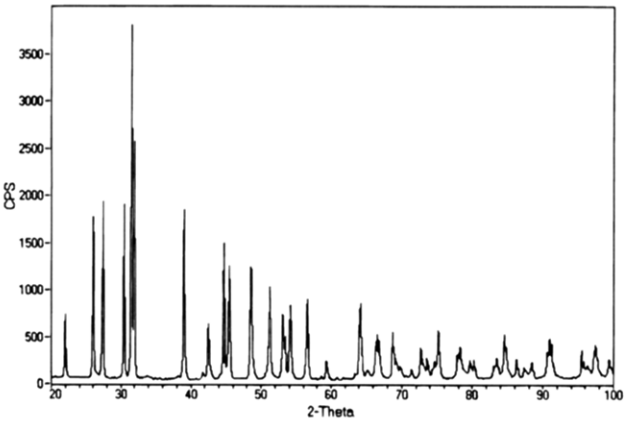

Figure 2. SnS prepared from bis(triphenytin) sulfide.

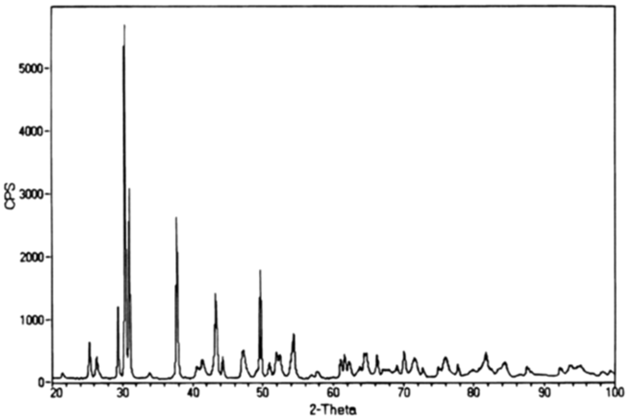

Figure 3. SnSe prepared from bis(triphenyltin) selenide.

spectra clearly show the formation of tetraphenyltin (^{119}Sn NMR ($CDCl_3$) Ph_4Sn: −127.5 ppm (lit.[15] −128.1 ppm)) and the stable six-membered tin−chalcogen ring systems that would be expected from such an intermediate (^{119}Sn NMR ($CDCl_3$) $(Ph_2SnS)_3$: +17.1 ppm (lit.[23] +16.8 ppm) and $(Ph_2SnSe)_3$: −44.7 ppm (lit.[24] −44 ppm)). While the final product distribution in the tellurium case seems to support this mechanism, the ^{119}Sn NMR did not show the presence of the $(Ph_2SnTe)_3$ ring system, (lit.[25] (C_6D_6) −204.3 ppm). This is not surprising considering its relative instability.

Careful analysis of the product mixture showed neither biphenyl nor hexaphenylditin. This suggests that if phenyl or tin radicals are present, they do not play an important role in the pyrolysis mechanism. In the case of $(Ph_3Sn)_2Se$ a small amount (<5%) of $Ph_3SnSePh$ was identified by GC-MS and the ^{119}Sn NMR resonance in $CDCl_3$ at −78.6 ppm (lit.[26] −79.2 ppm). This is consistent with the product distribution reported from the pyrolysis of the $(Ph_2SnSe)_3$ ring.[11]

X-ray Diffraction (XRD) Analysis of SnX Powders. The X-ray diffractograms of SnS, SnSe, and SnTe are in very good agreement with the observed and calculated reference patterns in Set 43 of the ICDD Powder Diffraction File (PDF, Figures 2−4). SnS and SnSe are isostructural and crystallize in the GeS structure type. SnTe crystallizes in the NaCl structure type. The unit cell parameters, obtained from the measured peaks (corrected with the internal diffractometer standard) compared well with the values given in the PDF and other sources (Tables 2−4).

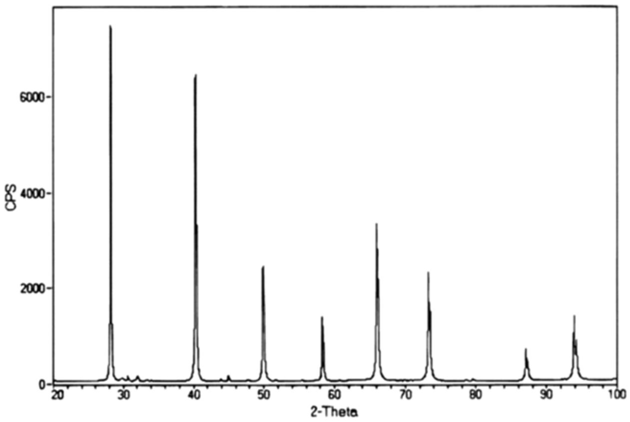

Figure 4. SnTe prepared from bis(triphenyltin) telluride.

Table 2. XRD Measured Unit-Cell Parameters for SnS[a]

referenced work	*a*, Å	*b*, Å	*c*, Å	vol, Å^3
PDF 33-1375	4.3340	11.2000	3.9870	193.53
PDF 39-354	4.3291(2)	11.1923(4)	3.9838(2)	193.03
DelBucchia[29]	4.329	11.180	3.982	192.72
Mosburg[30]	4.328	11.190	3.987	193.09
this study	4.3268(9)	11.1927(3)	3.9862	193.05

[a] SnS, orthorhombic [GeS] structure type, space group *Pbnm*, $Z = 4$.

Table 3. XRD Measured Unit-Cell Parameters for SnSe[b]

referenced work	*a*, Å	*b*, Å	*c*, Å	vol, Å^3
PDF 32-1382	4.46	11.42	4.19	213.4
Okazaki[31]	4.46	11.57	4.19	216.2
Nesterova[32]	4.47	11.48	4.19	215.0
Wiedemeier[33]	4.445	11.501	4.153	212.31
this study	4.440(1)	11.4975(9)	4.1533(9)	212.03(4)

[b] SnSe, orthorhombic [GeS] structure type, space group *Pbnm*, $Z = 4$.

Table 4. XRD Measured Unit-Cell Parameters for SnTe[c]

referenced work	*a*, Å	vol. Å^3
PDF 8-487	6.303	250.40
this study	6.3171(85)	252.098(9)

[c] SnTe, cubic [NaCl] structure type, space group *Fm*3*m*, $Z = 4$.

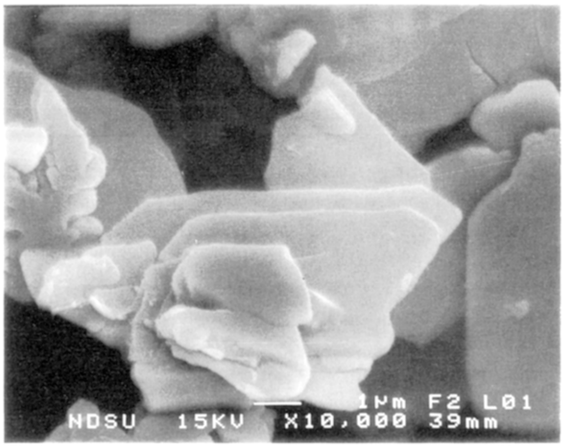

Figure 5. SnS prepared from bis(triphenyltin) sulfide.

Scanning Electron Microscopy. Electron micrographs taken of SnS and SnSe from these acyclic

---

(23) Schmidt, M.; Sersin, H. J.; Schumann, H. *Chem. Ber.* **1962**, *95*, 1428.

(24) Furue, K.; Kimura, T.; Yasuoka, N.; Kasai, N.; Kakudo, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 1661.

(25) Lockhart, T. P.; Puff, H.; Schuh, W.; Reuter, H.; Mitchell, T. N. *J. Organomet. Chem.* **1989**, *366*, 61.

(26) Chambers, R. F.; Scherer, P. C. *J. Am. Chem. Soc.* **1926**, *48*, 1054.

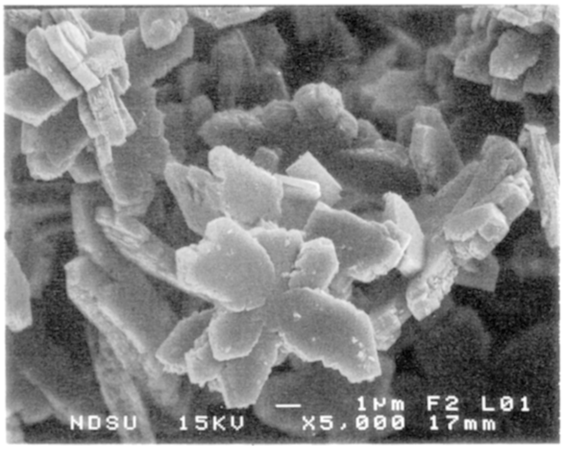

Figure 6. SnSe prepared from bis(triphenyltin) selenide.

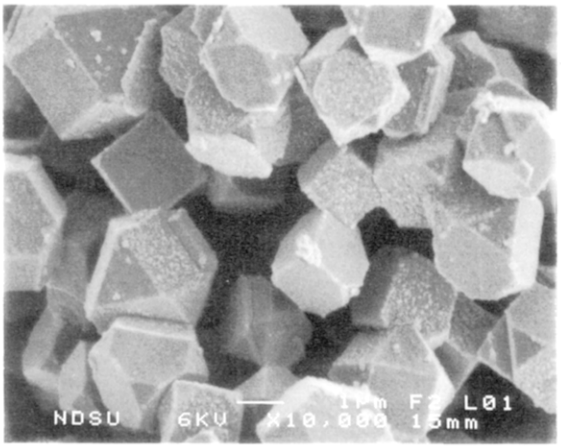

Figure 7. SnTe prepared from bis(triphenyltin) telluride.

precursors showed similar morphology to that obtained from the cyclic precursors.[11] Figure 5 shows the SnS powder produced from the pyrolysis of $(Ph_3Sn)_2S$ at 450 °C consists of microcrystalline plates in the 10 μm size range. The individual plates are 250−500 Å thick. Figure 6 shows the SnSe powder has a more prismatic habit with clusters in the range 10−100 μm. Each of the individual crystals are approximately 0.2−0.4 μm by 0.05 μm in size. Figure 7 shows that pyrolysis of $(Ph_3Sn)_2Te$ produces crystals that are combinations of cubic and octahedral forms with a typical size of approximately 0.3−0.6 μm.

Conclusions

Much effort has been directed to preparing precursors to binary materials in which *t*-butyl, *n*-butyl, *i*-propyl and ethyl groups are attached to main group elements so that gas phase thermolysis will lead to the efficient formation of isobutylene, n-butene, propylene and ethylene, respectively.[27] Our approach to the bulk synthesis of semiconductor materials from single source precursors differs in two major ways: 1) the precursor molecules are designed to take advantage of the migrating ability of the phenyl group rather than its ability to form stable degradation products, and 2) the thermolyses occur in the liquid phase. The successful syntheses of SnS and SnSe from $(Ph_2SnE)_3$ and $(Ph_3Sn)_2E$ systems and of SnTe from the easily prepared $(Ph_3Sn)_2Te$ suggested broader applicability for this approach. Recently we reported that GaAs and GaP can be similarly prepared from perphenylated precursors.[28] We have noted some advantages to working with these phenyl-substituted systems compared to the alkylated analogues: easier synthesis; increased stability toward oxygen and moisture; lower vapor pressures and therefore reduced transmission of toxic vapors; and, much reduced carbon content in the metal chalcogen powders.

Acknowledgment. Financial support from the Air Force Office of Scientific Research through Grants 91-0197 and F49620-92-J-0431 and the National Science Foundation through Grant No. EHR 9108770 is gratefully acknowledged. We thank Dean Grier and Jason Bender for help in acquiring and interpreting XRD patterns and Dr. Thomas Freeman and Kathy Iverson for obtaining SEM photographs.

---

(27) Cowley, A. H.; Jones, R. A. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1208 and references therein.

(28) Pan, Y.; Boudjouk, P. *206th National Meeting of the American Chemical Society*; Chicago, IL, Aug 22−27, 1993; Abstract, INOR 93.

(29) DelBucchia, P. S.; Jumas, J. C.; Maurin, M. *Acta Crystallogr.* **1981**, B37, 1903.

(30) Mosburg, S.; Ross, D. R.; Bethke, M.; Toulmin, P. *U.S. Geol. Surv., Profess. Papers* **1961**, *424-C*, 347.

(31) Okazaki, A.; Ueda, I. *J. Phys. Soc. Jpn.* **1956**, *11*, 470.

(32) Nesterova, Y. M.; Pashinkin, A. S.; Novoselov, A. V. *Russ. J. Inorg. Chem.* **1961**, *6*, 1031.

(33) Weidemeier, H.; Csillag, F. *Z. Kristallogr.* **1979**, *149*, 17.