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Solid solutions of $\text{M}_{2-2x}\text{In}_{2x}\text{S}_3$ ($\text{M} = \text{Bi or Sb}$) by Solventless Thermolysis

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† Electronic Supplementary Information (ESI) available: Thermogravimetric analysis for Bi(S2COEt)3, Sb(S2COEt)3, In(S2COEt)3 precursors, powder X-ray diffraction Patterns of Bi2S3, Sb2S3 and In2S3 materials, Rietveld refinement, EDX analysis and absorption spectra of $\text{M}_{2-2x}\text{In}_{2x}\text{S}_3$. See DOI: 10.1039/x0xx00000x

Tris(O-ethylxanthato) bismuth(III) [Bi(S2COEt)3], tris(O-ethylxanthato) antimony(III) [Sb(S2COEt)3] and tris(O-ethylxanthato) indium(III) [In(S2COEt)3], have been synthesized and employed for the preparation of Bi-In-S and Sb-In-S solid solutions by solventless thermolysis. $\text{M}_{2-2x}\text{In}_{2x}\text{S}_3$ (where $\text{M} = \text{Bi or Sb}$) alloys were obtained using a mixture of In(S2COEt)3 and M(S2COEt)3 molecular precursors, with different mole fraction of indium x ($0 \leq x \leq 1$) at 300 °C. The structural, compositional, optical and morphological properties of the synthesized $\text{M}_{2-2x}\text{In}_{2x}\text{S}_3$ samples have been characterized using a range of techniques.
including powder X-ray diffraction (p-XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, Raman spectroscopy and UV–Vis absorption spectroscopy. PXRD data suggests the incorporation of molar ratio of indium up to $x \leq 0.4$ into the $M_2S_3$ does not alter the orthorhombic crystal structure of $M_2S_3$. Higher quantities of indium ($x \geq 0.6$) changes the crystal structure to cubic $M_2S_3$. The estimated elemental compositions from EDX data are in line with the stoichiometric ratio expected. SEM images revealed that the morphology of $M_{2-2x}In_{2x}S_3$ ($0 \leq x \leq 1$) samples varied significantly with the changes in indium mole fraction in the precursor mixture. Elemental mapping of the mixed samples $M_{2-2x}In_{2x}S_3$ ($0 \leq x \leq 1$) revealed uniform elemental distributions of M, In and S in every sample investigated. The estimated band gap of $Bi_{2-2x}In_{2x}S_3$ films varied from 1.66 to 2.39 eV, while the band gap of $Sb_{2-2x}In_{2x}S_3$ films varied in the range $2.19 – 2.9$ eV, and the energy can be tuned by variation of the indium content.

**Introduction**

Bismuth sulfide ($Bi_2S_3$) and antimony sulfide ($Sb_2S_3$) are V-VI semiconductor materials with direct band gaps, that have attracted considerable interest due to their high absorption coefficients and good transport characteristics. They have found applications in solar cells, non-linear optical materials and for thermoelectric power generation.\(^1\)\(^-\)\(^7\) Extensive research has been undertaken in terms of exploratory synthesis of new ternary or quaternary bismuth and antimony sulfides, with numerous compounds with promising properties reported. For example, $K_2Bi_8S_{13}$ and $La_7Sb_9S_{24}$ show promising thermoelectric properties, $Ba_2BiInS_5$\(^1\(^0\) and $La_4InSbS_9$\(^1\(^1\) show particularly strong second harmonic generation in the IR range, whilst $KBiCu_2S_3$ presents good photoelectric behaviour and offers potential utility in photovoltaic devices.\(^1\(^2\)
Indium sulfides are promising semiconductor materials for various optoelectronic and photovoltaic application,\textsuperscript{13-15} as a result of their interesting electronic properties, including intense absorption of light, photoconductivity, and bandgap energies across the visible and IR spectrum.\textsuperscript{16-18} For instance, CuInS\textsubscript{2} is a commonly utilized absorber material in photovoltaic solar cells,\textsuperscript{19} while LiInS\textsubscript{2} is an important IR nonlinear optical material.\textsuperscript{20}

The incorporation of indium into V-VI binary compound semiconductors may produce materials with interesting properties and structures. Lin \textit{et al.} reported that the Bi-In-S ternary system possess nonlinear optical properties, which may prove promising materials in the mid-infrared nonlinear optical applications.\textsuperscript{21} Ali \textit{et al.} studied the optoelectronic properties of InBiS\textsubscript{3} thin films prepared by thermal evaporation. It was found that InBiS\textsubscript{3} possesses an optimal band gap for photovoltaic applications combined with a high absorption coefficient; this study suggests that this material can potentially be used as an alternative material for absorber layers in thin film solar cells.\textsuperscript{22}

In the Bi\textsubscript{2}S\textsubscript{3}–In\textsubscript{2}S\textsubscript{3} system, only a few compounds have been synthesized and these include BiInS\textsubscript{3}, Bi\textsubscript{4}In\textsubscript{2}S\textsubscript{9}, Bi\textsubscript{2}In\textsubscript{4}S\textsubscript{9}, Bi\textsubscript{3}In\textsubscript{5}S\textsubscript{12}, Bi\textsubscript{3}In\textsubscript{4}S\textsubscript{10}, Bi\textsubscript{14.7}In\textsubscript{11.3}S\textsubscript{38} and Bi\textsubscript{0.76}In\textsubscript{1.24}S\textsubscript{3}.\textsuperscript{22-26} The crystal structures of these compounds have been reported as being either orthorhombic or monoclinic.

These Bi-In-S materials were synthesized by annealing a mixture of different molar ratios of Bi\textsubscript{2}S\textsubscript{3} and In\textsubscript{2}S\textsubscript{3} at elevated temperatures (600-900 °C). The study of new ternary mixed antimony indium sulfide compounds (Sb-In-S) is even more limited currently.

The utilisation of single source precursors for synthesising binary and ternary metal chalcogenides has been an active research area for decades. It is somewhat advantageous over
other methods, due to its inherent simplicity, the avoidance of toxic and pyrophoric precursors, and yields products with high purity. As the process utilizes molecular scale precursors, there is much scope to explore the synthesis of doped materials with excellent control of stoichiometry and spatial distribution within a host matrix as compared with solid state reactions.

The use of metal xanthates as molecular precursors for the synthesis of metal sulfides is particularly attractive due to their low decomposition temperature, ease of synthesis, and their relatively clean decomposition pathway (Chugaev elimination). Xanthate complexes of bismuth, antimony and indium have been utilised for the synthesis of pure binary Bi$_2$S$_3$, Sb$_2$S$_3$ and In$_2$S$_3$ by different methods. Furthermore, ternary and quaternary sulfides have been prepared successfully through the use of metal xanthate complexes. For example, Rath et al. prepared two different copper antimony sulfide phases CuSbS$_2$ and Cu$_{12}$Sb$_4$S$_{13}$ utilising a mixture of copper and antimony xanthates. Solventless pyrolysis of metal xanthates is advantageous in that they have relatively low decomposition temperatures (< 200 °C) and the by-products of the decomposition are volatile gas-phase products, allowing the clean formation of ternary sulfides in a short amount of time compared to conventional solid-state reactions. Additionally, the molecular nature of the precursors allows alloying to proceed without phase separation or incomplete reaction and gives extremely homogeneous distributions of elements down to the nanoscale. Another advantage of metal xanthates is that they already contain the sulfur required for the preparation of the metal sulfide. Thus, no additional sulfur source, such as hydrogen sulfide, thiourea, thioacetamide, alkanethiols or elemental sulfur, is needed.
Here we report the use of Bi(S<sub>2</sub>COEt)<sub>3</sub>, Sb(S<sub>2</sub>COEt)<sub>3</sub> and In(S<sub>2</sub>COEt)<sub>3</sub> metal xanthates as molecular precursors for solventless synthesis of Bi-In-S and Sb-In-S solid solutions. Thermogravimetric analysis (TGA) revealed that ethylxanthates of bismuth, antimony and indium show complete decomposition within a similar temperature range (120-160 °C). Thus, it is possible to prepare ternary Bi-In-S and Sb-In-S systems with varying stoichiometry using a mixture of their xanthates. The M<sub>2-2x</sub>In<sub>2x</sub>S<sub>3</sub> (0 ≤ x ≤ 1, M = Bi, Sb) products from this facile synthetic route were characterised in detail using powder X-ray diffraction (p-XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), and Raman spectroscopy. To the best of our knowledge, this is the first report on the synthesis of ternary Bi-In-S and Sb-In-S systems using a combined single -source precursor approach.

**Experimental**

**Chemicals**

Potassium ethyl xanthogenate (96%), bismuth(III) chloride (BiCl<sub>3</sub>, ≥98%), antimony(III) chloride (SbCl<sub>3</sub>, ≥99.95%), indium(III) chloride (InCl<sub>3</sub>, 98%), methanol (99.8%), ethanol (95.0%), chloroform (CHCl<sub>3</sub>, ≥99%) were purchased from Sigma-Aldrich, and used with no additional purification. The synthesis of all precursors was carried out in air and no special handling was required. All the obtained products are air and moisture stable.

**Instrumentation**

Elemental analysis and thermogravimetric analysis were performed by the microanalytical laboratory of the University of Manchester. A Mettler Toledo TGA/DSC1 was used to obtain the TGA data between 30 - 500 °C with a heating rate of 10 °C min<sup>-1</sup> under N<sub>2</sub>. A Bruker X-Pert diffractometer equipped with a Cu-Kα source (1.54059 Å)
was used to acquire p-XRD data. Each of the samples was scanned between 10° and 75° with 0.02° steps and 3 s per step, at 40 kV and 30 mA. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) measurements were obtained via a Philips XL30 FEG SEM, with an accelerating voltage of 10-20 kV. Raman spectra were recorded using a Renishaw 1000 Micro-Raman microscope equipped with a 514 nm Argon ion laser.

**Synthesis of tris(0-ethylxanthato) bismuth(III), Bi[S₂COEt]₃.**

Potassium ethylxanthate (8 g, 49.9 mmol) was dissolved in ethanol (150 mL), followed by gradual addition of a bismuth(III) chloride (5.24 g, 16.6 mmol) solution in ethanol (50 mL) and stirred for one hour at room temperature. The reaction mixture was filtered, washed with ethanol and DI water, then dried under vacuum to give a bright yellow solid. The resulting product was recrystallised from chloroform to give dark yellow solid, yield 8.2 g, 86 %; m.p. 110 °C. Elemental analysis: calc. for Bi(S₂COEt)₃: C, 18.86%; H, 2.64%; S, 33.53%; Bi, 36.49%. Found: C, 19.14%; H, 2.65%; S, 33.46%; Bi, 36.47%; IR (cm⁻¹): 1206 ν(C=O); 1018 ν(C=S). ¹H NMR (CDCl₃): δ 4.69 (q, J = 7.1 Hz, 2H, CH₂), δ 1.49 (t, J = 7.1 Hz, 3H, CH₃). ¹³C NMR: δ 206.99 (S₂C), δ 71.3 (CH₂), δ 13.9 (CH₃).

**Synthesis of tris(0-ethylxanthato) antimony(III), Sb[S₂COEt]₃.**

Sb(S₂COEt)₃ was prepared using the method outlined above for Bi(S₂COEt)₃, however, antimony(III) chloride (3.79 g, 16.6 mmol) was used as the antimony source. The product was recrystallised from chloroform to give a yellow solid. Yield: 7.1 g, 88 %; m.p. 90.3 °C. Elemental analysis: calc. for Sb(S₂COEt)₃: C, 22.25%; H, 3.11%; S, 39.55%; Sb, 25.08%. Found: C, 22.61%; H, 3.07%; S, 39.71%; Sb, 24.15%. IR (cm⁻¹):
1220 ν(C–O); 1020 ν(C–S). \(^1\)H-NMR (CDCl\(_3\)): δ 4.61 (q, J = 7.1 Hz, 2H, CH\(_2\)), δ 1.44 (t, J = 7.1 Hz, 3H, CH\(_3\)). \(^{13}\)C NMR: δ 207.02 (S\(_2\)C), δ 72.07 (CH\(_2\)), δ 13.9 (CH\(_3\)).

**Synthesis of \textit{tris}(O-ethylxanthato) indium(III), In[S\(_2\)COEt]_3.**

In(S\(_2\)COEt)\(_3\)) was prepared following the same method outlined above for Sb(S\(_2\)COEt)\(_3\), however, indium(III) chloride (3.67 g, 16.6 mmol) was used as the indium source. Recrystallization from chloroform resulted in white solid, yield 6.5 g, 82 %; m.p. 135 °C, with decomposition. Elemental analysis: calc. for In(S\(_2\)COEt)\(_3\)): C, 22.6%; H, 3.2%; S, 40.2%; In, 23.9%. Found: C, 23.1%; H, 3.2%; S, 40.3%; In, 23.2%; IR (cm\(^{-1}\)): 1244 ν(C–O); 1017 ν(C–S). \(^1\)H NMR (CDCl\(_3\)): δ 4.49 (q, J = 7.1 Hz, 2H, CH\(_2\)), δ 1.48 (t, J = 7.1 Hz, 3H, CH\(_3\)). \(^{13}\)C NMR: δ 229.6 (S\(_2\)C), δ 76.2 (CH\(_2\)), δ 14.1 (CH\(_3\)).

**Synthesis of \textit{In}_2\textit{S}_3-\textit{Bi}_2\textit{S}_3.**

A mixture of In(S\(_2\)COEt)\(_3\) and Bi(S\(_2\)COEt)\(_3\) was used for the preparation of the Bi-In-S system using solventless thermolysis. In a typical procedure, the required molar ratios of In(S\(_2\)COEt)\(_3\) and Bi(S\(_2\)COEt)\(_3\) complexes (Supporting Information Table S1) were dissolved in 10 mL of chloroform for uniform mixing of the complexes. The chloroform solution was evaporated and the powder obtained was finely ground in air using pestle and mortar. The powder was then loaded into a ceramic boat inside a glass tube for heating. The powder was heated in a furnace up to the chosen temperature (250, 300 or 350 °C), under a flow of nitrogen. After one hour, the sample was allowed to cool to room temperature and the final product was collected.

**Synthesis of \textit{In}_2\textit{S}_3-\textit{Sb}_2\textit{S}_3.**

Similarly, the Sb-In-S system was prepared using a mixture of In(S\(_2\)COEt)\(_3\) and Sb(S\(_2\)COEt)\(_3\) complexes, in the required molar ratios (0 ≤ x ≤ 1) (Supporting
Information Table S2). The procedure for thermolysis of the powder to furnish the product is identical thereafter as for the In$_2$S$_3$-Bi$_2$S$_3$ system described above.

**Result and discussion**

**Synthesis of [M(S$_2$COEt)$_3$] (M = Sb, Bi, In).** Ethylxanthato complexes of Sb$^{+3}$, Bi$^{+3}$, and In$^{+3}$ were synthesised via the metathesis of the metal chloride with potassium ethylxanthate to furnish M(S$_2$COEt)$_3$ (where M = Sb, Bi, In). Elemental analysis indicated an acceptable purity of the complexes. The complexes are stable at room temperature and are all soluble in chloroform, dichloromethane and other common organic solvents.

**Thermogravimetric analysis (TGA).**

TGA was used to study the thermal decomposition behavior of the complexes, being undertaken between 25 to 500 °C under a nitrogen atmosphere (Supporting Information Fig. S1). In all cases the TGA profiles show the decomposition of the metal ethylxanthate complexes to the corresponding metal sulfide in one single step between 115 and 160 °C. The observed total mass loss of the Sb(S$_2$COEt)$_3$ complex after heating to 500 °C was 35 %, corresponding to the calculated value for Sb$_2$S$_3$ (35 %). For Bi(S$_2$COEt)$_3$, the observed percentage of the total residue weight (46 %) is in excellent agreement with the calculated percentage of Bi$_2$S$_3$ (45 %). Similarly, the In(S$_2$COEt)$_3$ provided 36 % residue which agrees with the calculated value for the formation of In$_2$S$_3$ (34 %).

**Binary systems: M$_2$S$_3$ (M = Sb, Bi, In).**

p-XRD patterns obtained from decomposition of Sb(S$_2$COEt)$_3$, Bi(S$_2$COEt)$_3$, and In(S$_2$COEt)$_3$ at 200, 250, 300 °C for one hour are presented in Supporting Information Fig. S2. The diffraction patterns of the products produced from the decomposition of
Sb(S₂COEt)₃ and Bi(S₂COEt)₃ matched well with the orthorhombic phase of Sb₂S₃ (ICDD: 01-075-1310) and with orthorhombic phase of Bi₂S₃ (ICDD: 01-089-8965) respectively at all temperatures. In contrast, decomposition of the complex In(S₂COEt)₃ at 200 and 250 °C afforded an amorphous product that did not show a crystalline diffraction pattern. At higher temperatures (300 and 350 °C) the formation of cubic In₂S₃ (ICDD: 03-065-0459) was observed based on the diffraction pattern obtained. On this basis, a temperature of 300 °C was selected going forward for preparation of the Bi-In-S and Sb-In-S systems.

In comparison to our results, Bessergenev et al. prepared In₂S₃ from isopropylxanthato indium(III) at different temperatures. It was found that a variation in synthetic temperature resulted in different phases of indium sulfide; cubic In₂S₃ was obtained at 230 °C, whereas the tetragonal phase was obtained at 250 °C and higher temperatures. Furthermore, the synthesis of In₂S₃ from both mono- and di-methyl isopropylxanthato indium(III) at 450 °C, yielded a mixture of tetragonal and cubic forms of In₂S₃. Our study indicates that the solventless pyrolysis of indium ethyl xanthate at varying temperatures produced only the cubic phase of In₂S₃. The diffraction peaks matched to cubic In₂S₃ at all synthesis temperatures employed, with no indication of impurities or secondary phases.

**Synthesis and characterisation of ternary bismuth-indium-sulfidse (Bi-In-S).**

The TGA results indicated that Bi(S₂COEt)₃ and In(S₂COEt)₃ decompose to their corresponding metal sulfide in the same temperature range. Furthermore, indium and bismuth have the same charge and the size of In³⁺ (0.80 Å) and Bi³⁺ (0.93 Å) are comparable. Therefore, a mixture of these complexes is likely to be appropriate for the preparation of the Bi-In-S system at varying ratios. Indeed, Bi₂-2xIn₂xS₃ was synthesised
via the solventless thermolysis at 300 °C by variation of the ratio of the Bi and In complexes.

The p-XRD patterns of the Bi$_{2-2x}$In$_{2x}$S$_3$ ($0 \leq x \leq 1$) samples are illustrated in Fig. 1. For $x = 0$ the p-XRD pattern is again assignable to orthorhombic Bi$_2$S$_3$ ($a = 11.170$, $b = 11.322$, and $c = 3.992$ Å, ICDD: 01-089-8965). In contrast, the pattern when $x = 1$ matches that of cubic In$_2$S$_3$ ($a = 10.771$ Å, ICDD: 03-065-0459). The introduction of indium, where $x = 0.2$, 0.4, shifts reflections associated with orthorhombic Bi$_2$S$_3$ at $2\theta = 22.3^\circ$, $24.8^\circ$, $28.5^\circ$, $31.7^\circ$, $32.8^\circ$, $35.5^\circ$, $39.8^\circ$, $45.4^\circ$, $46.5^\circ$ and $52.5^\circ$ to larger $2\theta$ implying a contraction of the lattice. This is accompanied by line broadening of the

**Fig. 1** p-XRD patterns of Bi$_{2-2x}$In$_{2x}$S$_3$ ($0 \leq x \leq 1$) produced by solventless thermolysis at 300 °C with variations in In/In+Bi molar ratios with standard patterns of Bi$_2$S$_3$ (bottom) and In$_2$S$_3$ (top).
reflections and a concomitant decrease in signal intensity. The introduction of higher quantities of indium (x = 0.6, 0.8) resulted in diffraction patterns similar to those obtained from pure In$_2$S$_3$ indicating that the crystal structure of the Bi$_{2-2x}$In$_{2x}$S$_3$ samples changes from orthorhombic to cubic, as x increases from 0 to 1. The phase change between orthorhombic Bi$_2$S$_3$ to cubic In$_2$S$_3$ structure occurs between x ≥ 0.4 and x ≤ 0.6. Rietveld refinement of XRD data for all Bi$_{2-2x}$In$_{2x}$S$_3$ samples was carried out in order to ascertain the changes in crystal structures in alloyed systems. A mixture of orthorhombic and cubic phases were observed for all samples. Increasing the indium concentration decreases the relative proportion of the orthorhombic phase in the final samples (Supporting Information Table S4). We estimate the errors in phase percentage that we report to be quite large because of the peak breadth due to the nanostructured crystalline grains found within the sample and the overlap of low angle reflections. The peaks were seen to fit well to a simple Vegardian model of continuous change apart from the {1 1 1} family of planes in the In$_2$S$_3$ phase. This leads to preferred orientation as-observed from the (222) reflection in all the diffraction patterns; crystal growth along the [111] direction is responsible for the observed preferred ordination and anisotropic peak broadening in this phase.

The composition of the Bi$_{2-2x}$In$_{2x}$S$_3$ (0 ≤ x ≤ 1) prepared using mixtures of Bi(S$_2$COEt)$_3$ and In(S$_2$COEt)$_3$ was determined via energy dispersive X-ray (EDX) spectroscopy. For x = 0 (Bi$_2$S$_3$), only Bi and S elements were found, with the atomic percentage of Bi:S being 40.7:59.3, close to theoretical (40:60) (Supporting Information Fig. S3). Similarly, for x = 1 (In$_2$S$_3$), no additional peaks of other elements except In and S are observed in the spectrum. The atomic ratio of In to S was determined to be 40.3:59.7, close to the theoretical value of In$_2$S$_3$ (40:60). For Bi$_{2-2x}$In$_{2x}$S$_3$ with x = 0.2, 0.4, 0.6 and 0.8, the
EDX spectra of the Bi$_{2-2x}$In$_{2x}$S$_3$ samples indicated the characteristic peaks of bismuth, indium, and sulfur. The ratios of bismuth, indium and sulfur in all compositions from EDX data was found to be in excellent agreement with the calculated stoichiometric ratio (Supporting Information Table S4). There is an approximately quantitative linear relationship between the amount of indium in the precursor powders and the amount of indium found by EDX in the Bi$_{2-2x}$In$_{2x}$S$_3$ ($0 \leq x \leq 1$) products from thermolysis (Fig. 2), indicating that the atom economy of the process with respect to the metal center is high. The latter is an important point to consider when choosing a processing route for sustainable manufacturing.

Fig. 2 Approximately linear correlation between the amount of indium in the precursor feedstock and the amount of indium found in Bi$_{2-2x}$In$_{2x}$S$_3$ ($0 \leq x \leq 1$) samples from EDX spectroscopy.
The morphology of the samples was investigated using scanning electron microscopy (SEM). Representative SEM images of Bi$_{2-2x}$In$_{2x}$S$_3$ (0 ≤ x ≤ 1) are presented in Fig. 3. The morphology of Bi$_{2-2x}$In$_{2x}$S$_3$ (0 ≤ x ≤ 1) samples varied significantly with the increasing of indium molar fraction. Fig. 3a shows an image of pure Bi$_2$S$_3$ (x = 0), revealing nanorod structures. Similar morphology was also observed by Koh et al. for Bi$_2$S$_3$ obtained from ethylxanthato bismuth(III). The introduction of indium (x = 0.2, 0.4) resulted in the formation of clusters of small nanorods (Fig. 3b and c). Samples with higher amounts of indium revealed small and large particles of undefined shape (Fig. 3d and e). Pure In$_2$S$_3$ (x = 1), consists of irregularly shaped larger particles (Fig. 3f). The morphological variation of the samples is likely the consequence of an alteration in the crystal structures from orthorhombic to cubic. Elemental mapping of the mixed samples Bi$_{2-2x}$In$_{2x}$S$_3$ with x = 0.2, 0.4, 0.6 and 0.8, showed an even microscale spatial distribution of Bi, In and S based on images produced from voxels of Bi M$_\alpha$, In L$_\alpha$ and S K$_\alpha$ emission (Fig. 4).

![SEM images of Bi$_{2-2x}$In$_{2x}$S$_3$ prepared by solventless thermolysis at 300 °C.](image)

Fig. 3  SEM images of Bi$_{2-2x}$In$_{2x}$S$_3$ prepared by solventless thermolysis at 300 °C. (a) x = 0, (b) x = 0.2, (c) x = 0.4, (d) x = 0.6, (e) x = 0.8 and (f) x = 1.
Raman spectroscopy was used to investigate the Bi$_2$In$_{2x}$S$_3$ (0 ≤ x ≤ 1) samples prepared from mixtures of antimony and indium xanthates at 250 °C (Fig. 5). The pure Bi$_2$S$_3$ sample shows a weak peak at 184 cm$^{-1}$ and two intense and convoluted peaks located at 235 and 255 cm$^{-1}$, in agreement with Raman spectra reported for Bi$_2$S$_3$. The low intensity peak at 184 cm$^{-1}$ is assigned to the A$_g$ symmetric bending mode, and the peaks at 235 and 255 cm$^{-1}$ are assigned to the A$_g$ and B$_{1g}$ anti-symmetric stretching modes, respectively.

Similarly, the Raman spectrum of In$_2$S$_3$ produced from indium xanthates gives seven modes of vibration at 135, 177, 245, 266, 307, 325 and 363 cm$^{-1}$ which correspond to the phonon modes of cubic In$_2$S$_3$. The three Raman peaks at 245, 307 and 363 cm$^{-1}$ are attributed to A$_{1g}$ modes, while the peaks at

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Fig. 4 EDX elemental mapping (20 kV) of Bi Mα, In Lα and S Kα emission lines for (a) x = 0.2, (b) x = 0.4, (c) x = 0.6 and (d) x = 0.8. Scale bars = 5 µm.
177 and 325 cm\(^{-1}\) can be ascribed to the F\(_{2g}\) mode and the peak at 266 cm\(^{-1}\) to the E\(_{g}\) mode.\(^{52-55}\) The Raman peaks at 245 and 307 cm\(^{-1}\) are ascribed to the symmetric stretching vibrations of InS\(_6\) octahedra and InS\(_4\) tetrahedra, respectively.\(^{52, 56, 57}\) The Raman spectra of Bi\(_{2-x}\)In\(_x\)S\(_3\) (x = 0.2 and 0.4) show very weak A\(_g\) symmetric bending modes, alongside two A\(_g\) and B\(_{1g}\) anti-symmetric stretching modes, which are equivalent with the phonon modes of orthorhombic Bi\(_2\)S\(_3\). The weak A\(_g\) symmetric bending mode disappears as the indium content increases in the samples from x = 0 to x = 0.4, whilst a small shift in the positions of the two dominant peaks were observed: the A\(_g\) mode is shifted from 235 cm\(^{-1}\) to 238 cm\(^{-1}\), and the B\(_{1g}\) mode is shifted from 250 cm\(^{-1}\) to 257 cm\(^{-1}\). We attribute these shifts to higher wavenumbers from the lower atomic mass of the indium dopants compared to Bi. Raman spectra of Bi\(_{2-x}\)In\(_x\)S\(_3\) (x = 0.6 and 0.8) manifest a broad hump in the range of 150-340 cm\(^{-1}\), suggesting the semi-amorphous nature of the samples, as observed by p-XRD and may include contributions from atomic
arrangements, residual stress, structural disorder or defects, all of which can affect the appearance of Raman-active phonon modes.\textsuperscript{58}

![XRD patterns of Sb\textsubscript{2-2x}In\textsubscript{2x}S\textsubscript{3} (0 ≤ x ≤ 1) produced by solventless thermolysis at 300 °C with variations in In/In+Sb molar ratios at 300 °C with standard patterns of Sb\textsubscript{2}S\textsubscript{3} (bottom) and In\textsubscript{2}S\textsubscript{3} (top).]

**Fig. 6** p-XRD patterns of Sb\textsubscript{2-2x}In\textsubscript{2x}S\textsubscript{3} (0 ≤ x ≤ 1) produced by solventless thermolysis at 300 °C with variations in In/In+Sb molar ratios at 300 °C with standard patterns of Sb\textsubscript{2}S\textsubscript{3} (bottom) and In\textsubscript{2}S\textsubscript{3} (top).

**Synthesis and characterisation of ternary antimony-indium-sulfides (Sb-In-S).**

From TGA data Sb(S\textsubscript{2}COEt)\textsubscript{3} and In(S\textsubscript{2}COEt)\textsubscript{3} have a comparable decomposition temperature range. Furthermore, both have the same formal charge and the ionic radii of In\textsuperscript{3+} (0.80 Å) and Sb\textsuperscript{3+} (0.90 Å) are comparable, indicating their suitability for preparing Sb-In-S solid solutions by variation of Sb and Bi ratios in the precursor mixture.
p-XRD patterns for Sb\textsubscript{2-x}In\textsubscript{2x}S\textsubscript{3} (0 ≤ x ≤ 1) prepared using Sb(S\textsubscript{2}COEt)\textsubscript{3} and In(S\textsubscript{2}COEt)\textsubscript{3} at 300 °C for one hour are presented in Fig.6. The p-XRD patterns of orthorhombic Sb\textsubscript{2}S\textsubscript{3} and cubic In\textsubscript{2}S\textsubscript{3} are presented in the same figure for comparison. Sb\textsubscript{2-x}In\textsubscript{2x}S\textsubscript{3} (x = 0.2 and 0.4) show a similar diffraction pattern to Sb\textsubscript{2}S\textsubscript{3}, with a slight shift of all reflections to higher 2θ, indicative of lattice contraction. The p-XRD patterns of Sb\textsubscript{2-x}In\textsubscript{2x}S\textsubscript{3} (x = 0.2 and 0.4) appear more similar to cubic In\textsubscript{2}S\textsubscript{3} (x = 1), but the intensity of the reflections is diminished and the lines broadened in comparison. In this case the transition from the orthorhombic to cubic unit cells occurs between x ≥ 0.4 and x ≤ 0.6. Rietveld refinement of the XRD patterns for the Sb\textsubscript{2-x}In\textsubscript{2x}S\textsubscript{3} samples revealed mixtures of orthorhombic and cubic phases. Table S5 in the supporting information.

\textbf{Fig. 7} Approximately linear correlation between the amount of indium in the precursor feedstock and the amount of indium found in Sb\textsubscript{2-x}In\textsubscript{2x}S\textsubscript{3} (0 ≤ x ≤ 1) samples from EDX spectroscopy.
The atomic percentages of antimony, indium and sulfur in Sb$_{2-2x}$In$_{2x}$S$_3$ ($0 \leq x \leq 1$) samples were measured using EDX spectroscopy. For $x = 0$ (pure Sb$_2$S$_3$), only Sb and S elements were found, and the atomic ratios of Sb to S was found as 40.6 : 59.4, close to the anticipated value of Sb$_2$S$_3$ (40 : 60). Similarly, for $x = 1$ (pure In$_2$S$_3$), the atomic ratio of In to S was determined as 40.3 : 59.7, close to the theoretical value of In$_2$S$_3$ (40 : 60). For Sb$_{2-2x}$In$_{2x}$S$_3$ ($x = 0.2$, 0.4, 0.6 and 0.8), the EDX spectra confirmed that the composition was Sb$_{2(1-x)}$In$_{2x}$S$_3$, with no emission from other elements observed in the spectra (Supporting Information Fig. S5). The estimated metal amount derived from EDX spectroscopy are in excellent agreement with precursor mixture (Supporting Information Table S5). An approximately linear relationship between the amount of indium in the precursor feed and the amount of indium found in Sb$_{2-2x}$In$_{2x}$S$_3$ ($0 \leq x \leq 1$) samples by using EDX, with the same comments regarding atom economy of the process applicable here as well.
The morphologies of the Sb$_{2-2x}$In$_{2x}$S$_3$ (0 ≤ x ≤ 1) samples prepared from a mixture of indium and antimony complexes are shown in Fig. 8. The SEM image of pure Sb$_2$S$_3$ (x = 0) showed that the crystallites have a pseudo-spherical morphology, with diameters of ca. 1.5 μm (Fig. 8a), possibly nanostructured by division into smaller spheres. Similar morphology has been observed by Castro et al. for Sb$_2$S$_3$ synthesised from ethylxanthato antimony(III).$^{37}$ Furthermore, pseudo-spherical crystallites were also observed in Sb$_{2-2x}$In$_{2x}$S$_3$ samples (x = 0.2 and 0.4, Fig. 8b and c), which change to irregularly shaped larger particles in Sb$_{2-2x}$In$_{2x}$S$_3$ (0.6 x ≤ 1, Fig. 8d-f). Elemental mapping of Sb$_{2-2x}$In$_{2x}$S$_3$ (x = 0.2, 0.4, 0.6 and 0.8), exhibited uniform microscale spatial distribution of Sb, In and S based on images produced from voxels comprising the Sb Lα, In Lα and S Kα emissions (Fig. 9).

![Fig. 9 EDX elemental mapping (20 kV) of Sb Lα, In Lα and S Kα emission lines for (a) x = 0.2, (b) x = 0.4, (c) x = 0.6 and (d) x = 0.8. Scale bars = 5 μm.](image-url)
The Raman spectrum of the pure Sb$_2$S$_3$ reveals peaks at 186, 250, 280, 301 and 448 cm$^{-1}$ corresponding to orthorhombic Sb$_2$S$_3$ (Fig. 10). The peak at 186 cm$^{-1}$ is assigned to the B$_{1g}$ anti-symmetric S-Sb-S bending modes, whilst the peak at 250 cm$^{-1}$ is ascribed to the A$_g$ symmetric S-Sb-S bending mode. The peaks at 280 and 301 cm$^{-1}$ are assigned to the A$_g$ and B$_{1g}$ anti-symmetric Sb-S stretching modes. Seven phonon modes were observed in the Raman spectrum of In$_2$S$_3$ at 135, 177, 245, 266, 307, 325 and 363 cm$^{-1}$ which correspond to the phonon modes of cubic of In$_2$S$_3$. The three Raman peaks at 245, 307 and 363 cm$^{-1}$ are attributed to A$_{1g}$ modes of the cubic structure of In$_2$S$_3$, while the peaks at 177 and 325 cm$^{-1}$ are ascribed to the F$_{2g}$ mode and the peak at 266 cm$^{-1}$ to the E$_g$ mode. The Raman peaks at 245 and 307 cm$^{-1}$ are ascribed to the symmetric stretching vibrations of InS$_6$ octahedra and InS$_4$ tetrahedra, respectively. For x = 0.2 and 0.4 samples, the A$_g$ and B$_{1g}$ modes were obtained, which are associated with the vibration of metal and sulfur atoms (Sb-S), whilst the antisymmetric and symmetric S-Sb-Sb bending modes (B$_{1g}$ and A$_g$) were decreased and shifted to lower wavenumbers.
The addition of 0.6 and 0.8 mole fractions of indium resulted in a broad hump in the range of 200 - 370 cm\(^{-1}\). This potentially indicates that long range order is lost after \(x > 0.6\) Sb.

**Optical band gaps of \(M_{2-2x}In_{2x}S_3\) (\(M = Bi, Sb\)) thin films**

For optical bandgap measurements, thin-film samples of \(M_{2-2x}In_{2x}S_3\) \((0 \leq x \leq 1)\) \((M = Bi, Sb)\) were prepared by spin coating different molar concentrations of metal xanthates on glass substrates which were then heated under nitrogen in a quartz tube at 300 °C for 1h. Optical absorption spectra of these samples were recorded using UV-visible spectrometer in the wavelength of 300-900 nm (Supporting Information Fig. S6a and b). The band gap of the films can be calculated using the Tauc relationship, \((\alpha h\nu)^n = A(h\nu - E_g)\), where \(E_g\) is the optical band gap, \(h\nu\) is the photon energy, \(\alpha\) is the absorption coefficient, \(A\) is a constant characteristic of the material, and \(n = 2, \frac{1}{2}\) for allowed direct and allowed indirect transitions, respectively. \(In_2S_3\), \(Bi_2S_3\) and \(Sb_2S_3\) are all direct band gap materials.\(^{64-66}\) Plots of the \((\alpha h\nu)^n\) versus \(h\nu\) for \(n = 2\) and \(\frac{1}{2}\) show a linear behaviour for \(n = 2\), which confirm the presence of a direct allowed transition in the \(Bi_{2-2x}In_{2x}S_3\) and \(Sb_{2-2x}In_{2x}S_3\) samples for all compositions. Supporting Information Fig. S7a and b represent the band gaps for \(Bi_{2-2x}In_{2x}S_3\) and \(Sb_{2-2x}In_{2x}S_3\) samples in the indium compositional range \(x = 1, 0.2, 0.4, 0.6, 0.8,\) and 1.

Values of direct band gap of 1.66, 2.19 and 2.39 eV were estimated for the binary \(Bi_2S_3\), \(Sb_2S_3\) and \(In_2S_3\), respectively. The estimated bandgap values are very close to the reported values for these materials.\(^{32, 64, 65, 67-72}\) For \(Bi_{2-2x}In_{2x}S_3\) samples, the values of the band gaps for the mixed samples were estimated to be 1.8, 1.9, 1.98 and 2.2 eV for \(x = 0.2, 0.4, 0.6\) and 0.8, respectively, which lies between those of pure \(Bi_2S_3\) and \(In_2S_3\) (Fig. 11). The band gaps increase with the indium content increase in the samples.
On the other hand, the estimated band gaps for Sb$_{2-2x}$In$_{2x}$S$_3$ ($0 \leq x \leq 1$) samples shows two different tendencies with x composition (Fig. 11). In the composition range ($0 \leq x \leq 0.6$), the band gaps increased from 2.19 eV ($x=0$) to 2.9 eV ($x=0.6$). Whereas in the composition range ($0.6 \leq x \leq 1$), the value of the band gaps decreased from 2.9 eV ($x=0.6$) to 2.39 eV ($x=1$). The reason for the band gap variation might be related to the effect of many factors including grain size, thickness, structural disorder, lattice strain and carrier concentration due to doping.$^{55, 57, 73}$

![Fig. 11 Variation of the direct band gaps for Bi$_{2-2x}$In$_{2x}$S$_3$ ($0 \leq x \leq 1$) samples as a function of $x_{In}$, and the inset shows the variation of the band gap for Sb$_{2-2x}$In$_{2x}$S$_3$ ($0 \leq x \leq 1$) samples as a function of $x_{In}$.](image)
Conclusion

Antimony, bismuth and indium complexes of ethylxanthates of the form M(S$_2$COEt)$_3$ (where M = Sb(III), Bi(III), In(III)) have been utilised as molecular precursors for the synthesis of Bi-In-S and Sb-In-S systems via a solventless route, at 300 °C. The decomposition temperature range of these complexes are similar, making them suitable for the preparation of M$_{2-2x}$In$_{2x}$S$_3$ (0 ≤ x ≤ 1) samples with different mole fraction of indium x. According to the p-XRD analysis, at lower mole fraction of indium (x = 0.2, 0.4) no significant change in the p-XRD patterns were observed. However, at a higher mole fraction of indium (x = 0.6, 0.8), changes in the diffraction patterns were observed, indicating that the crystal structure of M$_{2-2x}$In$_{2x}$S$_3$ (0 ≤ x ≤ 1) samples transformed from orthorhombic to cubic, as x increases from 0 to 1. SEM images revealed that the morphology of M$_{2-2x}$In$_{2x}$S$_3$ (0 ≤ x ≤ 1) samples differed considerable in relation to the increased indium molar fraction. The estimated compositions from EDX are in excellent agreement with the feed ratio in the precursor mixture. Elemental mapping of the mixed samples M$_{2-2x}$In$_{2x}$S$_3$, with x = 0.2, 0.4, 0.6 and 0.8, exhibited uniform distribution of M, In and S throughout the entire sample at the microscale. The process we have developed is an excellent way to produce these materials in a simple and atom-efficient manner with respect to the metals used, which is important for sustainable synthesis.

Conflicts of interest

There are no conflicts to declare.

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Notes and references


