

Molecular pathways for technologically important tin chalcogenide nanostructures

Gourab Karmakar,^a Adish Tyagi,^{*a,b}

^aChemistry Division, Bhabha Atomic Research Centre, Mumbai- 400 085, India

^bHomi Bhabha National Institute, Anushaktinagar, Mumbai- 400 094, India

Email: tyagia@barc.gov.in

Received: July 22, 2024 | Accepted: August 30, 2024 | Published online: September 6, 2024

Abstract

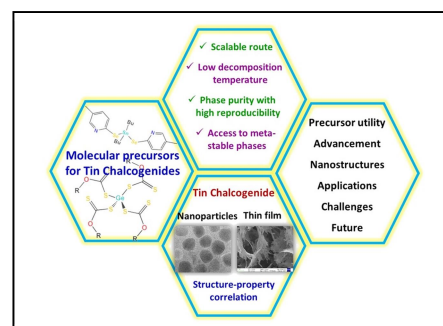
Tin chalcogenides have been projected as promising energy materials owing to their interesting physico-chemical properties. It is needed to evolve a cost effective route to fully harvest their commercial potential. Single source molecular precursors (SSP) offer a versatile route to functional materials. This mini review is intended to summarize various SSPs reported so far for tin chalcogenides. The effect of different ligand systems, capping agents in modulating the properties of tin chalcogenides have been discussed. Finally, the applications of SSP derived tin chalcogenides have also been included in this account.

Keywords: Single Source Molecular Precursor, Tin Chalcogenide, Nanomaterials, Thin Films, Energy Application.

1. Introduction

Since the discovery of graphene, 2D layered materials have garnered significant attention due to their distinct properties, such as unique electronic structures, large specific surface areas, and the quantum confinement of electrons due to their ultrathin nature compared to bulk materials.¹⁻⁴ These characteristics have opened new avenues for developing the next generation of electronic, optical, optoelectronic, and flexible systems. However, absence of band gap in graphene has impeded its application in photovoltaics, nanoelectronics etc. This has diverted the attention of research fraternity towards other layered materials particularly metal chalcogenide.⁴ Layered metal chalcogenides exhibit a wide array of unique chemical and physical properties, making them suitable for various applications including optoelectronic and photovoltaic devices, thermoelectric devices, transistors, lithium-ion batteries, and hydrogen generation through photocatalytic water splitting.⁵⁻¹⁶

Among the metal chalcogenides, group 14 metal chalcogenides comprising of GeE, GeE₂, SnE, SnE₂ and PbE (E = S, Se, Te) have shown great potential for high performance electronic, photonic as well as energy conversion and storage devices.¹⁷⁻²² Traditionally, Pb chalcogenides were favored for various applications, but environmental concerns associated with Pb²³ and the scarcity of Ge have led researchers to explore tin chalcogenides (SnE) as a more sustainable alternative. Practical application of any material is governed by economical synthetic route to



access that material with high phase purity and reproducibility, in addition to the fundamental nature of the material itself. (Figure 1).

To achieve controlled synthesis of tin chalcogenides, researchers have explored a variety of methods. These methods include hydrothermal and solvothermal synthesis, heat-up techniques, hot-injection methods, plasma-assisted routes, solid-state pyrolysis, and both chemical and physical vapor deposition (CVD and PVD) processes.^{20,22,24-27} Broadly, these approaches can be categorized into two main strategies: the multi-source strategy and the single-source molecular precursor strategy. The multi-source (or dual-source for binary materials) strategy utilizes separate organic or inorganic molecules or salts for each constituent elements. These precursor materials are often air-sensitive, toxic, or pyrophoric, necessitating careful handling during the synthesis process. In contrast, the single-source precursor (SSP) strategy employs metal-organic or organometallic molecules that incorporate all the necessary elements within a single compound, typically connected by direct covalent bonds. Occasionally, these elements may exist in an unbound state within the molecule.²⁸ The SSP method offers several distinct advantages over the dual-source method.^{19,29-32} Given the rapid growth of research on group IV metal chalcogenides (MCs) and the significance of the solid-state precursor (SSP) method for their synthesis, a systematic review on SSPs for this class of nanomaterials is essential.

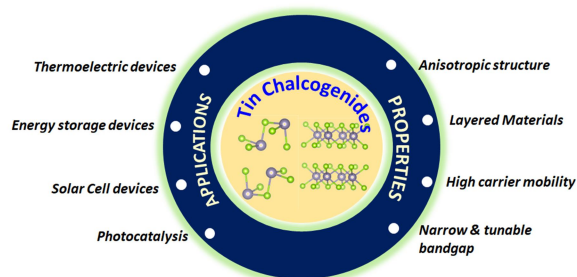


Figure 1. Promising properties and applications of tin chalcogenides.

In this mini-review, we provide a thorough examination of recent advancements in the development of tin chalcogenide nanostructures derived from SSPs. We begin by exploring the intriguing physical properties of tin chalcogenides, followed by an in-depth discussion on the fundamental principles of the SSP strategy. Next, we delve into various synthetic approaches that leverage SSPs for the efficient transformation into desired nanostructures, highlighting the factors influencing the final product's characteristics. We then analyze significant SSPs utilized in the synthesis of tin chalcogenides. The review concludes with a summary and future research directions in this field.

2. Crystal structure and physical properties of tin chalcogenides

Tin chalcogenide compounds, including SnE (SnS, SnSe, SnTe) and SnE₂ (SnS₂, SnSe₂), represents a significant category of 2D layered materials. These compounds exhibit robust covalent bonding within their planes, while weak Van der Waals forces prevail between the layers. This structural arrangement is similar to other two-dimensional materials. Tin chalcogenides can crystallize in various phases, such as orthorhombic, hexagonal, monoclinic, and cubic, each characterized by the oxidation state of the tin atoms.

Tin monochalcogenides (SnS, SnSe) adopt an orthorhombic crystal structure with a P_{nma} space group at ambient temperature (Figure 2a).³³ These structures originate from a distorted rock salt (NaCl) framework, mainly due to the influence of the lone pair of electrons in the valence orbitals of the Sn²⁺ ions. Within this framework, atoms are arranged in double layers, forming a zig-zag accordion-like pattern.³⁴ In these 2D layered materials, the bonds between Sn and S/Se within each layer are predominantly covalent, with each Sn atom linked to three S/Se atoms. Meanwhile, the layers themselves are held together by weak Van der Waals forces, allowing for easy cleavage into sheet-like forms.

The unit cell features SnS₇ or SnSe₇ distorted polyhedra with three short and four long bonds. The lone pair present of tin cation occupies a symmetric positions which leads to anisotropic crystal packing along the b and c axes.

Notably, both SnS and SnSe exhibit 2nd order displacive phase transition from the orthorhombic α phase which is less symmetric to more symmetric β phase at higher temperature.²⁹ In the β phase, each atom is evenly coordinated with four neighboring atoms within the x-y plane. Additionally, SnS is known to have a rocksalt structure (F_{m-3m}) and a metastable zinc blende structure (F_{-43m}). In the cubic phase, the Sn and S atoms occupy four distinct crystallographic positions due to the strong asymmetric bonding influenced by the lone pair on Sn²⁺. Unlike SnS and SnSe, SnTe prefers a cubic structure ($a = 6.32 \text{ \AA}$, F_{m-3m} space group) (Figure 2c), stable up to 1000 K, at which point it melts congruently.³⁵ However, SnTe exhibit soft chemical bonds originating from delocalization of electron density which interacts with lone pair present on Sn leading to distortion of the crystal structure.

Tin dichalcogenides (SnE₂), akin to their monochalcogenide counterparts (SnE), exhibit a remarkable layered structure. They crystallize in a CdI₂-type layered structure with a P_{-3m1} space group, in which E–Sn–E trilayers with internal covalent bonding are held together by Van der Waals forces (Figure 2b).²⁰ In this arrangement, Sn atoms are sandwiched between two layers of chalcogenide atoms, creating SnE₆ polyhedra at the edges. The bonding within these layers is predominantly covalent between Sn and E, with weak Van der Waals forces present between the layers, allowing for easy separation into thin sheets.³⁶ SnE₂ bonding involves Sn atoms contributing four electrons to the bonding molecular orbitals, resulting in oxidation states of +4 for Sn and -2 for E. The lone pair electrons on the chalcogen atoms terminate the surfaces of the layers, preventing the formation of dangling bonds and making these layers resistant to surface oxidation.²⁹

In addition to mono and dichalcogenides, tin also forms sesquisulfide (Sn₂S₃), commonly referred to as ottemannite. This mixed-valence tin sulfide boasts a distinctive ribbon-like structure. In this arrangement, Sn(II) atoms display a trigonal pyramidal geometry while Sn(IV) atoms are coordinated octahedrally.²⁹

Due to such unique anisotropic crystal structure and resonant bonding, tin chalcogenides are projected as environment friendly thermoelectric substitute of lead chalcogenides.¹⁷ A remarkable zT of 2.6 at 923K was achieved in p-type SnSe which has re-ignited quest in lead free tin chalcogenides as thermoelectric materials. In addition to their applications in thermoelectrics, the layered structure of tin chalcogenides with tunable spacing, high theoretical capacity and good electronic conductivity, has garnered significant attention as promising anode materials in energy storage devices.³⁷ Furthermore, the high absorption coefficient, solar spectrum compliant appropriate band-gap, high charge carrier concentration and efficient carrier mobility renders tin chalcogenides as material of choice for photovoltaics and optoelectronic applications.^{38,39}

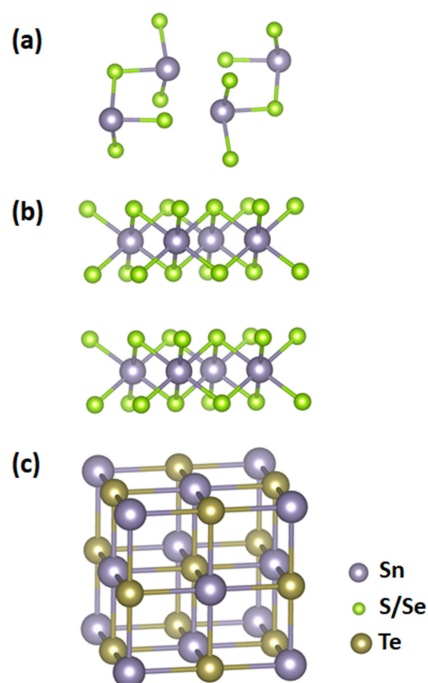


Figure 2. Crystal structure of (a) SnE and (b) SnE₂ (E = S/Se); (c) SnTe.

3. SSP: A versatile approach for nanostructured materials and thin films

Several synthetic methods including conventional solid-state methods, microwave-assisted synthesis, low temperature wet chemical approach have been adopted for the preparation of tin chalcogenide nanomaterials. However, most of these approaches often result in poor control over the composition, crystallite size, morphology, as well as chemical, optical and electronic properties of tin chalcogenides. A more effective approach is to design suitable single-source molecular precursors (Figure 3). The presence of pre-formed bond between the tin and chalcogen lowers the nucleation activation energy and thereby provide a low temperature route to access these materials.²⁹ These pre-formed bonds ensure better phase purity, lower defect concentration, improved stoichiometric control, and high reproducibility in the final product.⁴⁰ In addition to this, single source molecular precursors are equally viable for deposition of thin films via aerosol assisted chemical vapor deposition (AACVD). They bring additional advantage of by-passing complicating factors such as pre-reaction in the vapor phase, a common problem faced with dual precursor.³³ In the uncommon scenario, where no direct bond exists between the desired constituent elements in the molecule, product formation is aided by the reduced diffusion distances between these elements needed to form the lattice.²⁸ It is important to note that most of the SSPs can be conveniently used in various synthetic protocols such as heat up, hot injection, hydrothermal, co-precipitation methods, solid state pyrolysis as well as conventional and modified chemical

vapor deposition techniques.²⁹ However, this approach can introduce significant carbon content in the final materials due to the organic ligands in the precursor. This carbon typically forms non-conducting amorphous carbon, which remains separate from the metals rather than mixing intimately.⁴¹ Nevertheless, such low-temperature molecular precursor approaches have been proven to be beneficial to improve the activity and stability of active materials for photovoltaics, thermoelectric, energy storage devices, and other applications.

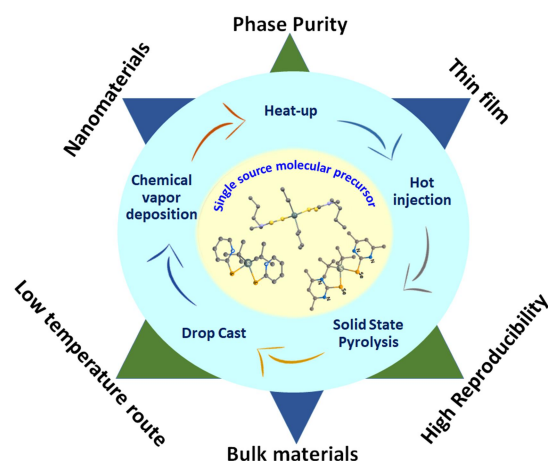


Figure 3. Versatility of single source molecular precursor (SSP) approach.

The decomposition profile of single-source precursors (SSPs) can be fine-tuned through various methods. The stability of the molecular complex can be modified using ancillary ligands. It has been observed that groups such as tertiary butyl, iso-propyl, and benzyl attached to the tin center can significantly accelerate the decomposition rate.^{42,43} The nature of the chalcogen ligands greatly influences the stability of molecular precursors. Generally, aliphatic ligands like xanthates and dithiocarbamates decompose at lower temperatures, although they can occasionally promote oligomerization. Conversely, a special class of ligands known as internally functionalized hemilabile ligands resists oxidation, prevents oligomerization by chelating the metal center, and ensures low-temperature decomposition of the precursor.²⁹

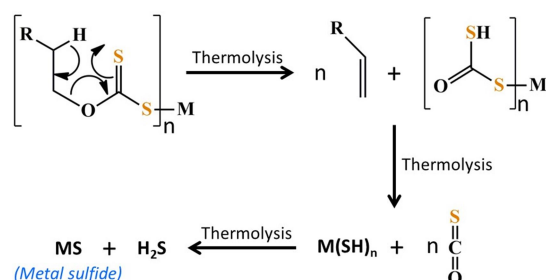
Additionally, the reaction solvent profoundly affects the decomposition signature of SSPs and the final product's crystallite size, composition, morphology, and optical properties. Solvents such as oleylamine (OAm), dodecanethiol (DDT), and dodecylamine (DDA), which also act as capping agents, participate in the thermolysis reaction. These solvents facilitate SSP decomposition through nucleophilic attack on the metal center, initiating a complex cascading effect in the decomposition reaction. Other capping agents, like trioctylphosphine oxide (TOPO), oleic acid (OA), and octadecene (ODE), commonly used in thermolysis experiments, play a crucial role in tuning the size

and optical properties of the final product.^{44,45} Careful selection of solvents can promote the targeted synthesis of specific compositions and phases of nanomaterials.^{43,46}

In the following section, we will explore the precursors that offer an efficient pathway to tin-chalcogenide nanostructures and delve into their applications.

4. Synthetic approaches to access tin chalcogenides from SSPs

SSP approach for metal chalcogenide material permits a high degree of liberty for design and synthesis with subtle but effective variation in the ligand system. The advantages and the production of material via SSP route relies upon the ligand system and the substitution on the later. In case of chalcogen containing ligands, there are only few common sulfur-based ligands, which are commercially available. These are mostly based on diethyldithiocarbamates, xanthates, thiobenzoic acid, thioethers and thiols. Thus, it is also crucial to synthesize new ligands with tailor made substituents to develop new molecular complexes which can be utilized as SSPs. With genuine protocol, ligands containing S, Se and Te, with assorted substituents (i.e., functional groups, halogens etc.) can be synthesized.



Scheme 1. Decomposition mechanism of metal xanthate precursors by the Chugaev elimination pathway to produce metal sulfide.

Metal xanthates and thiocarbamates are two of the many types of complexes, which are well studied and are among the very first SSPs developed for the fabrication of metal chalcogenide materials. The decomposition pathways of these complexes are also established. For instance, production of metal sulfide nanomaterials from metal xanthate precursors follows Chugaev elimination pathway (Scheme 1).⁴⁷ Hogarth and co-workers have carried out detailed experimental and DFT studies to unravel the decomposition mechanism of metal dithiocarbamate complexes in presence of primary amine.⁴⁸ They found the formation of dithiocarbamate intermediate specie formed due to proton migration from amine nitrogen to sulfur in complex, as the driving force behind the decomposition. The dithiocarbamate intermediate quickly transform into dimeric

metal thiolate [Ni{S₂CN(H)R}(μ-SH)]₂ which further convert into metal thiolate stabilized by amine. This metal thiolate, at elevated temperature finally produced metal sulfide materials.

Adeyemi *et al.* have isolated a series of mixed dithiocarbamate dimethyltin complexes, which serves as efficient single source precursors for tin sulfide nanomaterials.⁴⁹ The complexes, [(CH₃)₂Sn{S₂CN(C₄H₉)Ph}{S₂CN(CH₃)Ph}], [(CH₃)₂Sn{S₂CN(C₄H₉)Ph}{S₂CN(C₂H₅)Ph}] were prepared at room temperature, with crystal structure elucidation of the former. These complexes were thermolyzed under solventless and solvent-assisted conditions to isolate SnS and SnS₂ nanoparticles respectively. This shows that SSPs are quite versatile and can lead to tunable compositions and morphologies by subtle change in reaction conditions. In another study, Ramasamy *et al.* have prepared a series of diorganotin dithiocarbamate complexes of the type: [Sn(C₆H₅)₂(S₂CN(RR')₂)₂] (R, R' = ethyl; R, R' = butyl; R = methyl, R' = butyl; R = methyl, R' = hexyl) and [Sn(C₄H₉)₂(S₂CN(RR')₂)₂] (R, R' = ethyl; R, R' = butyl; R = methyl, R' = butyl; R = methyl, R' = hexyl) (Figure 4).³³ These complexes were used as SSPs for the deposition of phase pure orthorhombic SnS thin films by AACVD technique. A variable temperature range (400-530°C) was employed for the deposition to study the effect of temperature on the physical and chemical properties of the deposited film.

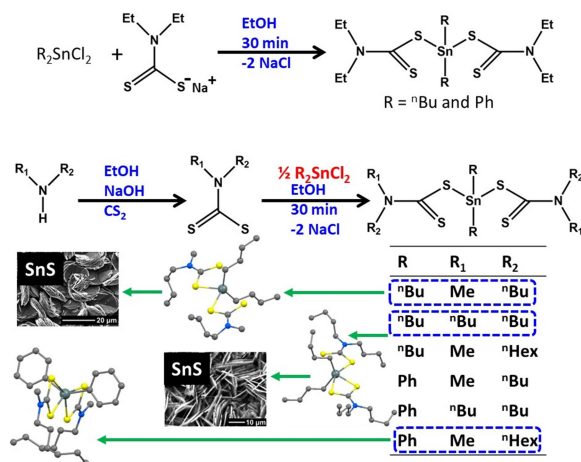


Figure 4. Synthesis of SnS thin films via AACVD from diorganotin dithiocarbamate complexes. Adapted with permission from Reference 33. Copyright ACS Publishers.

Apart from the well studies xanthate and thiocarbamate ligand systems, there are a plethora of ligand backbones, which make exotic class of tin complexes as SSPs for tin chalcogenides with tunable properties. For instance, Boudjouk *et al.* synthesized phenylated ring containing tin complexes with S and Se: (Ph₂SnS)₃ and (Ph₂SnSe)₃. Pyrolysis of the SSPs led to the formation of phase pure orthorhombic SnS and SnSe bulk powder.⁵⁰ O'Brien's group have designed thiosemicarbazone based tin

compounds, viz., Bz_3SnCl (saltscz) and Bz_3SnCl (4-Clbenzscz) (where Bz = benzyl, saltscz and 4-Clbenzscz are thiosemicarbazones of salicylaldehyde and thiosemicarbazone of 4-chlorobenzaldehyde respectively). These SSPs were subjected to AACVD for the deposition of SnS thin film over glass substrate.⁵¹ Robinson *et al.* have developed the organotin complexes: ${}^nBu_2Sn(SnBu)_2$ and ${}^nBu_3SnE{}^nBu$ (E = S and Se). Low pressure chemical vapour deposition (LPCVD) was adapted to fabricate SnS and SnSe thin films over fused silica substrates from these SSPs.⁵¹ These thin films were found to possess high Seebeck coefficient, which pose them as efficient thermoelectric materials for waste heat conversion.

In addition to these complexes, there is a separate class of ligands, called internally functionalized hemilabile ligands and their corresponding tin complexes, which have gained paramount attention as efficient SSPs for tin chalcogenide materials for energy applications. These chelating ligands featuring unsubstituted or substituted pyridyl/pyrimidyl/pyrazinyl moieties have been extensively explored by Tyagi *et al.* as suitable SSPs for tin chalcogenide materials for various applications. For example, Di-tert-butyltin complex with the ligand 2-pyrazinyl thiolate (2- $C_4H_3N_2SH$), i.e., ${}^tBu_2Sn(2-SC_4H_3N_2)_2$ was synthesized and structurally characterized. The SSP was versatile enough to not only yield binary SnS nanomaterials but also ternary Cu_2SnS_3 nanospheres, when co-thermolized in OAm with a Cu analogue of the ligand.⁵² Extending to the pyridyl and pyrimidyl system, their research group have isolated a series of bis and mono chloro substituted organotin complexes, namely, $[{}^tBu_2SnCl(2-SC_5H_4N)]$, $[{}^tBu_2Sn(2-SC_5H_4N)_2]$, $[{}^tBu_2SnCl(2-SC_5H_2(Me-4,6)_2N)_2]$ and $[{}^tBu_2Sn(2-SC_5H_2(Me-4,6)_2N)_2]$. These complexes have been successfully employed for the synthesis of SnS nanoplatelets under varied thermolysis conditions. A prototype photoelectrochemical (PEC) cell fabricated using these materials exhibited good photo-switching characteristics and responsivity, which pose them as fine materials for photodetectors.⁵³ As-prepared material exhibit high lithium uptake capacity, when employed as anode materials in LIB. Additionally, SnS thin films over glass and silica wafers were also grown utilizing these SSPs.⁵⁴

This strategy was further extended for synthesizing Se analogues of hemilabile chelating ligands with the aim to synthesize tin selenide materials. Notable among them is the SSP $[{}^tBu_2Sn(2-SeC_5H_3(Me-5)N)_2]$, which could be transformed into both SnSe and SnSe₂ nanomaterials under tunable solvent conditions. Furthermore, the dimethyl analogue of this complex, i.e., $[Me_2Sn(2-SeC_5H_2(Me-4,6)_2N)_2]$, was utilized to isolate morphology tuned SnSe nanosheets, which was employed as negative electrode in LIB. The material exhibits an initial specific capacity of 1134 mAhg^{-1} at a current density of $50 \text{ mA}g^{-1}$ with a capacity retention of 380 mAhg^{-1} even after 70 cycles with 100% efficiency.⁵⁵ Another series of complexes having the composition $[R_2Sn(2-SeC_5H_2(Me-4,6)_2N)_2]$ were also explored. These complexes were found to undergo

redistribution reaction with excess R_2SnCl_2 to yield another class of monochloro complexes: $[R_2SnCl(2-SeC_5H_2(Me-4,6)_2N)_2]$.⁴² SnSe₂ nanosheets and thin film with nanoflower growth were fabricated using these SSPs (Figure 5).

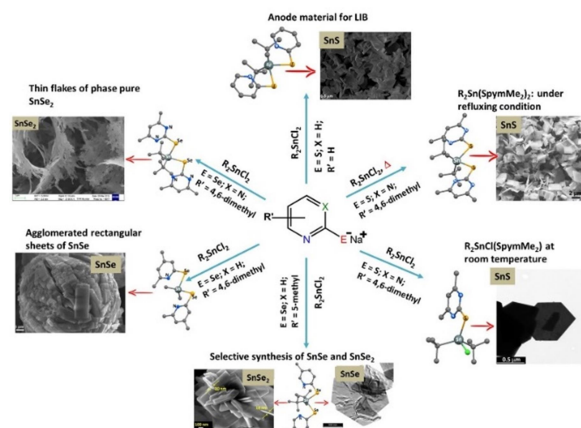
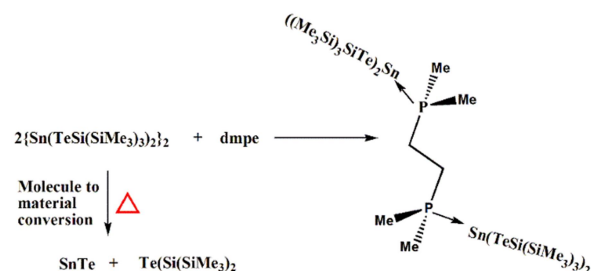


Figure 5. Di-organotin complexes derived using internally functionalized ligands and their facile conversion into shape and size tunable tin chalcogenide nanomaterial. Adapted with permission from Reference 29. Copyright Elsevier Publisher.

Extrapolating the work towards ternary Sn based semiconductor materials, co-thermolysis of the complex $[Me_2Sn(2-SeC_5H_3(Me-3)N)_2]$ along with the Cu analogue of the complex resulted into the formation of phase pure Cu_2SnSe_3 nanospheres. Optical studies divulge an optimal band gap of 1.4 eV for Cu_2SnSe_3 materials. SQUID (superconducting quantum interference device) analyses supported the magnetic nature of the ternary nanoparticles. A prototype photoelectrochemical (PEC) cell, fabricated with the pristine ternary material exhibited photovoltaic behaviour with efficiency (η) = 1.7%; open-circuit voltage (V_{oc}) = 339 mV; Current density (J_{sc}) = $33.3 \mu Acm^{-2}$ and fill factor (FF) = 0.3, which proved the suitability of SSP derived materials as absorber layer in next generation solar cells.⁵⁶

Tin telluride (SnTe) among the IV-VI narrow-bandgap semiconductor, has also garnered much attention and has been recommended as a promising alternative to PbTe due to similar crystal structure and relatively less toxicity and high abundance.⁵⁷ Furthermore, SnTe exhibits remarkable thermal and chemical stability, direct narrow band gap of 0.18 eV, large Bohr radius (95 nm), small effective electron-hole mass.^{58,59} Owing to these properties, SnTe finds relevance in quantum dot solar cell, high performance photodetector, thermoelectric devices and non-linear optics.⁶⁰ However, till date, very few precursors have been reported for the preparation of SnTe nanostructures, unlike tin sulfide and selenides. These include Hexabenzylcyclotristannatellurane, $(Bn_2SnTe)_3$, synthesized by Boudjouk *et al.*⁶⁰ The precursor was pyrolyzed at different temperatures and for different durations to afford SnTe in high yield and phase pure state. Subsequently, the same group reported bis(triphenyltin) telluride which produced

medley of cubic and octahedral SnTe at relatively lower temperature.⁶¹ The structurally characterized SSPs [Sn{TeSi(SiMe₃)₃}₂]₂ and (PMe₃)Sn[TeSi(SiMe₃)₃]₂ reported by Seligson *et al.* were found to be useful in accessing SnTe through solid state as well as solution phase route. However, little contamination from Te[Si(SiMe₃)₃]₂ was also observed in the final product (Scheme 2).⁶²



Scheme 2. Schematic representation of synthesizing homoleptic tin tellurolate and its conversion into tin telluride.⁶²

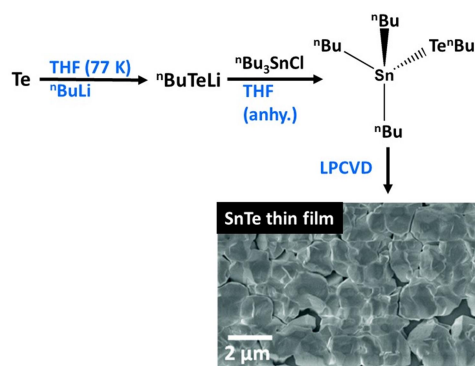


Figure 6. Synthesis of the SSP ⁿBu₃SnTeⁿBu and fabrication of thermoelectric SnTe thin film. Adapted under CC BY 3.0 license from Reference 65.

In addition to above literatures, there are few more reports dealing with the molecular precursor derived SnTe nanostructures. Thompson *et al.* reported the molecular complex [(PhTe)₂Sn{N(SiMe₃)₂}₂] with tin centre in pseudo-tetrahedral coordination environment, obtained from the reaction of tin(IV)bis(hexamethylsilylamide) with diphenylditelluride. The complex was successfully utilized for the preparation of amorphous Sn rich SnTe nanoparticles.⁶³ Afterwards, Ahmet *et al.* have prepared tin mono telluro compounds [(ⁱPrNC(NMe₂)NR)Sn(Te)] by the oxidative addition of elemental tellurium with tin(II) guanidate complexes. The complex was employed for the deposition of cubic SnTe via AACVD.⁶⁴ The decomposition process proceeds through two electron reduction process. However, the thin film obtained, were very thin and some SnO contamination was also observed. Recently, Reid and co-workers have prepared a molecular reagent [ⁿBu₃Sn(TeⁿBu)] and demonstrated its utility for the preparation of SnTe via low pressure CVD (Figure 6).⁶⁵ The film obtained found to be continuous and strongly adherent to the substrate.

Thermoelectric performance of the film was found to be decent and comparable to the bulk SnTe. The study paved way for the development of thin film based thermoelectric devices fabricated using SSPs. These instances proves that the materials synthesized using SSPs are not only of good quality, but can be used in actual energy and environmental fronts.

5. Conclusion and Future Outlook

In the current century, the development of environmentally friendly, high-performance, earth-abundant materials is essential for advanced energy conversion and storage devices. Tin chalcogenides represent a promising class of materials for this purpose. To fully harness their potential, high-quality and scalable synthesis methods are needed. The single source molecular precursor (SSP) approach offers a solution to this challenge.

The reactivity of SSPs can be tailored in various ways, with the nature of the ligand playing a significant role. The ligand in metal complexes controls the coordination behavior and rate of chalcogen atom transfer during material preparation. Whilst, the chelating ligand promotes the formation of monomeric complexes, the monodentate ligands facilitate oligomerization by coordinating through bridging mode. This variability affects the stability of the complex, influencing the temperature needed for its thermal breakdown, which in turn impacts reaction kinetics and the crystallinity of the final product. Additionally, the nature of the reaction solvent significantly affects the morphology and composition of the final product.

Research in this area could establish robust protocols for synthesizing tin chalcogenides with precise composition, morphology, and size. Currently, few SSPs for tin chalcogenides have been developed, and even fewer exist for SnTe, a material with significant potential for thermoelectric and photodetector applications. Thus, efforts should focus on developing efficient molecular precursors for SnTe, which is seen as a potential alternative to the already established PbTe. Furthermore, ternary tin chalcogenides are gaining importance in energy applications, yet precursors for their nano-scale preparation are scarce, indicating numerous research opportunities.

In summary, tin chalcogenide-based materials are poised to be leaders in energy-related applications. This mini-review presents a versatile approach to accessing these promising materials, discussing key factors that influence precursor reactivity and alter the final product

6. Acknowledgements

We thank Dr. R. Mishra, Head, TPMS, ChD; Dr. N. Choudhury, Head, ChD and Prof. A. K. Tyagi, former Director, Chemistry Group and Dean, HBNI for encouragement of this work.

7. Notes and References

- Novoselov, K. S.; Geim, A. K.; Morozov, S. V.; Jiang, D.; Zhang, Y.; Dubonos, S. V.; Grigorieva, I. V.; Firsov, A. A., *Science* **2004**, 306, 666.
- Choi, J.; Zhang, H.; Choi, J. H., *ACS Nano* **2016**, 10, 1671.
- Ji, Q.; Zhang, Y.; Liu, Z., *Chem. Soc. Rev.* **2015**, 44, 2587.
- Li, X.; Chen, C.; Yang, Y.; Lei, Z.; Xu, H., *Adv. Sci.* **2020**, 7, 2002320.
- Chhowalla, M.; Jena, D.; Zhang, H., *Nat. Rev. Mater.* **2016**, 1, 16052.
- Lv, R.; Robinson, J. A.; Schaak, R. E.; Sun, D.; Sun, Y.; Mallouk, T. E.; Terrones, M., *Acc. Chem. Res.* **2015**, 48, 56–64.
- Hu, Z.; Neill O., R.; Lesyuk, R.; Klinke, C., *Acc. Chem. Res.* **2021**, 54, 3792-3803.
- Heine, T., *Acc. Chem. Res.* **2015**, 48, 65-72.
- Shah, A. Y.; Kedarnath, G.; Tyagi, A.; Betty, C. A.; Jain, V. K.; Vishwanadh, B., *ChemistrySelect* **2017**, 2, 4598-4604.
- Karmakar, G.; Tyagi, A.; Wadawale, A. P.; Shah, A. Y.; Kedarnath, G.; Srivastava, A. P.; Singh, V.; *J. Mater. Sci.* **2020**, 55, 15439-15453.
- Karmakar, G.; Tyagi, A.; Shah, A. Y.; Nigam, S.; Wadawale, A.P.; Kedarnath, G.; Vats, B. G.; Kumar, N. N.; Singh, V.; *Dalton Trans.* **2022**, 51, 12670.
- Thomas, A.; Karmakar, G.; Shah, A. Y.; Lokhande, S. V.; Kulkarni, A. Y.; Tyagi, A.; Chauhan, R. S.; Kumar, N. N.; Singh, A. P., *Dalton Trans.* **2022**, 51, 12181.
- Kulkarni, A. Y.; Karmakar, G.; Shah, A. Y.; Nigam, S.; Kumbhare, G.; Tyagi, A.; Butcher, R. J.; Chauhan, R. S.; Kumar, N. N.; *Dalton Trans.* **2023**, 52, 16224.
- Karmakar, G.; Tyagi, A.; Shah, A. Y.; Kumbhare, L. B.; Wadawale, A. P.; Kedarnath, G.; Singh, V., *RSC Adv.* **2022**, 12, 27292.
- Karmakar, G.; Tyagi, A.; Halankar, K. K.; Nigam, S.; Mandal, B. P.; Wadawale, A. P.; Kedarnath, G.; Debnath, A. K., *Dalton Trans.* **2023**, 52, 1461.
- Karmakar, G.; Pathak, D. D.; Tyagi, A.; Mandal, B. P.; Wadawale, A. P.; Kedarnath, G., *Dalton Trans.* **2023**, 52, 6700.
- Banik, A.; Roychowdhury, S.; Biswas, K., *Chem. Commun.* **2018**, 54, 6573-6590.
- Rundle, J.; Leoni, S., *J. Phys. Chem. C* **2022**, 126, 33, 14036–14046.
- Lewis, D. J. Kevin, P.; Bakr, O.; Muryan, C. A.; Malik, M. A.; O'Brien, P., *Inorg. Chem. Front.* **2014**, 1, 577-598.
- Zhou, X.; Zhang, Q.; Gan, Li.; Li, H.; Xiong, J.; Zhai, T., *Adv. Sci.* **2016**, 3, 1600177.
- Palchoudhury, S.; Ramasamy, K.; Han, J.; Chen, P.; Gupta, A., *Nanoscale Adv.* **2023**, 5, 2724-2742.
- Shi, W.; Gao, M.; Wei, J.; Gao, J.; Fan, C.; Ashalley, E.; Li, H.; Wang, Z., *Adv. Sci.* **2018**, 5, 1700602.
- Roychowdhury, S.; Samanta, M.; Perumal, S.; Biswas, K., *Chem. Mater* **2018**, 30, 5799–5813.
- He, F.; Klein, E.; Bartling, S.; Saeidpour, S.; Corzilius, B.; Lesyuk, R.; Klinke, C., *J. Phys. Chem. C* **2022**, 126, 20498-20504.
- Zhang, J.; Zhu, H.; Wu, X.; Cui, H.; Li, D.; Jiang, J.; Gao, C.; Wang, Q.; Cui, Q., *Nanoscale* **2015**, 7, 10807-10816.
- Liu, G.; Li, Y.; Li, B.; Tian, H.; Fan, C.; Zhang, Y.; Hua, Z.; Wang, M.; Zheng, H.; Li, E., *J. Mater. Chem. C* **2018**, 6, 10036-10041.
- Moore, S.; Kobayashi, K.; Takahashi, M.; Higashimine, K.; Meanosono, S., *J. Phys. Chem. C* **2023**, 127, 12394–12403.
- Karmakar, G.; Tyagi, A.; Kedarnath, G.; Kumar, N. N.; Phadnis, P. P.; Mishra, R.; Kumar, M., *Inorg. Chim. Acta* **2022**, 529, 120668.
- Karmakar, G.; Tyagi, A.; Shah, A. Y., *Coord. Chem. Rev.* **2024**, 504, 215665.
- Matthews, P. D.; McNaughton, P. D.; Lewis, D. J.; O'Brien, P., *Chem. Sci.* **2017**, 8, 4177-4187.
- Khan, M. D.; Malik, M. A.; Revaprasadu, N., *Coor. Chem. Rev.* **2019**, 388, 24-47.
- Jain, V. K.; *Dalton Trans.* **2020**, 49, 8817-8835.
- Ramasamy, K.; Kuznetsov, V. L.; Gopal, K.; Malik, M. A.; Raftery, J.; Edward, P. P.; O'Brien, P., *Chem. Mater.* **2013**, 25, 266-276.
- Peters, M.J.; Mcneil, L.E., *Phys. Rev. B: Condens. Matter Mater. Phys.* **1990**, 41, 5893–5897.
- Breternitz, J.; Gunder, R.; Hempel, H.; Binet, S.; Ahmet, I.; Schorr, S., *Inorg. Chem.* **2017**, 56, 11455–11457.
- Zhong, H.; Yang, G.; Song, H.; Liao, Q.; Cui, H.; Shen, P.; Wang, C.X.; *J. Phys. Chem. C* **2012**, 116, 9319–9326.
- Wei, Z.; Wang, L.; Zhuo, M.; Ni, W.; Wang, H.; Ma, J., *J. Mater. Chem. A* **2018**, 6, 12185-12214.
- Kumar, A.; Ranjan, R.; Mishra, V. K.; Srivastava, N.; Tiwari, R. N.; Singh, L.; Sharma, A. K., *Renew. Energy* **2024**, 226, 120462.
- Antunez, P. D.; Buckley, J. J.; Brutchey, R. L., *Nanoscale*, **2011**, 3, 2399–2411.
- Brune, V.; Raydan, N.; Sutorius, A.; Hartl, F.; Purohit, B.; Gahlot, S.; Bargiela, P.; Burel, L.; Wilhelm, M.; Hegemann, C.; Atamturk, U.; Mathur, S.; Mishra, S., *Dalton Trans.* **2021**, 50, 17346-17360.
- Ghosh, S.; Dasgupta, B.; Walter, C.; Menezes, P. W.; Driess, M., *Small Sci* **2023**, 3, 2200115.
- Tyagi, A.; Kedarnath, G.; Wadawale, A.; Shah, A. Y.; Jain, V. K.; Vishwanadh, B., *RSC Adv.* **2016**, 6, 8367-8376.
- Tyagia, A.; Karmakar, G.; Wadawale, A.; Shah, A. Y.; Kedarnath, G.; Srivastava, A. P.; Singh, V.; Jain, V. K., *J. Organomet. Chem.* **2018**, 873, 15-21.
- Chen, O.; Chen, X.; Yang, Y.; Lynch, J.; Wu, H.; Zhuang, J.; Cao, Y. C., *Angew. Chem. Int. Ed.* **2008**, 47, 8638-8641.
- Shah, A. Y.; Karmakar, G.; Tyagi, A.; Kedarnath, G., *New J. Chem.* **2022**, 46, 19817-19823.
- Karmakar, G.; Shah, A. Y.; Tyagi, A.; Wadawale, A. P.; Kedarnath, G.; Kumar, N. N.; Bahadur, J., *New J. Chem.* **2022**, 46, 3871-3881.
- Makin, F.; Alam, F.; Buckingham, M. A.; Lewis, D. J., *Sci. Rep.* **2022**, 12, 5627.
- Hollingsworth, N.; Roffey, A.; Islam, H.-U.; Mercy, M.; Roldan, A.; Bras, W.; Wolthers, M.; Catlow, C. R. A.; Sankar, G.; Hogarth, G.; de Leeuw, N. H., *Chem. Mater.* **2014**, 26, 6281-6292.
- Adeyemi, J. O.; Onwudiwe, D. C.; Hosten, E. C., *J. Mol. Struct.* **2019**, 1195, 395-402.
- Bahr, S. R.; Boudjouk, P.; McCarthy, G. J., *Chem. Mater.* **1992**, 4, 383-388.
- Robinson, F.; Curran, P. J.; (Kees) de Groot, C. H.; Hardie, D.; Hector, A. L.; Holloway, K.; Huang, R.; Newbrook, D.; Reid, G.; *Mater. Adv.* **2021**, 2, 4814-4823.
- Tyagi, A.; Kole, G. K.; Shah, A. Y.; Wadawale, A.; Srivastava, A. P.; Kumar, M.; Kedarnath, G.; Jain, V. K., *J. Organomet. Chem.* **2019**, 887, 24-31.
- Karmakar, G.; Tyagi, A.; Shah, A. Y.; Wadawale, A. P.; Kedarnath, G.; Singh, V., *Polyhedron* **2022**, 220, 115833.
- Tyagi, A.; Karmakar, G.; Mandal, B. P.; Pathak, D. D.; Wadawale, A.; Kedarnath, G.; Srivastava, A. P.; Jain, V. K., *Dalton Trans.* **2021**, 50, 13073-13085.
- Karmakar, G.; Halankar, K. K.; Tyagi, A.; Mandal, B. P.; Wadawale, A. P.; Kedarnath, G.; Srivastava, A. P.; Singh, V., *Dalton Trans.* **2021**, 50, 15730-15742.
- Tyagi, A.; Shah, A. Y.; Kedarnath, G.; Wadawale, A.; Singh, V.; Tyagi, D.; Betty, C. A.; Lal, C.; Jain, V. K., *J. Mater. Sci.: Mater. Electr.* **2018**, 29, 8937-8946.
- Reiss, P.; Carrière, M.; Lincheneau, C.; Vaure, L.; Tamang, S., *Chem. Rev.* **2016**, 116, 10731.
- Ahmed, S.; Qiao, J.; Cheng, P. K.; Saleque, A. M.; Hossain, M. I.; Zeng, L. H.; Zhao, J.; Qarony, W.; Tsang, Y. H., *Adv. Opt. Mater.* **2021**, 9, 2001821.

59. Kannaujya, R. M.; Khimani, A. J.; Chaki, S. H.; Chauhan, S. M.; Hirpara, A. B.; Deshpande, M. P., *Eur. Phys. J. Plus* **2020**, 123, 1.
60. Boudjouk, P.; Remington, M. P.; Grier, D. G.; Triebold, W.; Jarabek, B. R.; *Organometallics* **1999**, 18, 4534–4537.
61. Boudjouk, P.; Seidler, D. J.; Bahr, S. R.; McCarthy, G. J., *Chem. Mater.* **1994**, 6, 2108–2112.
62. Seligson, A. L.; Arnold, J., *J. Am. Chem. Soc.* **1993**, 115, 8214–8220.
63. Thompson, J. B.; Ahmet, I. Y.; Johnson, A. L.; Kociak-Kohn, G., *Eur. J. Inorg. Chem.* **2016**, 4711.
64. Ahmet, I. Y.; Hill, M. S.; Raithby, P. R.; Johnson, A. L., *Dalton Trans.* **2018**, 47, 5031.
65. Robinson, F.; Newbrook, D. W.; Curran, P.; (Kees) de Groot, C. H.; Hardie, D.; Hector, A. L.; Huang, R.; Reid, G.; *Dalton Trans.* **2021**, 50, 998-1006.

published 49 research articles in peer-reviewed journals and contributed five book chapters. He is the recipient of Young Applied Scientist Award-2020 (DAE-GOI), CRS Bronze Medal, SMC Bronze Medal and elected NASI Member.

Article Note: A collection of invited papers based on *Award Lecture* presentations in the International Symposium *Science Beyond Boundary: Invention, Discovery, Innovation and Society 'Rasayan 19'* held at IISER Kolkata during July 29-30, 2024.

8. About the author(s)



Dr. Gourab Karmakar received his M.Sc. degree in Chemistry from IIT Roorkee. He obtained Ph.D. degree from HBNI. He is currently serving as Scientific Officer (D) in Chemistry Division, BARC. He is actively involved in the design and development of

efficient single source molecular precursor for metal chalcogenide nanomaterials and thin films. His research interest also include Metal Organic Framework and Porous Materials for environmental applications. He has published several research papers and conference papers as well as presented his research work at various scientific platforms. He has received SMC Emerging Scientist Award in 2024.



Dr. Adish Tyagi, a Scientific Officer (F) at the Bhabha Atomic Research Centre (BARC), Mumbai, completed his post-graduation in Chemistry from Delhi University and joined BARC in 2011 after successfully finishing a one-year orientation course at the BARC Training

School. Since then, he has been actively working in the frontier areas of chemical sciences, focusing on expanding the horizons of molecule to material transformation. His work includes designing molecular precursors and their conversion into intricate metal chalcogenide nanostructures for energy conversion and storage applications. In pursuit of this objective, he has successfully designed a multitude of chalcogen-bearing complexes encompassing transition & main-group metals. Various materials crafted by him, have proven successful as anode materials in LIBs, exhibiting commendable charge-discharge capacity and high cyclability. His innovative approach extends to scalable pathway for highly photoresponsive ternary nanostructures. Towards teaching and promotion of science, Dr. Tyagi is a faculty at Homi Bhabha National Institute, Mumbai and a visiting faculty member at UM-DAE CEBS, Mumbai. He serves as an executive council member of the Society for Materials Chemistry (SMC) and Indian Chemical Society (Mumbai, Branch) and has guest-edited three bulletin editions. He has