Synthesis of (Bi$_{1-x}$Sb$_x$)$_2$S$_3$ solid solutions via thermal decomposition of bismuth and antimony piperidinedithiocarbamates†

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The synthesis of the complete range of (Bi$_{1-x}$Sb$_x$)$_2$S$_3$ solid solutions, where 0 ≤ x ≤ 1, by the variation of the mole ratio of bismuth and antimony piperidinedithiocarbamate complexes is reported. There was a near linear expansion of a and c lattice parameters as the mole ratio of the antimony precursor was increased. The composition of the particles directionally followed the amount of precursor ratio used. When the composition of particles was compared to cell parameters, a slight deviation from Vegard’s law was observed with a corresponding contraction of the b parameter and an approximately 3.5% reduction of the lattice volume. The nanorods obtained showed aspect ratios that depend on the composition of the material. The Bi and Sb rich materials had high aspect ratios of 16.58 and 16.58 respectively with a minimum aspect ratio of 2.58 observed for x = 0.50.

Sodium ion batteries,16–22 solar cells based on Sb$_2$S$_3$ films have been fabricated with power conversion efficiency of 4.3%.23,24 Despite the significant difference in their sizes Bi and Sb form a full range solid solution series between stibnite and bismuthinite.25–26 The formation of a solid solution between the two compounds is due to their similarity in charge, ability to crystallize in the same orthorhombic lattice with space group Pnma, having typical lattice parameters of a = 11.269 Å, b = 3.9717 Å and c = 11.2270 Å for bismuthinite and a = 11.2990 Å, b = 3.8313 Å and c = 11.2270 Å for stibnite.27–29 Their orthorhombic unit cell volume differs by 3.5%.29–32 Analysis on various stibnite and bismuthinite samples from various localities show that replacement of Sb with Bi goes up to 55 moles% giving a limiting miscibility range of (Bi$_{0.45}$Sb$_{0.55}$)$_2$S$_3$ in naturally occurring Bi$_2$S$_3$–Sb$_2$S$_3$ solid solution.25,32,33 This paucity of representation covering the whole solid solution range in natural samples is attributed to the different geological conditions under which bismuthinite and stibnite are deposited in nature.25–34 Kyono et al. synthesised a full range (BiSb)$_2$S$_3$ solid solution series with a nearly statistical substitution of Sb by Bi from a starting mixture with the same Bi$_2$S$_3$:Sb$_2$S$_3$ molar ratio. This observation of large deviations from linear trends in the lattice constants was in contradiction to earlier work by Nayak et al. that showed good agreement with Vegard’s law on the entire solid solution range by depositing thin films of the solid solution by a dip-dry method.35 Colloidal synthesis of nanostructures in surface passivating agents has proven to be an efficient route as it provides easy control over size and...
shape.\textsuperscript{35,36} Wang et al. used a dual precursor source route to synthesize a full range solid solution of (Bi\textsubscript{1-x}Sb\textsubscript{x})\textsubscript{3}S\textsubscript{3} with aspect ratios that depended on their compositions.\textsuperscript{3} Patra et al. did similar work using diethylthiocarbamate complexes in oleylamine and thiol.\textsuperscript{4} However, they did not investigate the influence of the Sb substitution on the lattice constant.\textsuperscript{27} Khan et al. prepared the entire range of (SnS\textsubscript{1-x}Se\textsubscript{x}) from bis(selono-benzoato)dibutyltin(IV) and bis(thiobenzoato)-dibutyltin(IV) complexes by colloidal and melt methods and showed that the colloidal method provided superior control over composition, though both methods showed compositional dependence in the variation of the lattice parameters.\textsuperscript{28} In our earlier work, we showed that addition of a small amount of dodecanethiol was efficient in directing the shapes of Bi\textsubscript{2}S\textsubscript{3} rods from single source precursors by thermal decomposition of bismuth dithiocarbamate complexes in high boiling point coordination solvents.\textsuperscript{39} This paper examines the effect of substituting antimony for bismuth on the structure of the bismuthinite–stibnite solid solution prepared by bismuth pipedrine and antimony pipedrine dithiocarbamate complexes.

Experimental section

Bismuth trichloride (98\%, Sigma-Aldrich), antimony trichloride (99\%, Sigma-Aldrich), carbon disulphide (99.9\%, Sigma-Aldrich), piperidine (99.5\% Sigma-Aldrich), oleylamine (98\% Sigma-Aldrich), 1-dodecanethiol (98\% Sigma-Aldrich), ethanol (99.8\% Sigma-Aldrich), chloroform (99.8\% Sigma-Aldrich), chloroform-d\textsubscript{4} (99.8\% Sigma-Aldrich), and sodium hydroxide (97\% Fisher Scientific) were used as supplied without further purification.

Synthesis of the precursors

Preparation sodium pipedrine dithiocarbamate (1). The synthesis of (1) followed previously reported procedure with modifications.\textsuperscript{39} In a typical synthesis, carbon disulfide (0.1 mol, 6.0 mL) was added to an equimolar mixture of sodium hydroxide (0.1 mol, 4.0 g) and pipedrine (0.1 mol, 9.9 mL) cooled to 0 °C. After 15 min, the white precipitate formed was filtered, dried in air and recrystallised from acetone/petroleum ether. Na(S\textsubscript{2}CPip); yield: 92\%/mp 295 °C. Significant IR bands: \textnu\textsubscript{C=O} = 3377 (O–H), 964 (C=S), 1468 cm\textsuperscript{-1} (C=N); elemental analysis (\%) for C\textsubscript{18}H\textsubscript{32}N\textsubscript{3}O\textsubscript{6}Bi; calc; C 30.54, H 4.56, N 5.94, S 27.18, Bi 29.52. Found; C 30.99, H 4.28, N 5.98, S 26.80, Bi 29.39.

Preparation of tris(piperidindithiocarbamato)bismuth(m) (2). The synthesis of (2) followed our previous procedure with modifications.\textsuperscript{39} BiCl\textsubscript{3} (5.0 mmol, 1.58 g) was suspended in ethanol (15.0 mL), and added dropwise to a solution of the pipedrine dithiocarbamate ligand (15.0 mmol, 2.75 g) in ethanol (25.0 mL). The resultant solution was stirred for 1 h. The pale-yellow precipitate formed was collected by filtration and recrystallized from chloroform.

Sb(PipDtc)\textsubscript{3}:3H\textsubscript{2}O: yield 82\% mp 239 °C. Significant IR bands: \textnu\textsubscript{C=O} = 3377 (O–H), 967 (C=S), 1476 cm\textsuperscript{-1} (C=N); elemental analysis (\%) for C\textsubscript{18}H\textsubscript{30}N\textsubscript{6}S\textsubscript{8}Sb; calc; C 32.72, H 5.84, N 6.47, S 30.14, Sb 19.15.

Synthesis of (Bi\textsubscript{1-x}Sb\textsubscript{x})\textsubscript{3}S\textsubscript{3} solid solutions

(Bi\textsubscript{1-x}Sb\textsubscript{x})\textsubscript{3}S\textsubscript{3} solid solutions were prepared by variation of the mole ratio of (2) and (3). In a typical experiment, a mixture of (2) and (3) totalling 0.29 mmol was dispersed in a mixture of oleylamine (4.0 mL) and 1-dodecanethiol (0.2 mL). This was injected into 8.0 mL of hot oleylamine (230 °C) under N\textsubscript{2}. After 30 min the reaction was quenched, and the ensuing black precipitate washed three times with ethanol (12.0 mL), centrifuged (11 000 rpm) and dispersed in toluene (5.0 mL).

Instrumentation

Fourier transform infrared spectroscopy was performed using a Thermo Scientific Nicolet iS5 instrument (4000–400 cm\textsuperscript{-1}, resolution 4 cm\textsuperscript{-1}). Optical measurements were performed on a Shimadzu UV-1800 spectrophotometer. Elemental analysis was performed with a Thermo Flash 2000 and Carlo Erba EA 1108 elemental analysers (Department of Chemistry University of Manchester). Melting points were recorded on a Stuart SMP10 Melting point apparatus. Thermogravimetric analysis was performed on a Seiko SSC5200/S220TG/DTA model, at a heating rate of 10 °C min\textsuperscript{-1} from 30 °C to 600 °C, under nitrogen.

XRD patterns of the thin films were collected on a PANalytical X’Pert PRO powder diffractometer (Material Science University of Manchester) with a Cu K\alpha radiation source (\lambda = 1.5406 Å). The samples were mounted flat and scanned over the 2\theta range of 10–70° in a step size of 0.05.

X-ray photoelectron spectroscopy (XPS) was performed using an Axis Ultra Hybrid (Kratos Analytical, United Kingdom) using 10 mA emission (150 W) of monochromated Al K\alpha radiation (1486.6 eV). Samples were pressed onto carbon tape, and a charge neutraliser was used to replenish electrons at the surface and remove the effects of differential charging under the X-ray beam. High resolution spectra were collected using an electron energy analyser pass energy of 20 eV and survey spectra with 80 eV pass energy.

X-ray photoelectron spectroscopy (XPS) data were analysed using CASAXPS (www.casaxps.com): the binding energy scales were calibrated using the principle C 1s peak associated with hydrocarbon at 284.8 eV, Shirley backgrounds were fitted where appropriate, and atomic concentrations were calculated using relative sensitivity factors incorporating the photoionization
cross section for each core electron orbital, as well as the transmission function of the electron energy analyser. Peak fitting using Voigt-approximation Gaussian–Lorentzian products was performed to obtain binding energy positions for chemical species determination.

Transmission electron microscope (TEM) images, high resolution transmission electron microscope (HRTEM) images, selected area electron diffraction (SAED) patterns and energy dispersive X-ray spectroscopy (EDS) spectra were obtained with an FEI Talos F200A microscope (PSI, University of Manchester) equipped with an X-FEG electron source and Super-X SDD EDS detectors. The experiment was performed using an acceleration voltage of 200 kV and a beam current of approximately 5 nA. Images were recorded with a FEI CETA 4k × 4k CMOS camera. Single crystal X-ray data were collected on a dual source Rigaku FR-X rotating anode diffractometer using Cu Kα wavelength at 150 K and reduced using CrysAlisPro 171.39.30c. Absorption correction was performed using empirical methods (SCALE3 ABSPACK) based upon symmetry-equivalent reflections combined with measurements at different azimuthal angles. The structure was solved and refined using Shelx-2016 implemented through Olex2 v1.2.9.2.3.

Results and discussion

Characterization of the precursors

The reaction of piperidine dithiocarbamate with BiCl₃ and SbCl₅ gave tris(piperidinedithiocarbamato)bismuth(m) [Bi(S₂CIPip)₃] (2) and tris(piperidinedithiocarbamato)antimony(m) (Sb(S₂CIPip)₃) (3) respectively. The presence of the dithiocarbamate moiety in the two complexes was shown by the characteristic thiourea band v(C=–N) around the 1450–1500 cm⁻¹ region and the v(C=S) band around the 960–1000 cm⁻¹. These bands appeared shifted to higher frequencies in the spectrum of the corresponding free ligand. The bidentate nature of the coordination of the dithiocarbamate ligand was shown by the band around 960–1000 cm⁻¹ which appeared unsplit. Broad bands around 3300–3500 cm⁻¹ in the spectra of the ligands as well as the antimony piperidine complex is due to the presence of moisture in the compounds.

Single crystals of complex (3) were grown in chloroform/ethanol mixture, and their X-ray crystal structure was determined at 150 K. The low temperature structure of tris(piperidinedithiocarbamato)antimony(m) (Sb(S₂CIPip)₃), crystallizes into a six coordinate Sb complex surrounded by three piperidinedithiocarbamato groups bonded through S donor atoms. There are three short Sb–S distances of ~2.53 Å and three long Sb–S distances of ~2.9–3.0 Å. There is a stereoelectronically active lone pair on the Sb atom such that the (seven) steric groups (6 S donors and 1 lone pair) occupy the vertices of an ‘elongated triangular pyramid’ in which there are parallel triangular sets of S donors with the lone pair pointed normal to the planes of 3 S atoms (the short Sb–S and the long Sb–S). A similar structure was reported by Liu and Tieckink at a much higher temperature of 223 K. The three short Sb–S bond length was found to be ~2.52 Å and that of the three long Sb–S bonds were 2.86 Å, which favourably compares to those of complex (3). The mean intercalate S–Sb–S bond angles of 93.60 of complex (3) is also comparable to 92.32 of the reported structure. The crystal structure, some selected bond lengths together with the crystallographic data and structural refinement parameters for complex (3) are shown in ESI 2, 3 and 4 respectively.

The thermogram of complex (2) shows a three-step decomposition pattern. The first mass loss of 3.05% (2.56% calculated) at 128 °C corresponds to the loss of H₂O molecules. The second mass loss of 59.47% (58.56% calculated) at 281 °C corresponds to the loss of the organic moiety and sulfur, while the third mass loss of 10.41% (11.09% calculated) at 464 °C is attributed to the additional loss of sulfur with the formation of a final residue of 33.67% (35.9% calculated) corresponding to Bi₂S₃. Complex (3) shows a two-step decomposition pattern, with the first mass losses of 8.68% (8.14% calculated) at 100 °C corresponding to the loss of the three water molecules and a second mass loss of 70.49% (72.44% calculated) attributed to the loss of the organic moiety and sulfur with the formation of a residue of 26.16% (25.56% calculated) which corresponds to Sb₂S₃ (Fig. 1).

Compositional characterization

The EDX data (Fig. 2) where the sampling depth is ≫ the nanorod diameter shows that the composition of the particles synthesised is in close agreement with the mole fraction of precursors used. This result is unusual with single source precursors as the difference in metal–sulfur bond strengths normally governs the rate of decomposition and consequentially skews the composition to the more reactive metal–sulfur bond. A plot of Sb precursor mole fraction against the proportion of antimony in the particles gave a close to straight line (Fig. 2b) with full details in Table 1. Many of the samples were sulfur rich which is possibly due to the relatively low reaction temperature which prevented evaporation of sulfur, a situation commonly observed in samples prepared at a much higher temperature.42,43

The X-ray diffraction patterns obtained for all the Bi/Sb ratios correspond well to the orthorhombic crystal system, with peaks for the Bi–Sb–S system falling between previously reported patterns of orthorhombic bismuthinite (α (a = 11.2690 Å, b = 3.9717 Å and c = 11.1290 Å) and orthorhombic stibnite (β (a = 11.2290 Å, b = 3.8313 Å and c = 11.2270 Å), Fig. 3a. Sb₂S₃ and

![Fig. 1. Thermogram of complexes (2) and (3).](image-url)
Bi$_2$S$_3$ both crystallize in the same orthorhombic lattice system with a difference in cell volume of 3.5% due to Sb$^{3+}$ possessing a smaller ionic radius than Bi$^{3+}$. The enlarged portion of the XRD pattern of the samples show a shift in the peak position confirming the successful incorporation of Sb into the Bi$_2$S$_3$ lattice and the movement through the entire compositional range of the (Bi$_{1-x}$Sb$_x$)$_2$S$_3$ solid solution, Fig. 3b. A plot of the d-spacing for the (112) plane shows a gradual decrease from Bi$_2$S$_3$ to the Sb$_2$S$_3$ end with a percentage difference of 2.26% (ESI 5†).

Refinement of the powder XRD data shows that all three axes of the unit cell vary linearly (Fig. 4). Upon increased incorporation of antimony, $a$ and $c$ increase whereas $b$ decreases which is the expected behaviour when moving between Bi$_2$S$_3$ and Sb$_2$S$_3$. All three cell parameters show a linear dependency on the amount of antimony in the solid solution which agrees with Vegard’s law. The subtle deviations in $a$ and $c$ from ideal behaviour may be due to the contrasting effect of the stereochiometric active lone pair of the 5s$^2$ and 6s$^2$ electrons of the antimony and bismuth atoms, which is positioned in the $a$–$c$ plane of the lattice.$^{37,44}$ With an increased concentration of antimony, there is expansion of the inter-rod space due to the expression of the stereochiometrically active lone electron pair with a resulting expansion of the $a$ and $c$ parameters.$^{39}$ However, the $b$ axis which is least affected by the stereochiometric active lone pair experiences a continuous contraction on Sb substitution, probably due to decrease in the shortest M–S bond as we move from the Bi$_2$S$_3$ to the Sb$_2$S$_3$ end.$^{26}$ There is a general shrinkage of the overall cell volume of (Bi$_{1-x}$Sb$_x$)$_2$S$_3$ as Bi is replaced by Sb (Fig. 4d).

The high-resolution transmission electron microscopy (HRTEM) images of the samples together with their selected area electron diffraction (SAED) patterns reveal the formation of highly polycrystalline powders showing two-dimensional lattice fringes (Fig. 4). Measured $d$-spacings of 3.69 and 4.98 Å were obtained for pure Bi$_2$S$_3$ (Fig. 5a) corresponding to the (011) and (102) planes (SG $Pnma$ with $a = 11.2690$ Å, $b = 3.9717$ Å and $c = 11.1290$ Å) while for pure Sb$_2$S$_3$ (Fig. 5i) a $d$-spacings of 3.50 Å corresponding to the (111) (SG $Pnma$ with $a = 11.2990$ Å, $b = 3.8313$ Å and $c = 11.2270$ Å) plane was recorded.

XPS is a much more surface sensitive technique than EDX, with sampling depths varying 6.3–9.0 nm for Sb, Bi and S,$^{45}$ which is much less than the nanorod diameter. Bi 4f coincides with the S 2p region, and Sb 3d coincides with O 1s. Fig. 6 shows a pile-up of the Bi 4f/S 2p and Sb 3d/O 1s regions for Bi$_2$S$_3$, Sb$_2$S$_3$ and (Bi$_{1-x}$Sb$_x$)$_2$S$_3$.

### Table 1 Structural data for Bi$_2$S$_3$, Sb$_2$S$_3$ and (Bi$_{1-x}$Sb$_x$)$_2$S$_3$ solid solution

| $X_{Bi}$ (%) | $X_{Sb}$ (%) | Chemical composition (EDX) | $a$ (Å) | $b$ (Å) | $c$ (Å) | $V$ (Å$^3$) |
|-------------|-------------|---------------------------|--------|--------|--------|----------|
| 100.0       | 0.0         | Bi$_{1.99}$S$_{3.05}$     | 11.24  | 3.97   | 11.13  | 496.68   |
| 87.5        | 12.5        | Sb$_{0.38}$Bi$_{1.66}$S$_{3.05}$ | 11.24  | 3.95   | 11.14  | 494.32   |
| 75.0        | 25.0        | Sb$_{0.58}$Bi$_{1.42}$S$_{3.08}$ | 11.24  | 3.93   | 11.14  | 492.90   |
| 62.5        | 37.5        | Sb$_{0.79}$Bi$_{1.15}$S$_{3.06}$ | 11.25  | 3.92   | 11.16  | 491.88   |
| 50.0        | 50.0        | Sb$_{0.97}$Bi$_{0.95}$S$_{3.08}$ | 11.26  | 3.91   | 11.19  | 492.00   |
| 37.5        | 67.5        | Sb$_{1.22}$Bi$_{0.75}$S$_{3.04}$ | 11.26  | 3.87   | 11.19  | 487.13   |
| 25.0        | 75.0        | Sb$_{1.49}$Bi$_{0.51}$S$_{3.00}$ | 11.26  | 3.86   | 11.21  | 489.03   |
| 12.5        | 87.5        | Sb$_{1.80}$Bi$_{0.24}$S$_{2.96}$ | 11.27  | 3.82   | 11.22  | 487.23   |
| 0.0         | 100.0       | Sb$_{1.93}$S$_{3.07}$     | 11.27  | 3.82   | 11.22  | 483.22   |

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Fig. 2 (a) EDS spectra of (Bi$_{1-x}$Sb$_x$)$_2$S$_3$ nanorods at different Bi : Sb mole ratios (b) particle composition $x$ obtained from EDS against precursor mole fraction.
In all cases the Bi 4f doublet required two chemical species (two sets of spin–orbit–split doublets) in order to obtain an adequate fit, with positions for the Bi 4f7/2 photoelectron peaks at 158.1 eV (associated with Bi2S3 and 158.8 eV (associated with oxidized Bi2O3. Likewise, the Sb 3d doublet required two chemical species for adequate fitting, with peak positions for 3d5/2 at 259.1 eV (associated with Sb2S3 and 530.1 eV (associated with oxidized Sb2O3). Note that O 1s photoelectron peaks are close to the Sb 3d5/2 signal, typically with binding energy positions at ~530.5 eV associated with metal oxides (i.e., BiOx, SbOx), ~532 eV associated with C–O contamination, and ~533 eV associated with C=O contamination. A variety of (Bi,Sb)xS3 samples were measured, and consistently a peak-fitting model including sulfide and oxide species was required for both Bi and Sb. However, no oxidation was seen for S, only one species for the S 2p doublet was observed for all the samples measured, with the peak position for 2p3/2 at ~161.0 eV associated with sulfide, and in the spectra there is a clear absence of any signal associated with sulfate which is expected in the binding energy region 168–170 eV. Also, when calculating the atomic ratios of Bi : Sb : S, there is consistently an absence of S as expected for (Bi1–xSb)xS3. In Fig. 6 the (Bi,Sb)xS3 sample exhibits a Bi : Sb : S ratio of 3 : 3 : 4 (or 1 : 1 : 1.3, short of the expected 1 : 1 : 1.5). This indicates that there is an absence of sulfur atoms at the surface of
the nanorods hence the atomic concentrations (Table 2) are skewed from the bulk measurement by EDX analysis. This also explains the lack of sulfur oxidation while a small amount of Bi and Sb atoms at the surface of the nanorods are susceptible to oxidation. For the range of \((\text{Bi}_{1-x}\text{Sb})_2\text{S}_3\) nanorod materials measured, the amount of oxidation of Bi and Sb observed varied between 10–40% (with an average value of 20% for Bi and 26% for Sb).

**Morphological characterization**

TEM analysis on the samples showed the presence of particles with a rod-shaped morphology, Fig. 7a–i. When the bismuth precursor was exclusively used, uniform elongated cylindrical nanorods of Bi\(_2\)S\(_3\) were obtained however the antimony precursor gave long sheaf-like collections of Sb\(_2\)S\(_3\) rods in the sub-micrometre range (Fig. 7i and 8e).

There was a conspicuous change in the aspect ratio of the rods as the Bi : Sb precursor mole ratio was varied, Table 3. With a Bi : Sb precursor mole ratio of 7 : 1, there was a considerable reduction in both the length and aspect ratio of the nanorods compared to pure Bi\(_2\)S\(_3\) until a mole ratio of 1 : 1, which gave an aspect ratio of 2.58 (Table 3). Wang *et al.* prepared \((\text{Bi}_{1-x}\text{Sb})_2\text{S}_3\) 1-d rods, by reacting bismuth chloride, antimony chloride, sulphur powder, oleylamine and thiols and observed composition dependant aspect ratios.\(^\dagger\) Sun *et al.* synthesized flower-like architectures Sb\(_2-\)Bi\(_2\)S\(_3\) by solvothermal treatment of bismuth and antimony diethyldithiocarbamate complexes. They proposed a mechanism in which 3-d flowers grow through an epitaxial growth on Sb\(_2-\)Bi\(_2\)S\(_3\) core.\(^5\) When we increased the precursor mole ratio of Sb beyond 1 : 1, the aspect ratio increased along with the length of the rods. At a mole ratio of 1 : 7 the longest rods of the solid solution were observed. Sb\(_2\)S\(_3\) has a partial fractal splitting growth habit which often lead to the formation of sheaf-like morphologies.\(^6\) However, the inclusion of Bi ions alters the growth dynamics by inducing complete splitting growth and consequently changes morphology from very long sheaf-like sub-micrometre Sb\(_2\)S\(_3\) rods to shorter separate nanorods. The particle size distribution of the as synthesized nanorods are shown in ESI 6.\(^\dagger\) TEM images of intermediate Bi : Sb ratio to those reported are shown in ESI 7.\(^\dagger\)

**Table 2** Relative percentage concentrations of Bi, Sb and S for Bi\(_2\)S\(_3\), Sb\(_2\)S\(_3\) and \((\text{Bi}_{1-x}\text{Sb})_2\text{S}_3\) solid solution

| Sb/(Sb + Bi) | Bi-S% | Bi-O% | Total Bi% | Sb-S% | Sb-O% | Total Sb% | S% |
|-------------|-------|-------|----------|-------|-------|----------|-----|
| 0           | 49.79 | 18.69 | 68.49    | 0.00  | 0.00  | 0.00     | 31.51 |
| 0.125       | 49.11 | 9.33  | 58.43    | 4.44  | 0.49  | 4.93     | 36.64 |
| 0.25        | 45.20 | 8.61  | 53.81    | 7.86  | 1.56  | 9.43     | 36.76 |
| 0.375       | 37.32 | 8.25  | 45.57    | 17.53 | 1.76  | 19.29    | 35.14 |
| 0.5         | 34.86 | 5.81  | 40.67    | 15.53 | 1.67  | 17.21    | 37.60 |
| 0.625       | 27.85 | 5.32  | 33.17    | 20.94 | 7.39  | 28.34    | 38.49 |
| 0.75        | 27.45 | 3.40  | 30.85    | 23.36 | 6.67  | 30.03    | 39.13 |
| 0.875       | 17.09 | 1.66  | 18.74    | 29.75 | 11.16 | 40.91    | 40.35 |
| 1           | 3.56  | 0.00  | 3.56     | 38.20 | 12.14 | 50.34    | 46.10 |

**Table 3** Dimensions of synthesised nanorods of Bi\(_2\)S\(_3\), Sb\(_2\)S\(_3\) and \((\text{Bi}_{1-x}\text{Sb})_2\text{S}_3\) solid solution

| Sb/(Sb + Bi) | Length (nm) | Width (nm) | Aspect ratio |
|-------------|-------------|------------|--------------|
| 0           | 474.4 ± 92.62 | 28.61 ± 12.90 | 16.58         |
| 0.125       | 104.99 ± 46.38 | 19.79 ± 9.13 | 5.31          |
| 0.25        | 65.13 ± 13.52 | 23.69 ± 6.50 | 2.75          |
| 0.375       | 57.00 ± 11.12 | 15.35 ± 4.07 | 3.66          |
| 0.5         | 60.38 ± 12.60 | 23.38 ± 4.38 | 2.58          |
| 0.625       | 25.04 ± 7.37  | 5.56 ± 1.09  | 4.51          |
| 0.75        | 142.81 ± 56.58 | 28.56 ± 5.03 | 5.00          |
| 0.875       | 386.32 ± 137.43 | 40.05 ± 11.08 | 9.65          |
| 1           | 2880.47 ± 550.22 | 137.09 ± 44.82 | 21.01         |
Optical properties

Bi$_2$S$_3$ and Sb$_2$S$_3$ possess direct band gaps of approximately 1.3 and 1.7 eV respectively, corresponding to 954 and 729 nm. The band gap of the ternary (Bi$_{1-x}$Sb$_x$)$_2$S$_3$ solid solutions made using different ratios of Bi and Sb should be a linear interpolation of the two parent materials. Fig. 9a shows the UV-visible absorption spectra of the as-prepared ternary (Bi$_{1-x}$Sb$_x$)$_2$S$_3$ in which a strong broad absorption was seen within the wavelength range of 300–1100 nm. In general, the absorption edge of (Bi$_{1-x}$Sb$_x$)$_2$S$_3$ nanorods is blue-shifted with the increase of Sb ratio.

However, a plot of the absorption maximum against the antimony mole fraction shows a marked deviation from the expected linear behaviour of the band gap of ternary semiconductor materials (Fig. 10). This phenomenon known as band gap bowing is often ascribed to local compositional fluctuations which occur on substitution. The extent of such local atom displacements usually brings about nonlinear dependence on optical properties in ternary materials. O’Brien et al. synthesize Bi$_{2-2x}$Sb$_{2x}$S$_3$ solid solutions from solvent less thermolysis of metal xanthate precursors and showed a slight deviation from linearity in the energy band gap on Sb substitution due to stoichiometric variations in the synthesized solid solution.

The Raman spectra of the particles are shown in Fig. 11. In case of pure Bi$_2$S$_3$ sample, a minor peak was observed at 184 cm$^{-1}$ and two prominent peaks at 236 and 256 cm$^{-1}$, which is in agreement with the previously reported Raman data for Bi$_2$S$_3$. The minor peak is assigned as A$_g$ symmetric bending mode, whereas the dominant peaks (236 and 256 cm$^{-1}$) are B$_{1g}$ and B$_{1g}$ anti-symmetric stretching modes, respectively. Similarly, one minor and two major peaks at 186, 272 and 294 cm$^{-1}$ were observed for pure Sb$_2$S$_3$, which are in good agreement with the previous reports. The peak at 186 cm$^{-1}$ can be assigned to the B$_{1g}$ anti-symmetric S–Sb–S bending modes, whereas the peaks at 272 and 294 cm$^{-1}$ are assigned to the A$_g$ and B$_{1g}$ anti-symmetric Sb–S stretching modes, respectively. The solid solutions consisting of 25% antimony show mainly one broad band around 240 cm$^{-1}$, which shift to higher frequencies of 253 and 260 cm$^{-1}$ when the percentage of antimony is increased to 50 and 75% respectively. The shift towards the higher wavenumber is due to lower mass of Sb as compare to Bi and shorter Sb–S bond respectively.

Conclusions

By the thermal decomposition of bismuth and antimony piperidinedithiocarbamates in oleylamine nanorods of the entire compositional range of (Bi$_{1-x}$Sb$_x$)$_2$S$_3$ of solid solutions have been produced by varying the bismuth and antimony precursor mole fraction. The morphologies of the nanorods

Fig. 9 Elemental mapping of the particles synthesized at Bi : Sb mole ratio of 1 : 1 showing distribution of atoms (a) SE, (b) Sb, (c) Bi and (d) S.
dependent on their compositions, and aspect ratios that decreased to a minimum of 2.58 with maxima of 16.58 when using just the bismuth precursor and 21.01 when using the antimony precursor.

The XRD peaks at all ratios correspond to the orthorhombic crystals system and fall between those of orthorhombic Bi$_2$S$_3$ and orthorhombic Sb$_2$S$_3$. The gradual shift in the peaks position in combination with compositional data from EDX confirms the successful incorporation of antimony into bismuth sulphide which almost adheres to Vegard’s law.

**Conflicts of interest**

There are no conflicts to declare.

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