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Structural investigations of SnS$_{1-x}$Se$_x$ solid solution synthesized from chalcogeno-carboxylate complexes of organo-tin by the colloidal and solvent-less routes

Malik Dilshad Khan, a,b Mohammad Aamir, a,b Ghulam Murtaza, c Mohammad Azad Malik d* and Neerish Revaprasadu a*

Tin chalcogenides are important semiconducting materials due to their non-toxic nature, cost effectiveness and layered structure. In this study, a facile synthetic route has been employed for the synthesis of a bis(selenobenzoato)dibutyltin(IV) complex, and used along with the bis(thiobenzoato)dibutyltin(IV) complex, as single source precursors, to prepare binary tin chalcogenides and their solid solution (SnS$_{1-x}$Se$_x$) in the entire range. The synthesis of the solid solution was carried out by the colloidal and melt methods. The comparative analysis of the solid solution obtained from both routes, indicate that the colloidal method provides superior control over composition. The UV-Vis-NIR analysis showed a gradual change in band gap, while moving from SnS to SnSe.

Introduction

Nanostructured layered materials are 2-dimensional materials with interesting mechanical, catalytic and electronic properties. 1-4 Besides graphene, many metal chalcogenide layered materials have gained attention due to their flexibility in the nature of metals and their oxidation states. 4-7 Depending upon the kind of metal and its oxidation state, a layered material can exist in different polymorphic geometries, such as octahedral, trigonal prismatic, rhombohedral and orthorhombic (also considered as the distorted rock salt structure) crystal lattices. 8, 9

Tin chalcogenides belong to the IV-VI class of semiconductors and exists in either the MX ($+2$ oxidation) or MX$_2$ ($+4$ oxidation) form. However, tin(II) chalcogenides have attracted considerable interest due to their suitable band gaps and intense absorption in the electromagnetic spectrum, which make them suitable candidates for photovoltaic and optoelectronic applications. 10, 11 Moreover, they have low toxicity, are relatively earth abundant and cost effective materials, properties that render them promising materials in nanocrystal based photovoltaics. 12 Hence, tin chalcogenides are highly desirable as thin films, nanocrystals and alloys with controllable morphology, size and composition for tunable electronic properties. 13, 14

SnS and SnSe are both isostructural and exist in the orthorhombic structure, and each unit cell consists of eight atoms. 15-17 SnS has both direct and indirect band gaps of around 0.9 eV and 1.3 eV respectively. 18 SnSe has been used in solar cells, memory switching and as an anode material. 19-21 Similarly, SnS is also a promising solar material with an absorption coefficient of the order 10$^3$-10$^4$ and its band gap is commensurate to that of silicon. 22 Due to the identical crystal structure of both the materials, a solid solution over the entire range is also known.

SnS$_{1-x}$Se$_x$ alloy thin films were deposited by the electrodeposition method, using sodium thiosulfate (Na$_2$S$_2$O$_3$), selenium dioxide (SeO$_2$) and stannous chloride (SnCl$_2$). 14, 21, 22 The effect of the different parameters, such as, potential, deposition time and composition on the electronic properties of the solid solution were studied. Another common method to prepare solid solutions is solid state synthesis, whereby the elements are mixed in stoichiometric quantities and heated at high temperature for a prolonged time. 13, 23-25 The resultant alloy solid solution was used as electrodes for lithium/sodium based batteries, where significant enhancement was observed in the thermoelectric performance. The band gap was also tuned by changing the S:Se ratio. However, the solid state method has inherent problems, as the process is laborious, inefficient in terms of energy and also not suitable when one of the components is more volatile than others, eventually leading to the formation of a non-stoichiometric product.

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Electronic Supplementary Information (ESI) available: TGA, p-XRD and EDX, elemental mapping and Tables. See DOI: 10.1039/x0xx00000x
The gas phase laser photolysis method was also used for the composition tuned synthesis of the SnS$_{1-x}$Se$_x$ alloy. Although, a facile control on phase and composition was achieved, the method requires the use of highly toxic H$_2$S and dimethyl selenium. The use of single source precursors is often advantageous as it prevents the usage of noxious reagents and provides better control over phase and stoichiometry of thin films and nanomaterials. Unfortunately, the use of single source precursors for the synthesis of SnS$_{1-x}$Se$_x$ solid solution is not well explored and the only precursors used until the present are benzyl substituted tin chalcogenides. The precursors were not suitable to prepare a solid solution due to the use of elemental selenium, and traces of elemental tin were also observed in the final product obtained by the decomposition of these precursors.

The design and use of suitable chalcogeno- single source precursors for an efficient and composition controlled synthesis of SnS$_{1-x}$Se$_x$ is required. Previously, we have reported the use of bis[diphenylphosphinidenelecanoato]tin(II) complex for deposition of SnSe thin films, the synthesis requires the use of highly toxic and expensive diphenylphosphine. Recently, we have developed a new and an efficient route for the synthesis of a novel phosphine-free bis(selenobenzoato)dibutyltin(IV) complex.

The synthesis of a SnS$_{1-x}$Se$_x$ solid solution in the entire range of composition, from chalcogeno- (thio/seleno) benzoate complexes of organotin, by a colloidal hot injection method, using oleylamine (OLA) as capping agent is described. For comparison, the solid solution was also synthesized by the solvent-less melt method, to observe the effect of capping agents on the synthesized alloyed materials.

**Experimental**

**Materials**

The reagents and solvents *i.e.* oleylamine (OLA), dibutylindichloride, NaBH$_4$, KOH, elemental selenium, benzoyl chloride, thiobenzoic acid and ethanol were purchased from Sigma Aldrich and used as received.

**Synthesis of bis(selenobenzoato)dibutyltin(IV) complex**

NaHSe was prepared by slight modification of the reported method. An ethanolic solution of NaBH$_4$ (12.0 mmol in 15.0 mL ethanol) was added to an ethanolic solution of metallic Se powder (0.5 g, 6.0 mmol) under inert conditions. The resultant reddish solution became colourless within 5 min of stirring. Benzoyl chloride (6.0 mmol) was then added into the freshly prepared NaHSe solution, which resulted in the formation of the seleno-benzoate ligand. The stirring was continued for a further 15 min, after which Bu$_2$SnCl$_2$ (0.95 g, 3.0 mmol) in 15.0 mL ethanol was added dropwise. The oily product was formed after stirring for 15 min, while stirring. The stirring was continued for 15 min. at room temperature, after which an ethanolic (20.0 mL) solution of Bu$_2$SnCl$_2$ (2.3 g, 7.5 mmol) was added dropwise under inert conditions. The reaction mixture was stirred for further half an hour, to ensure completion of the reaction. Distilled water (50.0 mL) was added to the reaction mixture, the solution became turbid with the formation of an oily product. The product was separated by the solvent extraction method using chloroform, magnesium sulphate was added in chloroform to remove water molecules. The chloroform solution was evaporated and an off-white precipitate appeared as the product (complex 1). Yield: 83 %, Melting point 96-97 °C, $^{1}$H-NMR (CDCl$_3$) $\delta$ (ppm): 0.93 (6H, t, $J$=7.32 Hz, CH$_3$), 1.47 (4H, q, $J$=7.26 Hz, CH$_2$), 1.80 (4H, m, $J$=7.62 Hz, CH$_2$), 1.90 (4H, t, $J$=7.95 Hz, CH$_2$), 2.49 (4H, t, $J$=7.47 Hz, o-ArH), 2.72 (2H, t, $J$=7.35 Hz, p-ArH), 8.14 (4H, d, $J$=7.74 Hz, m-ArH). $^{13}$C-NMR (CDCl$_3$) $\delta$ (ppm): 13.5, 22.2, 26.2, 28.6, 28.7, 128.5, 128.7, 133.7, 139.9, 200.5. Elemental analysis cal. (%): for C$_{33}$H$_{40}$O$_2$Sn$_2$: C 53.46, H 5.41, Sn 19.74; Found: C 53.08, H 5.54, Sn 19.65.

**Synthesis of bis(thiobenzoato)dibutyltin(IV) complex**

The sodium salt of thiobenzoic acid was prepared by adding an ethanolic solution (25.0 mL) of KOH (0.85 g, 15.0 mmol) in an ethanolic solution (25.0 mL) of thiobenzoic acid (2.1 g, 15.0 mmol) while stirring. The stirring was continued for 15 min. at room temperature, after which an ethanolic (20.0 mL) solution of Bu$_2$SnCl$_2$ (2.3 g, 7.5 mmol) was added dropwise under inert conditions. The reaction mixture was stirred for further half an hour, to ensure completion of the reaction. Distilled water (50.0 mL) was added to the reaction mixture, the solution became turbid with the formation of an oily product. The product was separated by the solvent extraction method using chloroform, magnesium sulfate was added in chloroform to remove water molecules. The chloroform solution was evaporated and an off-white precipitate appeared as the product (complex 2). Yield: 83 %, Melting point 96-97 °C, $^{1}$H-NMR (CDCl$_3$) $\delta$ (ppm): 0.95 (6H, t, $J$=7.32 Hz, CH$_3$), 1.47 (4H, q, $J$=7.26 Hz, CH$_2$), 1.80 (4H, m, $J$=7.62 Hz, CH$_2$), 1.90 (4H, t, $J$=7.95 Hz, CH$_2$), 2.49 (4H, t, $J$=7.47 Hz, o-ArH), 2.72 (2H, t, $J$=7.35 Hz, p-ArH), 8.14 (4H, d, $J$=7.74 Hz, m-ArH). $^{13}$C-NMR (CDCl$_3$) $\delta$ (ppm): 13.5, 22.2, 22.9, 24.4, 25.6, 25.9, 26.0, 26.2, 26.3, 26.6, 27.3, 27.9, 28.6, 28.1, 128.3, 128.5, 128.7, 129.0, 132.7, 137.5, 200.1. Elemental analysis cal. (%) for C$_{33}$H$_{40}$O$_2$Sn$_2$: C 53.46, H 5.41, Sn 19.74; Found: C 53.08, H 5.54, Sn 19.65.

**Colloidal synthesis of SnS$_{1-x}$Se$_x$ solid solution**

The solid solution was synthesized by dispersing a mixture of complex (1) and (2) in appropriate molar compositions in OLA (2.0 mL) and injected into pre-heated OLA (8.0 mL) at 230 °C with continuous stirring, under a nitrogen environment (Supplementary Table S1). The temperature was maintained for 30 min., after which the reaction mixture was removed from the heating source for cooling. A mixture of acetone and methanol (1:1) was used for precipitation, and the synthesized material was washed and separated by centrifugation.

**Synthesis of SnS$_{1-x}$Se$_x$ solid solution by melt method**

In the melt method, the solid solution was prepared by the thermal decomposition of the complexes (1) and (2), mixed in required stoichiometric quantities (Supplementary Table S2).
For this purpose, both complexes were mixed together homogeneously, and placed in a ceramic combustion boat. The boat, in a glass tube, was placed inside the carbolite tube furnace. The end of the tube was sealed by a rubber septum and a vacuum was applied to remove air from the tube followed by filling of nitrogen gas. As complex (1) and (2) both have low melting points, the temperature was maintained at 100 °C for 10 min., to obtain a homogenized molten mixture of both complexes. Afterwards, the temperature was raised slowly to 330 °C and maintained for one hour under an inert atmosphere. After an hour, the heating was turned off and the combustion boat was allowed to cool naturally to room temperature. The tube was removed from the furnace and powder residue was collected for analysis.

Characterization

Microanalysis was performed using a Thermo Scientific Flash 2000 Organic Elemental Analyzer. \(^{1}\)H and \(^{13}\)C NMR were recorded on a Bruker 600 MHz instrument with TMS as external reference at room temperature. Thermogravimetric analyses were performed using a Mettler-Toledo TGA/DSC under nitrogen gas flow rate of 10 mL/min. X-ray diffraction was performed using a Bruker D8 Discover Diffractometer using CuKα radiation (\(\lambda = 1.54178 \text{ Å}\)), in a 2θ range from 10° to 70°. The data collected was used to determine the lattice parameters and crystal phase. Scanning electron microscopy (SEM) was carried out using a Philips XL30 FEG-SEM. Energy-dispersive X-ray (EDX) spectroscopy was performed using a DX4 detector. All samples were carbon coated using an Edwards coating system E306A prior to SEM analysis. UV-vis-NIR spectra were recorded using a PerkinElmer Lambda 1050 instrument, using quartz cuvettes with a path length of 1 cm.

Results and discussions

Amongst the metal complexes of chalcogeno carboxylic acids, considerable work has been done on the thio-analogues, \(^{39-41}\) however very little work has been done on the complexes of heavier chalcogen congeners. \(^{42}\) The primary reason is the difficulty of preparation, as the resulting acids are highly unstable. \(^{43}\) In this study, we have used a new and efficient route for the synthesis of a metal selenobenzoate complex and used it as suitable precursor for the synthesis of the respective metal selenide and alloy solid solution. Previously, sodium selenide was used to prepare selenobenzoate ligand, \(^{44}\) however, the synthesis of sodium selenide requires the use of sodium metal, a highly pyrophoric material. In addition, the completion of the reaction requires \(\approx\) 24 hours. Our method excluded the use of sodium metal, and the reaction can be completed within 30 minutes.

A solid solution can be generated by substitution of one or more components without destroying the crystal structure. However, slight distortions in the crystal lattice can be observed in the form of defects, which may arise due to the vacancies or stacking faults, subject to the reaction conditions. \(^{45}\) The lattice parameters are affected by the type of the substituent used, leading to the shrinkage or expansion of the cell. Generally for an alloy system, Vegard’s law is expected to be obeyed. \(^{45}\) The law emphasizes the fact that the sizes of the atoms, independent of the other parameters, have a marked effect on the crystal structure. A linear relationship between lattice constants-composition can be found in the alloys or solid solutions. The extent of solubility of a substituent component can be determined by Hume-Rothery rules, \(^{46}\) which states that the formation of the solid solution is facilitated by (a) analogous electronegativity of solute and solvent (b) the difference in radii of solute and solvent must be less than 15 % (c) similar valency, and (d) identical crystal structures of solute and solvent for complete solubility. The chalcogenide atoms (sulfur and selenium), fulfill these requirements and favours the formation of alloys of the type MS\(_1\),Se. Hence, the thio/seleno-carboxylate complexes of the organotin were used to generate the SnS\(_{1-x}\),Se, solid solution in the entire range.

The thermal stability of both complexes was analysed by thermogravimetric analysis (Supplementary Figure S1). The TGA curve for both complexes show decomposition in a single step, and the complete decomposition occurs around 315 °C. Complex (2) decomposes at a slightly higher temperature as compared to complex (1). The differential thermogravimetric analysis indicates that the maximum mass loss for complex (1) occurred at 290 °C, and a slight loss was indicated by a shoulder peak at 310 °C (Supplementary Figure S1(a)). Similarly, DTG curve for complex (2), indicates a comparatively higher stability of complex (1) and maximum weight loss was observed at 313 °C (Supplementary Figure S1(b)). The residual mass for both of the complexes was around 15 %, which is less than the expected masses required for SnSe (32.8 %) and SnS (29.7 %). The residual mass does not correspond to any other selenide or sulfide phase, elemental tin, sulfur, selenium or oxide based product. It was observed that both organotin complexes were volatile and undergo sublimation during the thermogravimetric analysis. There are some previous reports on the sublimating nature of the organotin complexes. \(^{6, 47}\) The mass loss during sublimation can prevent the accurate determination of the final residue, hence the nature of residue cannot be determined simply on the basis of percentage mass left at the end.

The nature of the residue was observed by heating both complexes separately from room temperature to 500 °C in a tube furnace, under continuous nitrogen flow for one hour. After an hour, the heating was turned off and the furnace was allowed to cool to room temperature. The black residue obtained after cooling was collected and analysed by p-XRD. The analysis of residual powder obtained from decomposition of complex (1) shows the formation of pure SnSe, whereas the decomposition product of complex (2) yields pure SnS (Supplementary Figure S2).

Colloidal synthesis of SnS\(_{1-x}\),Se solid solution

Oleylamine (OLA) is a strong coordinating agent and often catalyses the degradation of complexes at temperatures quite lower than their decomposition temperature, as indicated by their TGA profile. \(^{33, 48}\) During temperature optimization, it was
observed that the complexes show no sign of decomposition below 190 °C, whereas at 200 °C, both complexes decompose partially giving a small product. However at 230 °C, complete decomposition of the complexes occurred giving products with good crystallinity and yields. This indicates high stability of both complexes as some other thio/seleno-benzoate complexes are reported to decompose immediately in the presence of a primary amine, even at room temperature. Nevertheless, the breakdown of both complexes below their decomposition temperature, indicated by their TGA profile, shows the role of the OLA as a catalyst and decomposition initiator. Hence, all reactions as part of the colloidal synthesis were performed at an optimized temperature of 230 °C.

The p-XRD pattern of all the samples prepared by the colloidal synthesis is shown in Figure 1. The peaks were sharp for all the samples which confirm their crystalline nature and it is also helpful to observe the shift in the peaks. The mole fraction (x = 0) represents the p-XRD pattern of SnS (ICDD # 01-075-2115) and (x = 1) shows diffraction pattern of SnSe (ICDD # 00-014-0159), both match well with the standard pattern. It was interesting to note that, in the starting precursor, the Sn atom is in the +4 oxidation state but both of the complexes yielded tin monochalcogenide as the main product. It is probably due to the reductive nature of the OLA that Sn+4 was reduced to the Sn+2 state during the reaction.

The diffraction peaks for the SnSₓSnSeₓ solid solution lie intermediate of the diffraction peaks of SnS and SnSe. The peaks show a gradual shift with the change in the ratio of mole fraction. There was no indication of phase separation or multiple sets of peaks, only a single phased diffraction pattern was observed, which confirms the formation of the solid solution. The shift in the peaks is in agreement with Vegard’s law i.e. change in d-spacing with change in the composition. The peaks shifted towards a lower theta value with increase in selenium content, due to an expansion of the lattice parameters with substitution of the smaller sulfur atoms (1.84Å) by the larger selenium atoms (1.98Å).

The morphologies of the synthesized binary and alloyed SnSₓSnSeₓ system was observed by SEM analysis and images are shown in Figure 4. The images are marked with different compositions of selenium from x = 0 to x = 1, and all presented images are taken at the same magnification for comparison. SnS shows cubic sheet like structures, which is in the order of microns (Figure 4(a)). With the introduction of selenium, the sheets started transforming from cubic to a hexagonal morphology (Figure 4(b,c)). Further increases in selenium content result in a decrease in size of the sheets, eventually giving short sheets or plate like structures.

In general, all the samples showed sheet-like structure. Both SnS and SnSe are isostuctural and the growth of sheets can be explained on the basis of orientation and the type of interactions present in their building blocks. The preferential growth crystallization for SnS is an orthorhombic structure with Pnma space group. Virtually, the SnS structure can be viewed as a slightly distorted rock salt structure, due to the withdrawal of electron density from Sn to a more electronegative S atom. Furthermore, the presence of a lone pair of electrons on the Sn atom has a significant impact in the distortion of the rock salt structure to the distorted orthorhombic layered structure. In the layered structure, the Sn atom is strongly connected to S atoms within the layer, with short and strong Sn-S bonds (≈ 0.266 nm), whereas the layers are interconnected to each other by comparatively long and weak Van der Waals interactions (≈ 0.388 nm). As a result, the layers of SnS can be easily separated and cleaved perpendicular to the c-axis. SnSe has a similar structure and...
bonding structure, hence all the samples showed a sheet-like structure.

**Melt method for the synthesis of SnS\(_{1-x}\)Se\(_x\) solid solution**

The SnS\(_{1-x}\)Se\(_x\) solid solution was also synthesized by the solvent-less melt method. The melt method was used to observe the influence of the capping agent on the formation of the product. In the melt method, the compounds are heated under an inert environment and the reactive melt formed undergoes decomposition, with removal of organic moieties, leading to the formation of the pure product. Thermogravimetric analysis indicates that, both complexes decompose completely in the temperature range of 305-315 °C, therefore a slightly higher temperature of 330 °C was used to ensure the complete decomposition of the complexes and high crystallinity of the product. The decomposition of the precursors yielded tin monochalcogenides respectively. The p-XRD analysis of SnS, SnS\(_{1-x}\)Se\(_x\) and SnSe synthesized by the solvent-less method is shown in Figure 5.

The peaks were sharp and the diffraction patterns for the binary tin monochalcogenides i.e. for the mole fraction x = 0 (SnS) and x = 1 (SnSe), match well with the standard pattern and confirm the formation of the pure product. A shift in peak position was observed when the mixture of complexes was used to prepare a solid solution, however, when the diffraction peaks were zoomed in, multiple peaks were also observed as shoulders for the mole fraction value of x = 0.2 and x = 0.4. The splitting of the peaks present at 2θ = 30.5 to 32.5 shows that there is a presence of SnS, which exists along with the solid solution and results in the phase segregation of the synthesized material. The separation was prominent at lower concentration of selenium (i.e. x ≈ 0.2) and fades away at higher incorporation of selenium. The intensity profile was also different from the diffraction pattern observed for the samples synthesized by the colloidal method.

It was observed during TGA analysis that the complexes are volatile and undergo sublimation, making accurate residual mass determination difficult. Similarly, the volatile nature may be responsible for improper mixing, as some of the complex might have sublimed and decomposed on the walls of the ceramic combustion boat, and appear as an impurity in the final product. However, the selenium was also merged into the crystal lattice, which can be confirmed by the shift in the diffraction peaks due to the change in the d-spacing.

The expansion in the cell as a result of the change in lattice parameters was calculated from the data of the intense peaks present in the diffraction pattern (Figure 6). The change in the lattice parameters with respect to the composition was nonlinear, the maximum deviation occurred at the Se/(Se+S) composition of x = 0.2 and x = 0.4. The irregularity in the lattice parameters also compliments the p-XRD pattern, and the phase segregation can be seen clearly at these compositions. The change in volume of cell from SnS to SnSe was plotted against composition and as expected the alteration in the volume was also uneven.

The EDX analysis was conducted to have an insight of the composition of the solid solution synthesized by the solvent-less melt method (Supplementary Figure S6). The analysis reveals that the binary as well as ternary alloys were chalcogenide deficient materials. Although, the amount of both sulfur and selenium was less than the required value, it can be seen that the deviation in the case of selenium is even more as compared to sulfur. Furthermore, the composition of the binary compounds i.e. SnS and SnSe also shows higher deficiency of selenium in SnSe as compared to sulfur in SnS (Supplementary Figure 7). It shows that the sulfur is more competitive in the reaction conditions used for the melt method. The deficiency of the chalcogenides is probably due to the high temperature used, and high partial pressure associated with the chalcogens. It is a common observation that thin films of metal chalcogenides deposited at high temperature are often chalcogen deficient.\(^{53}\) Hence, the stoichiometry of the synthesized alloys by the melt method is significantly altered (Supplementary Table S2) as compared to the alloys prepared by the colloidal method.

The morphology as determined by SEM, indicates the formation of sheet-like structures for all samples, which shows that the morphology was not influenced by the difference in the method of preparation (Figure 7). The Van der Waals interactions between the sheets are too fragile to sustain under harsh conditions such as presence of strong nucleophilic ligand and/or high temperature. The control over size also becomes challenging in such situations. It can be seen that the size of the SnS sheets (Figure 7(a)) is in the micron range and unlike OLA capped SnS, which shows predominantly cube like sheets, a mixture of irregular and hexagonal shaped plates were observed.

After the inclusion of selenium in the lattice, the morphology of the sheets showed a hexagonal-like structure but with some eroded edges. At higher selenium concentration i.e. when x ≈ 0.6 and 0.8, the shape became more defined and the size of the crystallites was also decreased. The trend of decreasing size in moving from SnS to SnSe, was similar to the pattern observed for the samples synthesized by the colloidal synthesis.

The homogenized distribution of all the elements in the SnS\(_{1-x}\)Se\(_x\) system was observed by elemental mapping (Supplementary Figure S8). The images show uniform distribution of the elements throughout the material.

The optical behaviour of the solid solution series was investigated by the UV-Vis-NIR spectroscopy and is shown in Figure 8. The stoichiometry of the solid solution obtained by colloidal method was comparatively better, hence, only those samples were used for the optical studies. The band gap decreases slightly (from 1.48 to 1.1 eV) with addition of selenium, and it can be seen that there is a little difference in band gaps of SnS\(_{1-x}\)Se\(_x\) system. Similar observations have been reported earlier,\(^{26,54}\) and it can be assumed that it is due to the similar nature of their band structures.

Conclusions

This/seleno-benzoate complexes of organotin were synthesized and used as single source precursors for the
synthesis of SnS, SnSe and SnS<sub>x</sub>Se<sub>y</sub> solid solution over the entire range, by two different synthetic routes. Both complexes have a volatile nature and undergo sublimation, which results in ambiguity in accurate mass determination of the residue by TGA, but p-XRD indicates clean decomposition to SnS and/or SnSe. In the colloidal route, OLA was used as the capping agent which helps in the decomposition of the complexes at temperatures lower than their decomposition temperature. Whereas, the melt method requires a high decomposition temperature of 350 °C. The volatility of complexes causes some problems, such as, sublimation of the complexes, and the resultant decomposition products were also observed to be chalcogen deficient.

The single source precursors provide efficient incorporation of selenium and a better control over composition was achieved by colloidal hot injection method, as determined by EDX analysis and gradual change in lattice parameters. In comparison, the change in lattice parameters was not smooth for the product obtained by the melt method and EDX analysis also shows a wider deviation from the required percentage. A comparison of the composition of the alloys, obtained by colloidal and melt method against the required composition is provided in Table 1. The morphology was independent of the method used, and a similar trend in size and shape was observed for both approaches. The band gap shows an increase in moving from SnSe to SnS. The route can be used for scalability of the solid solution and can be extended to other systems as well.

Acknowledgements
The authors are grateful to the National Research Foundation (NRF) South African Research Chairs Initiative (SARChI) for financial support.

Notes and references
Figure 1. (a) p-XRD pattern of SnS (x = 0), SnS$_{1-x}$Se$_x$ and SnSe (x = 1) synthesized in OLA at 200 °C (b) extended part of the p-XRD to show the shift in the peaks.
Figure 2. Unit cell of (a) SnS (ICDD # 01-089-0821) and (b) SnSe (ICDD# 01-075-1310) along with their bonds and Vander Waals distances.

Figure 3. Lattice constants a, b, and c derived from diffraction peaks, and inset shows change in volume of the cell, as a function of Se concentration ‘x’ in the OLA capped SnS$_{1-x}$Se$_x$ alloy system.
Figure 4. SEM images of (a) SnS, (b-e) SnS$_{1-x}$Se$_x$ and (f) SnSe sheets synthesized by the hot injection method.
Figure 5. (a) p-XRD pattern of SnS (x = 0), SnS$_{1-x}$Se$_x$ and SnSe (x = 1) synthesized by solvent-less route at 330 °C (b) extended part of p-XRD to show the shift in the peaks.
Figure 6. Lattice constants a, b, and c derived from the intense p-XRD diffraction peaks, and (inset) change in the volume of the cell, as a function of Se concentration ‘x’ in the SnS$_{1-x}$Se$_x$ alloy system synthesized by the melt method.
Figure 7. SEM images of (a) SnS, (b-e) SnS$_{1-x}$Se$_x$ and (f) SnSe sheets synthesized by the melt method.
Figure 8. (a) The UV-Vis-NIR spectra and (b) band gaps of the solid solution prepared by colloidal method.
Table 1. Comparison of the compositions observed by the EDX analysis for samples synthesized by colloidal and melt method.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Target composition</th>
<th>Stoichiometry from colloidal method</th>
<th>Stoichiometry from melt method</th>
</tr>
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<tr>
<td>0 (SnS)</td>
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<td>Sn\textsubscript{1.02}S\textsubscript{0.98}</td>
<td>Sn\textsubscript{1.07}S\textsubscript{0.93}</td>
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<td>Sn\textsubscript{1.03}S\textsubscript{0.76}Se\textsubscript{0.21}</td>
<td>Sn\textsubscript{1.06}S\textsubscript{0.77}Se\textsubscript{0.17}</td>
</tr>
<tr>
<td>0.4</td>
<td>SnS\textsubscript{0.60}Se\textsubscript{0.40}</td>
<td>Sn\textsubscript{1.02}S\textsubscript{0.61}Se\textsubscript{0.37}</td>
<td>Sn\textsubscript{1.05}S\textsubscript{0.58}Se\textsubscript{0.37}</td>
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<tr>
<td>0.6</td>
<td>SnS\textsubscript{0.40}Se\textsubscript{0.60}</td>
<td>Sn\textsubscript{1.03}S\textsubscript{0.39}Se\textsubscript{0.58}</td>
<td>Sn\textsubscript{1.11}S\textsubscript{0.37}Se\textsubscript{0.52}</td>
</tr>
<tr>
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</tr>
<tr>
<td>1 (SnSe)</td>
<td>SnSe</td>
<td>Sn\textsubscript{1.03}Se\textsubscript{0.97}</td>
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