Binary and ternary metal chalcogenides for sustainable and inexpensive solar energy generation

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Abstract

Binary and ternary metal chalcogenide semiconductors like antimony, copper, iron and cobalt sulfide and their alloys have a wide range of applications especially in the solar cells field. These semiconducting materials offer earth-abundant, low toxic and cheap alternatives for photovoltaic devices fabrications, instead of commonly used highly toxic and expensive metals (such as Cd or Pb, Te and In). In this study, diethyldithiocarbamate complexes M(S₂CNEt₂)ₙ (where M= Sb (III), Cu (II), Fe (III), and Co (II)) were synthesized as molecular precursors for the preparation of binary and ternary metal sulfide materials. The samples Sb₂₋₂ₓM₂ₓS₃ (0 ≤ x ≤ 1) were prepared by solvent less synthesis and AACVD method by considering excellent stoichiometric control to develop thin films and nanoparticles.

This work is divided into six chapters, in which the first chapter provides a brief summary of the chalcogenide-based semiconducting materials and the different approaches for the synthesis of metal chalcogenide thin films and nanoparticles. This chapter also provides a complete literature review of all the single source precursors used until the present for the preparation of antimony as well as its ternary chalcogenide materials. The second chapter gave a brief description of the experimental techniques used throughout this work.

The third chapter, tested the efficacy of iron into Sb₂S₃ via the solventless thermolysis method at 450 °C. Sb (III), and Fe (III) complexes of diethyldithiocarbamate have been used as molecular precursors for the synthesis of Sb₂₋₂ₓFe₂ₓS₃ (0 ≤ x ≤ 1) in entire range with excellent stoichiometric control. The effect of the addition of Fe into the Sb₂S₃ on the chemical composition morphology and band gap was investigated. Magnetic properties of the nanomaterials prepared were also studied.

The fourth chapter, describes the formation of ternary Sb₂₋₂ₓCu₂ₓS₃ (0 ≤ x ≤ 1) solid solution in entire range with excellent stoichiometric control via solventless thermolysis using Sb (III) and Cu (II) diethyldithiocarbamate as molecular precursors. The structural analysis shows that copper was effectively introduced as a solid solution into antimony sulfide. Thin films were also deposited on glass substrates using AACVD. A single-phase pure chalcostibite (CuSbS₂) and tetrahedrite (Cu₁₂Sb₄S₁₃) were obtained using the solventless methods and phase of the ternary material changes from chalcostibite (CuSbS₂) and fematinite (Cu₃SbS₄) at a low Cu : Sb ratio to tetrahedrite (Cu₁₂Sb₄S₁₃) at a high Cu : Sb ratio using the AACVD method.

The fifth chapter studied the incorporation of cobalt into Sb₂S₃ using the solvent less thermolysis method. Sb (III), and Co (II) complexes of diethyldithiocarbamate have been applied as molecular precursors for the synthesis of Sb₂₋₂ₓCo₂ₓS₃ (0 ≤ x ≤ 1) solid materials. The effect of the chemical composition on morphology and magnetic properties of the materials were investigated. In addition to the solvent less synthesis, AACVD method was also used for the deposition of pure CoSbS thin films and the effect of the chemical composition on band gap were also studied.

Chapter six provides a brief conclusion of all the experimental chapters and the future work plan.
Declaration

I hereby declare that no portion of the work referred to in the thesis has been submitted in support of an application for another degree or qualification of the University of Manchester or any other university or other institute of learning.

Fadiyah Antar Makin
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<td>Multiple Exciton Generation</td>
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<td>SEM</td>
<td>Scanning Electron Microscopy</td>
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<tr>
<td>SQUID</td>
<td>Super Conducting Quantum Interference Device</td>
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<td>SSP</td>
<td>Single Source Precursors</td>
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<tr>
<td>TAS</td>
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Publications Arising from this Thesis


2. Journal article: Makin, F., Alam, F. Buckingham, M. A., & Lewis, D. Synthesis of ternary copper antimony sulfide via solventless thermolysis or aerosol assisted chemical vapour deposition using metal dithiocarbamates. Scientific Reports, 2022, 12, 5627.
Chapter 1. Introduction

1.1 Semiconducting materials

Semiconductors SC are the class of materials that exhibit electrical conductivity in the range $10^{-9}-10^{2} \Omega^{-1} \text{cm}^{-1}$. The conductivity value is used to estimate the metallic or insulator nature of the SC. If the measured conductivity of material is in the range $10^{2}-10^{10} \Omega^{-1} \text{cm}^{-1}$ the response is like metals while for insulator type materials the conductivity values should be less than $10^{-9} \Omega^{-1} \text{cm}^{-1}$. SC have two main classifications: pure SC (intrinsic) and impure/ doped SC (extrinsic).\(^1\) Interestingly the conductivity factor in SC could be altered by some factors such as temperature and chemical purity. Most insulators and some wide bandgap SC have similar electrical resistivity in the absence of an electric field. Generally, at high-temperature, a SC conductivity enhances, while at lower temperature their response is as insulator.\(^2\)

The SC exhibit chemical, physical, thermal, and electrical properties which depends on the structural phases opted during fabrication. Normally most of the SC exhibit diamond and Zinc- Blende type structure.\(^3\) The distinctive feature of SC are the inter-band energy band gaps (Fig.1. 1a). For metals, there is no specific band separation between valence bands to conduction band. In case of insulators, the bandgap is larger than 2.5 eV.\(^4\)

![Figure 1.1](image1.png)

**Figure 1.1** (a) Bandgap in insulators, semiconductors, and conductors \(^5\) (b) Direct and indirect band gap.\(^6\)
The bandgap can be a direct or indirect in nature depending on the electron crystal momentum (k vector) of the material (Fig. 1b). For direct band gaps, the bottom of the conduction band and top of the valence band have the same value of k, While for all other possibilities band gap are indirect in nature.\textsuperscript{7} SC have wide variety of applications in electronics industry.\textsuperscript{8} Direct band gap SC have novel applications in optoelectronics like in LED’s, optical sensors, UV protectors and optical coaters. The indirect band SC are used in resistors, thermistors, sensors, and power controllers.\textsuperscript{9} Optoelectronic devices involve interaction between photons and electrons. Direct bandgap semiconductors that show strong absorption/emission characteristics are best suited for such applications. Indirect band gap semiconductors involve phonon coupling effects which are not suitable for thin film optoelectronic applications due to the large thicknesses required for photon capture.\textsuperscript{9}

1.2 Applications of Semiconductors

Semiconductors SC have tuneable physical properties due to which they have provision of variety of application such as, Si and Ge based SC are used in as diodes, transistors, and integrated circuits.\textsuperscript{10} More advanced type includes GaSb and AlGaSb which are used in thermal imaging devices and environmental sensors. Optically active SC include GaAs, a strong candidate to be extensively used in as solar cells and light emitting diode (LEDs).\textsuperscript{11} ZnSe is used as green phosphor in television cathode ray tube, camera microwave devices, InP and InGaAs are used in optical imaging. ZnS(Mn) doped is used in the thin film electroluminescent (TFELs).\textsuperscript{11}

1.2.1 Solar Cells

In recent years, the rapid population growth has increased the demand of energy sources which leads the world to energy and power deficient crisis. The solution to this problem is to introduce renewable energy resource in coping up with this escalating energy demand consumption. The most abundant source of renewable energy is the sunlight which can be converted into a usable form of energy by two main routes. The first method is to convert the sunlight to heat and then the heat is converted to electricity, this route is called, solar-thermal route. The second method is converting the sunlight directly to electricity using semiconductor materials, this approach is called the solar-photovoltaic route.\textsuperscript{12} Theoretically all the parts of the visible spectrum which is from near-infrared to ultraviolet could be harnessed.\textsuperscript{13} Photovoltaic (PV) is a major player in the future of the clean energy economy because it is a promising, cheap, require little maintenance and attractive alternative to fossil fuels.\textsuperscript{14}

Since past four decades, photovoltaic technology has attracted much attention and the industrial developments in this process has classified these generations of photovoltaic technology namely, type I, II and III photovoltaics. Type I was typically based on crystalline silicon, it can give high power conversion efficiency, but the major drawback of this type is the high cost. On the other hand, type II which is based on
the thin films technology with films containing polycrystalline silicon, it is cheap but offers lower efficiency. Type III photovoltaic has the both advantages of the previous two types low cost and high efficiency. It is based on solution-processed semiconducting nanostructured materials. The basic structure of solar cell is illustrated in figure 1.2. When the sun light is allowed to interact with PV cell, the p-n junction region become active region and the energy of electrons is increased which causes inter-band transition by overcoming the energy-gap. At the p-n junction the electric field drives the electrons to the n-type layer while the holes are collected in the p-type layer. The front contact of the cells collects the electrons and the holes are collected at the back contacts.

Figure 1. 2 The basic structure of solar cells.

1.3 Nano crystalline materials

Nanotechnology has been a rapidly growing industry in the last two decades. Nano crystalline materials or nanoparticles is a term used for class of materials whose particle size falls in the range of nanometres. The attributes of nanoparticles are significantly dependent on the size which could be different than that of bulk counterparts. However, these effects are dealt as quantum confinement response of a material in which physical properties become size dependent.

Nanoparticles can be made of almost any kind of materials which include metals, SC, polymers, metal oxides, and biomaterials. The particle size or shape topology of nanomaterials may exhibit any shape like cylinders, spheres, platelets, tubes, wires, discs, and rods.
Nanoparticles may be prepared in a number of ways, which can be categorized as top-down and bottom-up shown in Fig. 1. 3. Top-down methods, such as etching and sputtering, attempt to decrease the bulk size of materials to particles. On the other hand, bottom-up techniques like chemical synthesis and self-assembly aim to construct particles from smaller building components such as atoms, molecules, or polymers. Both techniques have their merits and limitations, but the bottom-up strategy is preferred since it produces smaller particles. As a result, the bottom-up method is more cost-effective since the relevant procedures are more exact with low energy waste and a more regulated process.

1.4 Chalcogenide based Semiconductors

Metal chalcogenides are semiconducting materials that contain a chalcogen anion and at least one more electropositive metal element. They are crystalline semiconductors with attractive electrical properties. They have a wide range of applications in different areas such as solar cells, hydrogen evolution, photocatalytic degradation, and lithium-ion batteries. These applications are attributed to their excellent stability and optoelectronic responses. In the periodic table, group VIA is generally composed of chalcogens specifically, tellurites, sulfides, selenides.

Metal chalcogenides (MC’s) have different structures and properties which includes binary (M₂Eₚ), ternary (MₓM’ₚEₚ), and quaternary (MₓM’ₚM’’ₚEₚ) systems. Where M is a first transition metal, M’/M’’ is a second transition metal and E is (S, Se, or Te). Some examples of chalcogenides are Ti₂S, CdTe, Sb₂S₃, FeS, and Cu₂Se.
Metal sulfides have emerged as an attractive class of metal chalcogenide owing to the cheap cost of production and the abundance of essential ingredients. Binary metal sulfides such as pyrite (FeS₂), stibnite (Sb₂S₃) cobalt sulfide (CoS) and chalcocite (Cu₂S), nickel sulfide (NiS), zinc sulfide (ZnS), bismuth sulfide (Bi₂S₃) and cadmium sulfide (CdS) are SC that have been used in number of applications. Binary metal sulfides were extensively reported as thermoelectrically materials. In recent years, low-cost, reduced toxicity and adaptable thermoelectric characteristics of such materials have gain considerable attention. For example, zinc sulfide (ZnS) was fabricated around 170 years ago, has been extensively investigated and used in a variety of applications. On the other hand, bismuth Sulfide (Bi₂S₃) with its bandgap of ~1.1 eV and high absorption coefficient of 10⁵~10⁶ cm⁻¹ illustrates its promising photovoltaic applications.

Ternary metal chalcogenide TMC has also received much attention by researchers owing to their unique features which are not plausible in binary chalcogenides. TMCs are formed by replacing two metals with identical total charges (MₓM′ₙEn) for the metal in a binary metal chalcogenide system (MₓEn). Due to the existence of two distinct metals and by carefully controlling the composition of ternary sulfides, the band gap and physical characteristics can be controlled. The ternary complexes exhibit quantum confinement and response as quantum dots, these materials act with the whole solar spectrum through the energy modulation effects. This property is advantageous for TMC’s as well as other binary chalcogenides for potential applications such as light harvesting.

1.5 Synthesis of chalcogenide nanoparticles

Researchers have discovered a wide variety of synthetic methods for producing high-quality nanocrystals. Synthesis of nanoparticles with SC attributes have two main fabrication methods: physical and chemical approaches. Chemical deposition techniques include chemical vapour deposition (CVD), plasma-assisted deposition, atomic layer deposition, and sol-gel deposition. While, molecular beam epitaxy, sputtering, pulsed laser deposition, cathodic arc deposition, thermal evaporation, and electrohydrodynamic deposition are all physical methods. Each method has its own advantages and disadvantages. Chemical methods for the creation of metal chalcogenide nanoparticles enable atomic-level modification of materials. The capacity to combine elements at this level offers more precise control over the composition, particle size, and form of the particles. The synthetic routes can also be classified according to the condition of the reaction medium as follows: (i) solid phase approach, (ii) liquid phase approach, (iii) vapour phase method, and lastly (iv) two-phase approach. The vapour-phase and solid-phase techniques of creating well-defined semiconductor nanocrystals have been discovered to be less accurate than the liquid-phase method because of constraints in instrumentation, precursors, and control of the synthetic process and crystal quality. Colloidal semiconducting nanocrystals are also known as liquid-phase synthesised nanocrystal SC’s because the manipulation of precipitation processes in suitable solvents to produce unchanging solution with the help of surfactants or capping ligands to prevent the nanoparticles from expanding larger than the specified size range and aggregation. As a result, the liquid-phase technique offers a variety of advantages, such as adjustable
bandgap energies and strong polarizability along with optical absorption coefficients. The low-cost effectiveness and exceptionally high throughput of the method enable solution-based manufacturing processes to be used for commercial production of inkjet printers, spin coating, and roll-to-roll casting using stable colloidal suspensions. Liquid-phase synthesis methods are classified into three subtype specific to the reaction medium like aqueous synthesis, organic syntheses, and aqueous-organic syntheses. The main disadvantage of the aqueous technique is that the low temperature of the reaction might result in reduced nanocrystallinity of SC’s. For example, recently copper sulfide (CuS), cadmium sulfide, (CdS), cadmium selenide (CdSe), tin sulfide (SnS), bismuth sulfide (Bi₂S₃), zinc sulfide (ZnS) and copper tin sulfide (Cu₂SnS₃) nanoparticles were synthesized using aqueous solution method. Single-phase silver sulfide powders (Ag₂S) and colloidal solutions were synthesised successfully through chemical deposition from aqueous solutions of silver nitrate and sodium sulfide in the presence of sodium citrate. However, there are significantly large number of MC’s which are difficult to produce with this fabrication process. Organic-based procedures such as hot injection, heating up method and the solvothermal method manufacture nanocrystals with well-controlled morphologies using high-boiling organic solvents and organic ligands. Wang and Li et al. have described an improved hot-injection process that utilises octadecylamine (ODA) as a solvent, surfactant, and reducing agent simultaneously, allowing for the controlled synthesis of a broad variety of noble metal, metal oxide, and bimetallic NC’s. Aqueous-organic procedures involves dissolving the reactants into distinct phases and forming solid NC’s at the interface between the aqueous and organic layers. This technique includes precise stoichiometry and gentle reaction conditions which has been successfully used to synthesise NC’s. For the first time Mikulec et al. used organometallic method to prepare CdSe, CdS, and CdTe nanoparticles. The samples were prepared by controlling the temperature which results in the preparation of excellent quality and high clean NC’s. The drawback of this technique is that the dual precursors can be extremely toxic and expensive. Gas-phase synthesis techniques are used to deposit large size powder particles by the low-pressure evaporation of SC. Moreover, hydrothermal and solvothermal methods are also commonly known techniques to prepare semiconducting nanomaterials. These methods are preferred choices because they are inexpensive and particles morphology is easily controllable. Fig.1.4 shows commonly used experimental techniques to synthesize metal chalcogenide nanomaterials. The advantages and disadvantages of the experimental methods are linked directly to specific material fabrication for particular applications.
One of the most attractive methods for the production of nanoparticles with fewer defects of chalcogenides under temperature is the decomposition of the molecular precursors. To overcome sensitive air issues while heating the samples, a single-source precursor method is used. According to O’Brien et al., using a single-source precursor that includes both the necessary metal and chalcogen elements may be an effective way to avoid such issues and to produce high-quality and crystalline semiconductor nanoparticles. For example, cadmium sulfide and cadmium selenide, NC’s were synthesized from alkyl-cadmium-dithio and di-seleno carbamates, respectively. Furthermore, long-chain Bi(S₂CN[(CH₃)(C₁₈H₃₅)])₃ complexes were used to fabricate bismuth sulfide (Bi₂S₃) by the thermolysis method. Thus single-source precursor method has benefits including circumventing the use of toxic and pyrophoric metal alkyl organometallic compounds. By using this approach different morphologies of metallic NPs of chalcogenide are formed such as nanofibers, spheres, nanowires, nanoroads and nanodisks.
1.5.1. Solvent-less thermolysis

One of the most known approaches used for the synthesis metal chalcogenide nanoparticles is the solvent-less thermolysis. The solvent-less method is also known as melt method in which reactions are easy to handle, less harmful to the environment, more economical as there is no need for a solvent. In this method, heating of precursor materials to a high temperature in a furnace is gradually performed to generate a melt of the material. The melt is then rapidly cooled to form a crystalline metal chalcogenides structure. The quality of structure formed is highly dependent on the melting temperature, pace of cooling and the amount of the sample melted. The schematic diagram of the process in this method is presented in Fig. (1.5).

![Figure 1.5 Setup of solvent-less thermolysis.](image)

Solvent-less thermolysis is most commonly used to fabricate a wide range of metallic nanoparticles and their oxides because it offers a wide range morphologies such as spheres, rods, wires, fabrics, and disks. O’Brien and co-workers have reported a new methodology for the fabrication of a-symmetric cadmium dithiocarbamate via self-capping and a solvent-less approach. The temperature range in their work was 190 – 270 °C, the reaction was carried out under a vacuum environment, and the obtained particle size was around 5-7nm.

1.5.2 Thin film deposition approach

A thin film is a two-dimensional substance formed by condensing atomic/molecular/ionic species of matter one at a time, often to a thickness of less than few microns. Individual atoms are deposited on a substrate to produce thin films. Thin films have been extensively used in electronic devices, optical coatings, instrument hard coatings, and aesthetic components throughout the years. Due to the constant need to produce new materials, such as nanomaterials and artificial super lattices, thin film technology development continues on a regular basis. Different methods have been evolved since early deposition reports of \( \text{Cu}_2\text{ZnSnS}_4 \) using
sputtering method for the deposition of thin films. Since then, metal sulfide based thin films have gained considerable attention and has grown significantly using this approach. Other approaches used to deposit thin films are chemical vapour deposition (CVD), physical vapour deposition (PVD), and liquid phase epitaxy (LPE).

1.5.3 Chemical Vapour deposition (CVD)

CVD is generally used to produce semiconductor thin films materials. The layer is deposited on the material from vapours produced in a chemical reaction. The physical and chemical properties of the layer having a uniform thickness can be changed by fluctuating the parameters of the experiment such as deposition temperature, gas phase, the total pressure of the gas flow, the composition of the gas phase. Argon gas is used to transport the vapours of desired material into the substrate. The volatile chemicals react to form gas-phase reactants, where both the substrate and vapours from the reactant interact directly. The vaporized material is absorbed on the substrate and reacts to fabricate a film of the desired material.

The specific types of CVD methods are atmospheric pressure CVD (APCVD) in which the reaction is performed under atmospheric pressure. (ii) Plasma-enhanced CVD (PECVD) which allows the use of plasma at low temperature, photo-assisted CVD (PACVD) which activates the chemical reaction using light, low-pressure CVD (LPCVD) which is used to make thin films under ultra-low pressure, Metal-organic CVD (MOCVD) is used to prepare thin films or organo-metallic interfaces. Hybrid physical CVD (HPCVD) is done by the decomposition of the gas of the precursors and the solid source vaporization. and lastly aerosol-assisted CVD (AACVD) in which the films are produced using the aerosol of a chemical solution.

1.5.3.1 Aerosol assisted CVD (AACVD)

Aerosol-assisted chemical vapour deposition is used to fabricate different types of semiconductor thin film. The major benefit of this technique is its simplicity and economical deposition process. The main idea of AACVD is that a solution of precursors is solved in an organic solvent and its aerosol is generated ultrasonically and transported by a carrier gas (argon or nitrogen) into a substrate surface in a heated furnace where the precursors are thermally decomposed. AACVD is a suitable method for a non-volatile material or soluble in an appropriate solvent. The typical AACVD process is shown in Fig. 1.6. This technique is used to generate a variety of metallic chalcogenide thin films such as binary metallic chalcogenide (Bi$_2$Se$_3$, CdS, In$_2$S$_3$, PbS, NiS, FeSe, ZnS and MoS$_2$), ternary metallic chalcogenides as (InBiS$_3$, Cu$_2$SnSe$_3$, and AgInS$_2$), and quaternary metallic chalcogenides as (Cu$_2$ZnSnS$_4$, Cu$_2$FeSnSe$_4$ and Cu$_2$FeSnS$_4$).
1.6 Single Source Precursors (SSP)

Single source precursors have been used effectively to prepare a wide variety of binary, ternary and quaternary SC’s, NP’s and thin films. The SSP contain two or more elements in one molecule when these are used for the synthesis of thin films and nanoparticles. Furthermore, SSPs are very efficient for the production of high-quality crystalline nanoparticles with control over the decomposition temperature, easy purification, and reduced use of toxic gases. The crystalline materials obtained by the SSP method afford high purity products. While mixing the chamber, there is no need for pre-reaction, leading to clean decomposition. It can be used in solution or in solid form with the opportunity to use low deposition temperature. Most SSP’s are air and moisture stable with easier purification than dual-source precursors leading to the preparation of unique nanoparticles with smaller amount of impurities. In SSPs the pre-existing bonds that are programmed to form the target material can potentially improve stoichiometry and decrease the defects. Another advantage of SSP is that it can control the structure of materials because of the fixed geometry. Therefore, this route has attracted increasing attention because of these advantages over other methods. For example Bhide et al. has reported in detail that most SSPs are air and moisture stable leading to the preparation of nanoparticles with a smaller amount of impurities.

As Trindade and O’Brien firstly reported using single-source molecular precursors has shown to be an effective method to high-quality, crystalline monodispersed nanoparticles of semiconducting materials. O’Brien et al., prepared CdS nanoparticles using single-source precursors of alkylcadmium dithiocarbamate complex. Air-sensitive alkylcadmium dithio- and diseleno carbamate complexes were utilised as precursors for the synthesis of CdS and CdSe nanoparticles, with subsequent work expanding to the preparation of CuSe and CuInSe quantum dots and ZnSe nanoparticles through the use of zinc derivatives. Recently, air-stable (methylhexyldithio-/ diselenocarbamato) cadmium/zinc complexes have been employed as precursors for the deposition of thin films of II/ VI chalcogenides by metal organic chemical vapor deposition (MOCVD), as well as the formation of other nanoparticles chalcogenide.
1.6.1 SSP approach for fabrication of nanomaterials and thin films

The selection of suitable precursor should be made on the basis of thermal stability when it is transported and evaporated in the gas phase, high purity, good volatilility, low-cost availability, should be nontoxic and non-pyrophoric, long time storage capability without occurring degradation.\textsuperscript{118} SSP has been used to prepare several semiconductor nanomaterials and thin films with advantages over the other precursor types.\textsuperscript{109} Traditionally, metal chalcogenide nanomaterials and thin films are synthesised using a multi-source precursors. However, the majority of these precursors (metal alkyls and H\textsubscript{2}S, H\textsubscript{2}Se) are very toxic, pyrophoric, and there is difficulty in controlling stoichiometry, are moisture sensitive, and therefore can cause undesired side reactions.\textsuperscript{119} Efforts have been made to design precursors that limit hazardous risks, lower the temperature needed for synthesis, produce high-quality materials, and lower the cost of raw materials.

It has been shown that SSP containing the metal and chalcogen (S, Se, Te) in a single molecule may be used to synthesise a variety of metal chalcogenides.\textsuperscript{120} Compatibility issues between precursors, which are often encountered in multi-precursor techniques, may also be solved utilising single-source precursor pathways.\textsuperscript{121} Numerous classes of sulphur-based SSP, including dithiocarbamates\textsuperscript{122} xanthates\textsuperscript{123} dithiophosphates\textsuperscript{124} and thiobenzoates\textsuperscript{125} have been created for the synthesis of metal sulfides.\textsuperscript{126} Fig. 1.7 illustrates the chemical structures of the most frequently employed SSP for the synthesis of metal sulfides. Dithiocarbamate SSP alleviate issues with air sensitivity and stoichiometry that existed when dual-source precursors were used\textsuperscript{127}

![Figure 1.7 Some of the single source precursors ligands used to synthesis metal sulfides.\textsuperscript{128}](image)

Owing to their low decomposition temperatures, increased solubility xanthate complexes are advantageous for the production of metal sulfides.\textsuperscript{129} Metal xanthate complexes have garnered considerable interest over the past two decades because of their potential as molecular precursors in the synthesis of metal sulfide nanomaterials.\textsuperscript{129}

1.6.2 Dithiocarbamate (DTC) complexes as SSP

Dithiocarbamates (DTC) with a general formula [M(S\textsubscript{2}CN\textsubscript{2}R\textsubscript{2})\textsubscript{n}] are the most commonly used precursors for the fabrication of thin films and nanoparticles.\textsuperscript{130} DTC also show some activities in the analytical and biological process such as fungicides, antidotes for metal poisoning, anticancer and antibacterial.\textsuperscript{131} This is
owing to its ease of synthesis using readily accessible and affordable basic components. Additionally, by simply changing the amine substituents, their volatility, solubility, and breakdown characteristics can be modified.\textsuperscript{132} Complexes of DTC single source precursors are often used for the preparation of metal sulfide nanoparticles. These complexes have high thermal stability and high deposition temperature (more than 200 °C) due to the ability of stabilising a broad variety of oxidation states, which is not possible with similar ligands such as xanthates. DTC may include a variety of different R-groups, which may be advantageous for tweaking the chemical precursors to synthesise a variety of various structured nanoparticles. Another reason is that C-S bonds are comparatively simple to break in comparison to P-S bonds, in for example, dithiophosphate precursors which is important to create breakdown pathways that leave just metal and sulfur remains during nanoparticle formation.\textsuperscript{133} The symmetry of DTC is classified into three categories (i) symmetrically disubstituted, (ii) unsymmetrically disubstituted, and (iii) monosubstituted see Fig. 1.8.\textsuperscript{134}

![Examples of some different types of DTCs](image)

**Figure 1.8** Examples of some different types of DTCs (a) symmetrically disubstituted, (b) unsymmetrically disubstituted, and (c) monosubstituted.\textsuperscript{132}

### 1.6.3 Dithiocarbamate complex as single-source precursors

In general, dithiocarbamates are synthesised in one of two methods. The most often seen reaction is that of carbon disulfide with a secondary amine in the presence of a base, most commonly sodium or potassium hydroxide. At room temperature, reactions may be carried out in water, methanol, or ethanol and provide a high yield of aqueous soluble product. The second approach generates soluble dithiocarbamates in organic solvents by reacting carbon disulfide with two equivalents of secondary amine in the absence of any base. This results in the ammonium salt of the molecule $[\text{R}_{2}\text{NH}_2][\text{S}_2\text{CNR}_2]$, in which one amine equivalent functions as a base and the other as a nucleophile.\textsuperscript{133} Researchers have studied a wide range of metallic DTC and their applications as a precursor for the fabrication of metal chalcogenide nanoparticles and thin films such as NiS$_2$, In$_2$S$_3$, CoS, MnS, Ga$_2$S$_3$, SnS, ZnS, MoS$_2$, Fe$_2$S$_3$.\textsuperscript{135} DTC compounds may be used to synthesise metal sulfide nanomaterials using a variety of synthetic methods. The earliest instances of DTCs acting as SSP were reported around five decades ago.\textsuperscript{136,137} O’ Brien also pioneered the use of DTC complexes in the solvothermal
synthesis of nano dimensional metal sulfides.\textsuperscript{138,139} The complexes were decomposed upon heating to approximately 200 °C to yield ZnS or CdS nanoparticles.\textsuperscript{140} The similar strategy was quickly used to the deconstruction of additional DTC complexes, such as the production of PbS cubes from [Pb(S\textsubscript{2}CNBu\textsubscript{2})\textsubscript{2}].\textsuperscript{141} Lewis and co-workers\textsuperscript{142} recently reported the successful deposition of binary, ternary, and quaternary metal sulfides onto glass substrates using initial air-spray deposition approach followed by pyrolysis using diethyl DTC complexes. Numerous studies reported the use of DTC for the preparation of ternary metal sulfide such as CuInS\textsubscript{2},\textsuperscript{143} AgInS\textsubscript{2},\textsuperscript{144} CuFeS\textsubscript{2},\textsuperscript{145} AgBiS\textsubscript{3},\textsuperscript{146} Cu\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13}, and Cu\textsubscript{3}SbS\textsubscript{3}.\textsuperscript{147} Deng et. al,\textsuperscript{148} prepared high quality ternary metal sulfide NCs with controlled morphologies, sizes, crystalline and structure. For example, Solvothermal decomposition of [Cu(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{2}] and [Bi(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{3}] produce nanosheets and nanoparticles of Cu\textsubscript{3}BiS\textsubscript{3}, nanowires and nanoribbons of Cu\textsubscript{4}Bi\textsubscript{4}S\textsubscript{9}. The decomposition of [Cu(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{2}] and [Sn(S\textsubscript{2}CNEt\textsubscript{2})\textsubscript{4}] are resulted in the formation of orthorhombic nanorods Cu\textsubscript{3}SnS\textsubscript{4}.\textsuperscript{149}

1.7 Binary metal chalcogenide

Binary metal chalcogenide materials have gained considerable attention due to its properties and diverse applications in the field of transistors, sensors, solar cells, water treatment and photocatalysis.\textsuperscript{150} Numerous Binary metal chalcogenide have layered architectures that impart electrical and chemical characteristics and are discussed below

Copper zinc tin sulfide Cu\textsubscript{2}ZnSnS\textsubscript{4} (CZTS) is a low-cost non-toxic absorbing material with direct band gap and high absorption coefficient near-IR range.\textsuperscript{151} The material is suitable for IR sensors, optical reflectors and highly suitable for thin film based solar cells.\textsuperscript{152} Due to stoichiometry sensitivity developing CZTS is a significant challenge.\textsuperscript{153} For this reason, alternate materials with low cost and cheap fabrication methods need to be developed for suitable applications in as thermoelectric and solar cells.

Among many materials, V-VI chalcogenide semiconductors such as Sb\textsubscript{2}S\textsubscript{3} are promising candidate for wide range of potential applications.\textsuperscript{154} Particularly wide band gap Sb\textsubscript{2}S\textsubscript{3} (1.7 eV and above) chalcogenides have gained significant attention due to freedom of tuning the bandgap by adding suitable dopant element. These resulting chalcogenides have high absorption coefficients and Seebeck coefficient as compared to similar band gap compounds.\textsuperscript{155} These compounds have shown long-term stability and portrayed high absorption coefficients of 10\textsuperscript{5} cm\textsuperscript{-1}.\textsuperscript{156} The ranges of band gap and absorption coefficient is in accordance with the predicted values of efficient solar energy devices predicted by Shockley and Queisser.\textsuperscript{157}

1.7.1 Antimony sulfides (Sb\textsubscript{2}S\textsubscript{3})

Antimony chalcogenides (Sb\textsubscript{2}S\textsubscript{3}) is a group (V-VI) semiconducting material.\textsuperscript{158} The unique attributes of Sb\textsubscript{2}S\textsubscript{3} is its optical properties which have wide range of applications in LED’s, cameras, microwave devices, switching devices, and photovoltaic devices.\textsuperscript{158} It crystallises as orthorhombic crystal (see fig. 1.9) and has a melting point of 650 °C. It is commonly found in different colours under crystalline and amorphous phases.
The Sb$_2$S$_3$ crystals are normally found in grey-black solid with a metallic lustre, although the amorphous form may take on a variety of colours, including dark grey, orange-red, brilliant orange, reddish-brown, or violet. This colour variation is linked to the particle size and preparation process used of Sb$_2$S$_3$ NC’s. The band gap of Sb$_2$S$_3$ falls in the range 1.5 ~ 2.5 eV, depending on the form, size, and crystallinity of the nanostructures. For band gap ranges from 2.6–2.7 eV have multiple applications, e.g. blue LEDs, solar cells, and optical filters. All these features make Sb$_2$S$_3$, suitable candidate for solar energy conversion, optoelectronics, and thermoelectric devices.

***Figure 1.*** Crystal structure of Sb$_2$S$_3$ with the orthorhombic unit cell marked (a = 11.319 Å, b = 3.833 Å, c = 11.233 Å with α = β = γ = 90°) Blue atoms represent Sb and the yellow atoms are S.

1.7.2 Sb$_2$S$_3$ nanoparticles

Sb$_2$S$_3$ nanocrystals have been synthesised by hydrothermal, solvothermal, pyrolysis, pulsed laser ablation in liquid, and single-source methods. Recently, the single-source precursor route has drawn interest in the preparation of Sb$_2$S$_3$ nanocrystals. For example, in early 2000, Yang et. al used a single source precursor of antimony and thiourea complex to produce Sb$_2$S$_3$ nanorods by the solvothermal method. They formed amorphous nanoparticles of Sb$_2$S$_3$ with an average size of 65 nm at 120 °C by heating for 2 hours. Prolonged heating for 6 hours under 120 °C resulted in well-crystallized Sb$_2$S$_3$ nanorods with an average diameter of 60 nm. In later studies by Xie et. al, the hydrothermal method at a temperature ranging from 115-170 °C was used to produce Sb$_2$S$_3$ nanorods from single-source precursors of antimony dialkyl dithiocarbamate (Sb(S$_2$CNEt$_2$)$_3$). The nanorods of Sb$_2$S$_3$ with average diameter and length of 50-400 nm and 1-7 μm was synthesized, respectively. Their findings were in support that temperature and time of the reaction had a major effect on the topology of NC’s. On the other hand, Chen et. al, in 2005, reported the preparation of Sb$_2$S$_3$ nanowires using SbCl$_3$ as antimony source and L-cysteine (C$_3$H$_7$NO$_2$S) as a sulfur source, respectively, by the hydrothermal method. In 2007, high-quality Sb$_2$S$_3$ nanorods synthesized were reported by Lou et. al, using single-source precursors (SSP’s) of antimony di-n-octyl-dithiophosphates (Sb(S$_2$P(OC$_8$H$_{17}$)$_2$)$_3$) by the solvothermal method. The SSP’s were prepared using antimony trichloride with
ammonium O-di-n-octyl-dithiophosphate. The resultant complex was dissolved in an oleylamine to form a light-yellow solution which was heated at a temperature of 140 °C for more than 3.5 hours, producing an orthorhombic Sb$_2$S$_3$ nanorod with a length of 1 µm ± 100 nm and a diameter of 45 ± 5 nm. In 2008 Castro et al. 167 mentioned a significant relationship between the types of the precursors used, the preparation method, size, and morphology of synthesized Sb$_2$S$_3$ nanocrystals. In their study they used antimony (III) diethylidithiocarbamate and dithiophosphate complexes by both solvothermal and hydrothermal methods. Zhu et al. 172 in 2009, prepared flower and rodlike single-crystalline antimony trisulfide (Sb$_2$S$_3$) using antimony trichloride (SbCl$_3$) and thiourea with PEG 400 and Op-10 as surfactants. They obtained remarkable flower-like orthorhombic Sb$_2$S$_3$ structure with size of 9-10 µm, thickness of 0.05 - 0.2 µm and width of 0.8 – 22 µm. In the form of nano rods, the diameter ranges from 45~360 nm and length around 0.7~4 µm. The obtained bandgap of the nanorod structure was 1.52 eV which is potentially suitable for optoelectronic devices.

In 2013, Jasmine et Al. 173 prepared spherical and rod-like antimony sulfide nanostructures using single-source precursors of antimony thiosemicarbazone by pyrolysis and solvothermal methods. In pyrolysis, the precursor samples were pyrolyzed at 350 °C for 2 hours in a furnace and then cooled to room temperature to obtain a black-colored Sb$_2$S$_3$. While in the solvothermal method, their reported results show spherical and rod-like crystallized Sb$_2$S$_3$ from precursors which were dissolved in ethylene glycol and diphenyl ether under nitrogen gas.

Muneeb et. Al, 174 used antimony chloride and sodium sulfide to prepare visible light active Sb$_2$S$_3$ powder via a hydrothermal method, in order to use Sb$_2$S$_3$ as photocatalyst powder. They used different temperature ranges 105, 150, and 200 °C and reaction times of 4, 6, and 12 h to check the synthesized attributes of the material. While, Sun et. al 166, in 2015 prepared Sb$_2$S$_3$ nanoparticles by pulsed laser ablation without using any surfactants or capping agents. Their results portray that the solvent used and wavelength of the laser, has significant impact on altering the nature of the prepared NP’s. The imperative result obtained was that Sb$_2$S$_3$ nanoparticles showed well visible light absorption with optical bandgap of 1.75 eV suitable for photovoltaic applications. In 2019 Tahani et. al prepared pure Sb$_2$S$_3$ using tris(O-ethylxanthato)antimony(III) [Sb(S$_2$COEt)$_3$] single source precursors at different temperature ranging from 200 °C to 300 °C by the solvent less method 175 table (1.1) below summarise some of the method used to synthesis antimony sulfide Sb$_2$S$_3$ nanoparticles.

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Precursors</th>
<th>Synthesis temperature °C</th>
<th>Material</th>
<th>Morphology</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrothermal method</td>
<td>Antimony chloride SbCl$_3$ + Thioglycolicacid</td>
<td>100, 140, 180, 220</td>
<td>Sb$_2$S$_3$</td>
<td>Nanorods, Nanorods, Needlebeck+ microrods, Nanoparticles</td>
<td>167, 172, 173, 174, 175</td>
</tr>
<tr>
<td>Method</td>
<td>Antimony/Reagent</td>
<td>Temperature</td>
<td>Product</td>
<td></td>
<td></td>
</tr>
<tr>
<td>--------------------------------</td>
<td>-----------------------------------</td>
<td>-------------</td>
<td>--------------------------------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Solvothermal + hydrothermal</td>
<td>Antimony dithiocarbamates + dithiophosphates</td>
<td>140-197</td>
<td>Sb₂S₃ Nanorods Rod like Spherical</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrolysis + Solvothermal</td>
<td>Antimony thiosemicarbazone</td>
<td>350</td>
<td>Sb₂S₃ Spherical + nanorod</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hydrothermal method</td>
<td>Antimony chloride + Sodium sulfide</td>
<td>105-150</td>
<td>Sb₂S₃ Spherical particles</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulsed laser ablation</td>
<td>Antimony sulfide + Water</td>
<td>200</td>
<td>Sb₂S₃ Nanoparticles</td>
<td></td>
<td></td>
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<tr>
<td>Solvent less method</td>
<td>Tris(O-ethylxanthato) antimony(III)[Sb(S₂COEt)₃]</td>
<td>300</td>
<td>Sb₂S₃ Spherical particles</td>
<td></td>
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</tr>
</tbody>
</table>
1.7.3 Sb₂S₃ thin films

Antimony sulfide thin films are obtained using different methods such as chemical bath deposition, single-source route, spray pyrolysis, dip and dry method, laser-assisted chemical bath deposition and Aerosol assisted chemical vapour deposition (AACVD). The thin films of antimony sulfides are generally prepared by the colloidal and metal-organic precursors. In thin-film solar cells, Sb₂S₃ acts as a naturally occurring layer absorber. It is well known that Sb₂S₃ is an anisotropic material with a gap of 1.7 eV and adsorption coefficient of 1.15cm⁻¹ under 450 nm irradiated light. Furthermore, the stability of Sb₂S₃ in moisture, UV and high melting point at 550 °C makes a potential candidate for IR semi-transparent solar cells.

In 2008, Molloy et. al also used solvothermal, hydrothermal, and AACVD methods using antimony xanthate (Sb(S₂COR)₃), dithiocarbamate (Sb(S₂CNR₂)₃) and dithiophosphate precursors (Sb(S₂P(OR)₂) to prepare nano sizes stibnite Sb₂S₃. They found that AACVD provided a poor quality thin film and the use of antimony xanthate precursor was better than the antimony dithiocarbamate in producing oxide-free stibnite product.

A rod-shaped Sb₂S₃ thin film was deposited by Jasmine et. al in 2010 by the AACVD method, using a single source precursors of antimony(III) thiosemicarbazones, and cinnamaldehyde. They obtained a film at a temperature range of 300 °C to 500 °C. The thin film obtained has a bandgap of 3.48 eV. In the same year, Mehrzi et. al prepared Sb₂S₃ thin films using a simple chemical bath method by the deposition of the thin films on SnO₂/glass substrates at a low temperature ranging from 40 °C to 70 °C. The Sb₂S₃ thin film obtained has good optical properties with a refractive index ranging from 2.5 to 3.3 eV and a direct bandgap of about 2.30 eV. Murtaza et. al produced oxygen-free antimony sulfide thin film using tris(thiobenzoato) antimony (III) complex as a single source precursor by spin coating, AACVD and the doctor blade methods at a deposition temperature ranging from 300 °C to 400 °C. The orthorhombic structure (stibnite) thin films deposited has different morphology and size, depending on the technique and temperature used. The thin film deposited by AACVD techniques have a bandgap ranging from 1.81 to 1.90 eV see Fig 1.10.
Figure 1.10 The morphology of Sb$_2$S$_3$ thin films obtained from tris(thiobenzoato)antimony(III) using AACVD, spin coating, solid state melting and the doctor blade technique at 400°C.\textsuperscript{184}

Vinayakumar et al, studied the effect of rapid thermal processed (RTP) on antimony sulfide (Sb$_2$S$_3$) thin films prepared by chemical bath deposition of antimony thiosulfate on glass and Mo-coated glass substrates. The films were processed at different temperatures ranging from 325 to 700 °C for 1-5 minutes. XRD, XPS, and Raman spectroscopy were used to study the structure, morphology, elemental composition, optical and electrical properties of the films obtained. The optical band gap value of the resulting films was in the range of 1.7–2.1 eV.\textsuperscript{185} Just recently Murtaza et. al prepared pure Sb$_2$S$_3$ using Tris(N,N-diethylthiocarbamato) antimony(III) Sb(S$_2$CNEt$_2$)$_3$ single source precursors at different 450 °C by the air spray pyrolysis method\textsuperscript{142} table 1.2 below summarise some of the method used to synthesis binary antimony sulfide Sb$_2$S$_3$ thin films.

Table 1.2 Some of the method used to synthesis antimony sulfide Sb$_2$S$_3$ thin films

<table>
<thead>
<tr>
<th>Synthesis method</th>
<th>Precursors</th>
<th>Synthesis temperature °C</th>
<th>Material</th>
<th>Morphology</th>
<th>Reference</th>
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<tbody>
<tr>
<td>AACVD</td>
<td>Antimony thiosemicarbazone</td>
<td>320</td>
<td>Sb$_2$S$_3$</td>
<td>Rod shape</td>
<td>177</td>
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<tr>
<td>Spray pyrolysis</td>
<td>Antimony trychloride (SbCl$_3$) + Thiourea</td>
<td>250</td>
<td>Sb$_2$S$_3$</td>
<td>Uneven surface morphology</td>
<td>178</td>
</tr>
<tr>
<td>Method</td>
<td>Precursors</td>
<td>Temperature Range</td>
<td>Product</td>
<td>Notes</td>
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<td>---------------------------------------------</td>
<td>----------------------------------------------------------------------------</td>
<td>-------------------</td>
<td>---------</td>
<td>-------</td>
<td></td>
</tr>
<tr>
<td>Dip and dry method</td>
<td>Antimony trichloride (SbCl₃) + Thiourea</td>
<td>75-250</td>
<td>Sb₂S₃</td>
<td>Nanorods</td>
<td></td>
</tr>
<tr>
<td>Laser assisted chemical bath deposition method (LACBD)</td>
<td>SbCl₃ (Antimony trichloride) CH₃(CO)CH₃ (acetone) Na₂S₂O₃·5H₂O (sodium thiosulfate pentahydrate)</td>
<td>350</td>
<td>Sb₂S₃</td>
<td>Spherical particles</td>
<td></td>
</tr>
<tr>
<td>AACVD</td>
<td>Antimony xanthate (SbS₂COR) Antimony dithiocarbamate (Sb₂CNR) Dithiophosphate precursors (SbS₂P(OR)₂)</td>
<td>200-240</td>
<td>Sb₂S₃</td>
<td>Spherical particles</td>
<td></td>
</tr>
<tr>
<td>AACVD</td>
<td>Antimony thiosemicarbazon e + cinnamaldehyde</td>
<td>300</td>
<td>Sb₂S₃</td>
<td>Rod shape</td>
<td></td>
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<tr>
<td>Chemical bath deposition</td>
<td>Thiosulfate (Sb₂(S₂O₃)₃</td>
<td>40</td>
<td>Sb₂S₃</td>
<td>Spherical grains</td>
<td></td>
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<tr>
<td>Spin coating AACVD Doctorbalde</td>
<td>Tris(thiobenzoate) antimony (III)</td>
<td>300-400</td>
<td>Sb₂S₃</td>
<td>Sheets + Rod shape</td>
<td></td>
</tr>
<tr>
<td>Chemical bath deposition</td>
<td>SbCl₃ + Na₂S₂O₃</td>
<td>325-700</td>
<td>Sb₂S₃</td>
<td>Spherical shape</td>
<td></td>
</tr>
<tr>
<td>Air spray pyrolysis</td>
<td>Tris(N,N-diethylidithiacarbamato) antimony(III) Sb(S₂CNEt₂)₃</td>
<td>450</td>
<td>Sb₂S₃</td>
<td>Rod shape</td>
<td></td>
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</tbody>
</table>


1.8 Ternary SbₓSᵧ nanomaterial and thin films

Alloying of semiconductors to prepare ternary nanoparticles and thin films with different chemical compositions and crystalline structures has been widely studied over the past. Ternary nanoparticles and thin films have outstanding physical and optical properties which makes them potentially suitable materials in a variety of applications. Some binary semiconductors contain toxic elements such as Cd and Pb in the CdS and PbS that limit their applications. So preparation of ternary and quaternary materials with low toxicity is vital for their wide range of applications. Ternary materials have shown many advantages compared to the binary and bulk materials which make them a suitable choice for solar cell applications. In addition, due to their suitable band gap and their high absorption coefficient to the solar light, they are promising candidates in this area.

The synthesis of ternary and quaternary metal chalcogenide nanoparticles and thin films has been done using several methods including the use of SSPs. For example, a ternary CuInS₂ nanoparticle has been prepared using a SSP of (Ph₃P)₂Cu(μ-SEt)₂In(SEt)₂ via microwave irradiation method. Preparation of ternary antimony germanium sulfide thin films has been reported by Huang et al., in 2007, using GeCl₄/SbCl₅ and H₂S as a source for Ge, Sb, and S, respectively, via CVD method on silicon and glass substrates. They studied materials under different temperatures ranging from 120 °C to 400 °C to fabricate Ge–Sb–S thin films with varying thickness and phases and found that the change in the deposition temperature has an impact on the composition of Sb–Ge–S films. In 2010, Huang, et al. studied the optical properties of germanium antimony sulfide (Ge–Sb–S) thin films after preparing them on commercial glass substrates using the CVD method. In their study, GeCl₄, SbCl₅, and H₂S were used as a source for germanium, antimony and sulfur, respectively. The optical properties of prepared films were studied by the optical transmission spectra by UV–Vis-NIR spectrometer. The optical properties (direct band gap) of different films of GeSbS under concentration of Ge (5-20%) and Sb (15-20%) were reported for photovoltaic applications. In another study, Liu, et al., in 2014, reported the preparation of new ternary semiconductor nanoparticles (PbₓSbᵧS₁₇) for solar cells applications. The nanoparticles were synthesized on nano sized porous TiO₂ electrodes. Ternary tin-antimony sulfide (TAS) Sn–Sb–S compositions was a possible replacement of existing semiconducting materials because of their low processing cost and non-toxic elemental composition. In 2013 Ali et al. used the thermal evaporation technique to prepare SnSb₂S₄ thin film on a glass substrate to study their structural and optoelectronic properties. The films were annealed in sealed glass ampoules at 85 °C, 150 °C, 275 °C, and 325 °C in argon gas at low pressure. Polycrystalline films were annealed at low temperature, while amorphous films were annealed at high-temperature. The crystalline and amorphous films have shown similar photoconductivity responses with estimated bandgap ranging from 1.82–3.1 eV and n-type conductivity at all temperatures. Anitha, et al., in 2018, used antimony as a dopant material to fabricate hexagonal SbSnS₂ thin films on glass substrate by spray pyrolysis. The study reported that with an increase in Sb doping concentration the band gap...
value decreased, reaching a minimum bandgap of 2.5 eV from 2.75 eV in pure form. Rahayu et al.\textsuperscript{200} prepared NaSbS\textsubscript{2} nanoparticles for solar cells applications by the chemical synthesis of binary sulfides Na\textsubscript{2}S and Sb\textsubscript{2}S\textsubscript{3}. Single-phase NaSbS\textsubscript{2} nanoparticles were synthesized with an attractive feature such as ionic-electronic coupled switchable photovoltaic in solar material. Fabiola et al.\textsuperscript{201} prepared Sb\textsubscript{2}S\textsubscript{x}Se\textsubscript{3-x} (x = 0.7 – 2) thin films with a diameter ranging from 280-300 nm by vacuum thermal evaporation, using a solution of potassium antimony tartrate, thioacetamide, and selenosulfate. The bandgap of the film prepared was ranging from 1.43 – 1.6 eV and photoconductivity was 4 x 10\textsuperscript{-5} and 8 x 10\textsuperscript{-7} $\Omega^{-1}$ cm\textsuperscript{-1}. Tahani et al.\textsuperscript{175} prepared M\textsubscript{2-2x}In\textsubscript{2x}S\textsubscript{3} (where M = Bi or Sb) alloys using precursor mixture of In(S\textsubscript{2}COEt)\textsubscript{3} and M(S\textsubscript{2}COEt)\textsubscript{3} by the solventless method. The mole fraction in their work was used in the range of indium x as (0 ≤ x ≤ 1) at temperature 300 °C. They reported comprehensive details on the compounds including structural, compositional, optical and morphological properties of the synthesized M\textsubscript{2-2x}In\textsubscript{2x}S\textsubscript{3} samples. The results were analysed using X-ray diffraction, scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, Raman spectroscopy and UV-Vis absorption spectroscopy. They also reported the band gap energies of Sb\textsubscript{2-2x}In\textsubscript{2x}S\textsubscript{3} films which fall in the range of 2.19–2.9 eV. In another report by Tahani et al., a combined single-source precursor approach has been used for the preparation of the ternary Bi\textsubscript{2-2x}Sb\textsubscript{2x}S\textsubscript{3} (0 ≤ x ≤ 1) solid solution. The compositions are controlled by solventless thermolysis using the xanthates Sb[S\textsubscript{2}COEt]\textsubscript{3} and Bi[S\textsubscript{2}COEt]\textsubscript{3}. The obtained electronic band gaps of Bi\textsubscript{2-2x}Sb\textsubscript{2x}S\textsubscript{3} films were ranging from 1.66 eV (Bi\textsubscript{2}S\textsubscript{3}) to 2.19 eV (Sb\textsubscript{2}S\textsubscript{3}) see Fig1.11. This approach provides efficient synthesis route for the production of ternary sulfide materials.

**Figure 1.11** changing of the band gap for Bi\textsubscript{2-2x}Sb\textsubscript{2x}S\textsubscript{3} (0 ≤ x ≤ 1)) samples with the increase of antimony mole fraction (x).\textsuperscript{162}
1.8.1 Ternary copper antimony sulfide

Ternary copper antimony sulfides (Cu-Sb-S) have shown great potential as low-cost solar absorber materials. Particularly these materials have band gap falls in the range 2.22–2.55 eV and useful for green LED’s. The reason for this is high absorption coefficients across the NIR-Vis range, band gap energy suitable for efficient light harvesting and are composed of inexpensive non-toxic elements. CuSbS₂ (chalcostibite), Cu₁₂Sb₄S₁₃ (tetrahedrite), Cu₃SbS₃ (skinnerite), and Cu₃SbS₄ (fematinite) are the four ternary phases of the Cu-Sb-S system. All aforementioned phases exhibit a strong absorption coefficient and p-type electrical conductivity.

The preparation of copper antimony sulfide (CAS) NPs have been reported in recent years. In 2011 Garza, et. al prepared p-type CuSbS₂ thin films by heating Sb₂S₃/Cu multilayers in a vacuum. The thickness of the copper layer and the evaporation temperature showed a direct effect on the structure, morphology, optical, and electrical properties of the thin films. For example, the CuSbS₂ thin film with p-type conductivity and optical band gap of 1.5 eV suitable for IR optical sensors were successfully formed at 380 °C. Ornelas, et. al, in 2014, prepared ternary CuSbS₂ thin films by the heating glass/Sb₂S₃/Cu layers at 350, 375 and 400 °C in low vacuum (103 Torr) for 1 h in a vacuum furnace. Then, copper thin films of 50 nm thickness were deposited by thermal evaporation of 99.99 % pure copper. Cu thin films wire was grown on Sb₂S₃, coated glass substrates, and loaded in a high vacuum system to deposit Sb₂S₃/Cu multilayers by thermal evaporation at different temperatures. Suehiro et al, prepared Cu–Sb–S (CAS) NCs such as Cu₃SbS₂, Cu₃SbS₄, and Cu₁₂Sb₄S₁₃ by spin coating method under low temperature. Their results have shown that crystal phase and electronic structure were sensitive to temperature and chemical composition during fabrication. Cho et. al prepared four different phases of Cu–Sb–S (CuSbS₂, Cu₁₂Sb₄S₁₃, Cu₃SbS₄, Cu₁₂Sb₄S₁₃) using a non-vacuum hybrid ink method. Cu and Sb precursors were coated and sulfurized with rapid thermal annealing (RTA) using a solution of Cu (II) acetate (Cu(O₂CCH₃)₂), antimony acetate (Sb(O₂CCH₃)₃), methanol (CH₃OH), and monoethanolamine (NH₂CH₂CH₂OH). The XRD analysis confirmed that the change in the ratio of Cu and Sb led to the formation of different phases of Cu–Sb–S thin films (CuSbS₂, Cu₁₂Sb₄S₁₃, Cu₃SbS₄, Cu₁₂Sb₄S₁₃). This shows the flexible nature of the compounds that are sensitive to Cu and Sb content ratio in thin film fabrication. Hussain et. al prepared copper antimony sulfide (Cu₃SbS₃) thin films with a p-type conductivity and optical band gaps in the range of 1.38 to 1.84 eV, using successive thermal evaporation of Cu₂Sand Sb₂S₃ layers, followed by annealing in an argon atmosphere at four different temperatures ranging from 300 to 375 °C. All these properties of the films demonstrated it as a good absorber layer in solar cells. In literature there are several reports available which have used precursor-based routes for the synthesis of ternary Cu-Sb-S materials. By changing the solvents and the composition of precursors, CuSbS₂, Cu₁₂Sb₄S₁₃ and Cu₁₂Sb₄S₁₃ NC’s can be obtained using this approach. The nano sheets of CuSbS₂ (rectangular shaped) were obtained from diethylidithiocarbamates of Sb and Cu in oleylamine. Regulacio et. al and Bera et. al also employed Cu and Sb diethylidithiocarbamate precursors to synthesise high-purity tetrahedrite (Cu₁₂Sb₄S₁₃) nanostructures by the solvothermal and hot injection methods, respectively. The development of additional
ternary Cu–Sb–S phases in addition of the target material is a prevalent issue when utilising these techniques. The solvent oleylamine resulted in the formation of famatinite (Cu$_3$SbS$_4$), dodecanethiol (DDT) result in a combination of tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$) and skinnerite (Cu$_3$SbS$_3$) phases. Very recently, Alqahtani et. al in 2021, synthesised two distinct phases of Cu–Sb–S, chalcostibite (CuSbS$_2$) and tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$) nanostructures using a simple, economical and low temperature route. Both compounds were prepared by the decomposition of a mixture of bis(O-ethylxanthato) copper(II) and tris(O-ethylxanthato) antimony(III), without the use of solvent or capping ligands. Moreover, by tuning the molar ratio of Sb and Cu xanthates, single-phases of chalcostibite and tetrahedrite were obtained the crystal structures analysis in terms of powder XRD are presented in Fig 1.12 below.

1.8.2 Ternary cobalt and iron antimony sulfide

Iron pyrite (FeS$_2$) is a diamagnetic small band gap (0.95 eV) SC frequently used in photovoltaics near IR region optical devices. While, CoS$_2$ is a metallic itinerant ferromagnet. The solid solution Co$_x$Fe$_{1-x}$S$_2$ is of great interest due to paramagnetic at room temperature and intermixed properties of Fe and Co based pyrites in the entire range (0 ≤ x ≤ 1). Naderi A. et. al, developed Co$_x$Fe$_{1-x}$S$_2$ nano particles with different ratios of Co and Fe to be used in as OER catalyst in alkaline media. The results showed that mechanism of activation process consists of leaching of sulfide and formation of a cobalt-iron amorphous oxide layer on the surface of catalyst. Furthermore, Fe doping in CoS$_2$ raised the activity of the electro catalyst which has decreased the over potential correlation between the iron and cobalt atoms.

Abdin et. al in 2019, reported the effect of doping antimony trisulfide Sb$_2$S$_3$ with iron Fe using chemical bath deposition (CBD) technique at temperatures 0, 5 and 10 °C for 4 h and annealed at 500 °C for 2 h under N$_2$ environment. They found that, Fe affects the microstructure of the developed crystalline thin films, reducing...
particle size while increasing stresses and dislocation densities. Furthermore, Fe addition in Sb$_2$S$_3$ thin films enhances not only their morphological features, but also their band gap values, bringing them into the photoactive-visible range. To summarise, the energy gap values obtained for undoped and Fe-doped Sb$_2$S$_3$ thin films (1.53 eV – 1.85 eV (RED) and 1.79 eV – 1.97 eV (Orange), respectively) were found within the operating requirements of photovoltaics applications.

Jang Y. H. et. al $^{218}$ have reported CoSbS-based nano composites as anodes for Na-ion batteries (NIB’s). They found that transformation between CoSbS and Na$_x$CoSbS for $x \leq 1.6$ leads to highly stable cycling response (after testing for 100 cycles of charging discharging) for the NIB’s and a volumetric capacity of 480 mAh cm$^{-3}$. In another study, Karthikeyan et. al $^{219}$ reported the crystal structure determination and thermoelectric studies of new Co-Sb-Se ternary system. They found that pristine Co$_{2.0}$Sb$_{1.6}$Se$_{2.4}$ exhibits low thermal conductivity (~1.0 Wm$^{-1}$K$^{-1}$ at 300 K and ~0.7 Wm$^{-1}$K$^{-1}$ at 657 K) due to enhanced phonon scattering among Sb and Se disordered lattices. Thus, suitable structural modifications were required to improve the effectiveness of material by adding Zn and Sn doping in pristine Co$_{2.0}$Sb$_{1.6}$Se$_{2.4}$. They also reported in detail quantitative and qualitative structural analyses of compounds by Rietveld refinement. The results have shown that improved thermoelectric power factor of Co$_{2.0}$Sb$_{1.5}$Zn$_{0.1}$Se$_{2.4}$ compound at 657 K ternary chalcogenides. Liu, X. et. al $^{220}$ reported the fabrication of two new thioantimonates [Co(dien)$_2$][CoSb$_2$S$_{14}$] and [Co(dien)$_2$][Sb$_4$S$_9$]. Where diethylenediamine (dien) compounds reacted and synthesized solvothermally with Sb, Co and S at 160 °C. The optical properties of both compounds have shown excellent optical attributes after analysis with UV–Vis spectra. Thermoelectric chalcogenide materials have high demand nowadays due to their conversion efficiency of heat into desirable electronic applications. $^{221}$ The development of new materials has escalated since past few years specially for transition element doping. You et. al $^{222}$ studied the structure and thermoelectric properties of Te doped paracostibite CoSb$_{1-x}$Te$_x$S for low doped concentrations ($x = 0$–0.09) samples were prepared by vacuum melting, annealing and SPS processing. The results have shown that by increasing the doping content of Te on Sb site enhances the carrier concentrations up to 7.24 ×10$^{20}$ cm$^{-3}$ for CoSb$_{0.93}$Te$_{0.07}$S, which is much higher than that of pristine CoSbS. Furthermore, the power factor (ZT) of 0.43 at 900 K is reported for CoSb$_{0.93}$Te$_{0.07}$S compound, which is 139% higher than pristine CoSbS. Table 1.3 below summaries various methods used to synthesis different phases of ternary antimony sulfide thin films and nanoparticles.

<table>
<thead>
<tr>
<th>Method</th>
<th>Precursors</th>
<th>Temperature °C</th>
<th>Materials</th>
<th>Thin film/ Nanoparticles</th>
<th>Phase</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical vapour deposition</td>
<td>GeCl$_4$/SbCl$_5$ and H$_2$S</td>
<td>120-400</td>
<td>GeSbS</td>
<td>Thin films</td>
<td>Sb$<em>{20.3}$Ge$</em>{17.9}$S$_{61.6}$</td>
<td>$^{194}$</td>
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<tr>
<td><strong>Chemical vapour deposition</strong></td>
<td><strong>GeCl₄/SbCl₅ and H₂S</strong></td>
<td><strong>120-400</strong></td>
<td><strong>GeSbS</strong></td>
<td><strong>Thin films</strong></td>
<td><strong>Ge₂₁Sb₁₅S₆₄</strong>&lt;br&gt;<strong>Ge₁₇Sb₂₀S₆₃</strong>&lt;br&gt;<strong>Ge₁₂Sb₂₄S₆₄</strong>&lt;br&gt;<strong>Ge₁₁Sb₂₀S₆₃</strong>&lt;br&gt;<strong>Ge₅Sb₃₂S₆₃</strong></td>
<td>195</td>
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<td><strong>SALAR process</strong></td>
<td>Lead sulfide PbS&lt;br&gt;Antimony sulfide&lt;br&gt;Sb₂S₃</td>
<td><strong>350</strong></td>
<td><strong>PbSbS</strong></td>
<td><strong>Particles</strong></td>
<td><strong>Pb₂Sb₈S₁₇</strong></td>
<td>196</td>
</tr>
<tr>
<td><strong>Thermal technique</strong></td>
<td>Tin sulfide&lt;br&gt;Antimony sulfide</td>
<td><strong>85-125</strong></td>
<td><strong>SnSbS</strong></td>
<td><strong>Thin films</strong></td>
<td><strong>SnSb₂S₄</strong>&lt;br&gt;<strong>Sn₂Sb₂S₅</strong></td>
<td>197</td>
</tr>
<tr>
<td><strong>Thermal evaporation</strong></td>
<td>Tin sulfide&lt;br&gt;Antimony sulfide</td>
<td><strong>85-325</strong></td>
<td><strong>SnSbS</strong></td>
<td><strong>Thin films</strong></td>
<td><strong>SnSb₂S₄</strong></td>
<td>198</td>
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<tr>
<td><strong>Pyrolysis</strong></td>
<td>Tin sulfide&lt;br&gt;Antimony sulfide</td>
<td><strong>250</strong></td>
<td><strong>SnSbS</strong></td>
<td><strong>Thin films</strong></td>
<td><strong>SbSnS₂</strong></td>
<td>199</td>
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<tr>
<td><strong>Silar method</strong></td>
<td>Na₂S and Sb₂S₃</td>
<td><strong>350</strong></td>
<td><strong>NaSbS</strong></td>
<td><strong>Nanoparticles</strong></td>
<td><strong>NaSbS₂</strong></td>
<td>200</td>
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<td><strong>Vacuum thermal evaporation</strong></td>
<td>Potassium antimony tartrate&lt;br&gt;(K₂Sb₂C₈H₁₂·3H₂O)&lt;br&gt;Sodium selenosulfate (SS), Na₂SeSO₃</td>
<td><strong>850-900</strong></td>
<td><strong>SbSSe</strong></td>
<td><strong>Thin films</strong></td>
<td><strong>Sb₂₀.₇Se₂.₃</strong></td>
<td>201</td>
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<td><strong>Solventless method</strong></td>
<td>Indium xanthates&lt;br&gt;<strong>In(S₂COEt)₃</strong>&lt;br&gt;And&lt;br&gt;Antimony xanthates&lt;br&gt;Sb(S₂COEt)₃</td>
<td><strong>300</strong></td>
<td><strong>InSbS</strong></td>
<td><strong>Nanoparticles</strong></td>
<td><strong>Sb₂₋₂xIn₂xS₃</strong></td>
<td>202</td>
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<td><strong>Solvent less method</strong></td>
<td>Antimony xanthates&lt;br&gt;Sb[S₂COEt]₃&lt;br&gt;and bismuth xanthates&lt;br&gt;Bi[S₂COEt]₃</td>
<td><strong>300</strong></td>
<td><strong>BiSbS</strong></td>
<td><strong>Nanoparticles</strong></td>
<td><strong>Bi₂₋₂xBi₂xS₃</strong></td>
<td>203</td>
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<td><strong>Chemical bath deposition</strong></td>
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<td><strong>300-380</strong></td>
<td><strong>CuSbS</strong></td>
<td><strong>Thin film</strong></td>
<td><strong>CuSbS₂</strong></td>
<td>204</td>
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<tr>
<td><strong>Chemical bath decomposition</strong>&lt;br&gt;<strong>Thermal evaporation</strong></td>
<td>SbCl₃ + Na₂S₂O₃ + Cu</td>
<td><strong>350-400</strong></td>
<td><strong>CuSbS</strong></td>
<td><strong>Thin film</strong></td>
<td><strong>CuSbS₂</strong></td>
<td>205</td>
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<td>Solution phase synthesis technique</td>
<td>Cu(II) acetylacetonate + Sb(III) acetate + oleylamine</td>
<td>200</td>
<td>CuSbS</td>
<td>Nanocrystals</td>
<td>CuSbS2, Cu3SbS4, Cu12Sb4S13</td>
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<td>Nonvacuum hybrid ink</td>
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<td>450-520</td>
<td>CuSbS</td>
<td>Thin films</td>
<td>CuSbS2, Cu3SbS3, Cu5SbS4, Cu12Sb4S13</td>
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<tr>
<td>Thermal evaporation</td>
<td>Cu2S + Sb2S3</td>
<td>300-375</td>
<td>CuSbS</td>
<td>Thin films</td>
<td>Cu3SbS3</td>
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<td>Solvothermal method</td>
<td>Copper diethylthiocarbamate Antimony diethylthiocarbamate</td>
<td>80-200</td>
<td>CuSbS</td>
<td>Nanoparticles</td>
<td>Cu12Sb4S13</td>
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<td>Hot injection</td>
<td>Copper diethylthiocarbamate Antimony diethylthiocarbamate</td>
<td>250-260</td>
<td>CuSbS</td>
<td>Nanoparticles</td>
<td>Cu12Sb4S13, Cu5SbS4, Cu3SbS3</td>
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<tr>
<td>Solvent less method</td>
<td>bis(Oethylxanthato) copper(II) and tris(Oethylxanthato) antimony(III),</td>
<td>250</td>
<td>Cusbs</td>
<td>Nanoparticles</td>
<td>CuSbS2, Cu12Sb4S13</td>
<td></td>
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<tr>
<td>Chemical vapour deposition</td>
<td>SbCl3 and Na2S2O3+ Fe</td>
<td>500</td>
<td>FeSbS</td>
<td>Thin films</td>
<td>Fe: SbS2</td>
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<tr>
<td>Vacuum melting method</td>
<td>Co, Sb and Se 99.8% purity</td>
<td>80</td>
<td>CoSbSe</td>
<td>Nanocrystals</td>
<td>Co2.6Sb1.6Se2.4 and Co2.6Sb1.5M0.1Se2.4 (M= Zn, Sn)</td>
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1.9 Aims and Objectives of the thesis

The literature review demonstrates that solventless pyrolysis of metal dithiocarbamate complexes is advantageous because dithiocarbamate precursors have low decomposition temperatures and volatile byproducts, allowing for low temperature synthesis and clean formation of metal sulfides in a shorter time period than the conventional solid-state synthetic approach. Another distinguishing aspect of this technique is the absence of high-boiling solvents, which may provide an environmental and economic benefit on the melt route over solution-based processes. Hence, the aim of the present work is to develop a simple and cost-effective method for synthesising well-defined phases of binary and ternary metal sulfides employing metal dithiocarbamates as molecular precursors.

The review of literature also shows that the iron, copper, and cobalt doped ternary antimony sulfides offer promising, novel, low-toxic and earth abundant materials with properties commensurate for use in a wide range of technological applications. For example, these materials have low-phonon energy and generally transparent to incident light ranging between visible to infrared. In nanocrystalline form seven distinct photoinduced phenomena are observed like photo-decomposition, photo-crystallization, photo-expansion, photo-polymerization, photo-vaporization and photo-dissolution of metals in the chalcogenide. These attributes are accompanied by slight changes in the optical constants, electronic band gap and optical absorption coefficient. These materials could also be suitable for their possible role in as new materials in optical fibre. Especially when doped with rare earths, the advantage of low phonon energy and high refractive index is observed in these materials which results increased pumping efficiencies.

This thesis explores the use of metal dithiocarbamates as molecular precursors for the synthesis of binary Sb$_2$S$_3$, FeS, CuS, CoS at different range of temperature and to synthesise ternary Sb$_{2(1-x)}$Fe$_{2x}$S$_3$, Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ , in particular CuSbS$_2$, Cu$_{12}$Sb$_4$S$_{13}$ and Co$_{2x}$Sb$_{2(1-x)}$S$_3$ powders by the solvent less thermolysis at 450 °C these will be characterised by p-XRD, SEM and EDX. The aim is to investigate the effect of metal dopant on the structural, morphological and optical and magnetic properties of the host material Sb$_2$S$_3$ compared with the effect of the binary Sb$_2$S$_3$ sample. Finally, we will explore the use of metal dithiocarbamate complexes to synthesise fematinite (Cu$_3$SbS$_4$), tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$) and costbite (CoSbS) thin films from SSPs using AACVD methods. The effect of this route on the structural, morphological and compositional properties of the thin film will be investigated. There are no previous reports in the literature about the deposition of Cu$_3$SbS$_4$, Cu$_{12}$Sb$_4$S$_{13}$ and CoSbS films from SSPs using AACVD. The synthesised thin films will be characterised by p-XRD, SEM, EDX, Raman and UV-Vis spectroscopy.
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CHAPTER 2. EXPERIMENTAL TECHNIQUES

2.1 Elemental analysis

Elemental analysis was performed with a carbon, hydrogen, nitrogen, sulfur analysis (CHNS) elemental analyser (Flash 2000 Thermo Scientific elemental analyser). The bulk samples are put within a tin container in a furnace set to 1000 °C and oxygen is introduced into the furnace, where they burn and decompose. Carbon in the sample burns and is converted to other forms of carbon. Carbon dioxide, CO₂, hydrogen produces water vapour, H₂O, nitrogen, and sulphur are identified as the formation of the dioxide gases NO₂ and SO₂. Gas chromatography is used to analyse those gases to ascertain the composition of each element existing in the sample. A weighted volume of the required elements, such as antimony, copper, iron, and cobalt, were dissolved in acid and then transferred to a volumetric flask and dissolved in water to estimate the metal composition of samples. Inductively coupled plasma optical emission spectrometer (ICP-OES) was used to analyse the solution and identify the specific element concentrations within it. All elemental analysis was done by the School of Chemistry's microanalysis team throughout the investigation.¹

2.2 Thermogravimetric analysis (TGA)

TGA is an important method for the determination of the thermal characteristics of materials since it allows for the measurement of changes in a substance's physical and chemical properties as a function of temperature over time or as a function of time while the temperature remains constant. The analysis is performed using a thermal analyser that is heated in the presence of a flow of gas, which may be nitrogen, dioxygen, air, or a combination of gases. To calibrate the device, indium metal is utilised as a reference. TGA may be used to get information about physical properties for example vaporisation, absorption and sublimation. Moreover, it contains data on chemical processes for example breakdown, dehydration, solid-gas interactions, oxidation, and reduction. The approach may be used to display the material properties of a sample by analysing the breakdown patterns, degradation processes and reaction kinetics, as well as the organic and inorganic contents. TGA is used to detect certain properties of single-source precursors that are linked to mass loss or gain owing to breakdown, oxidation, or the volatiles loss for example water. Perkin Elmer TGA 4000 was used to complete these measurements at a temperature ranging from 30 to 800 degree Celsius with a rate of heating of ten degrees Celsius per minute in the presence of nitrogen.

2.3 Powder x-ray diffraction
Powder X-ray diffraction (p-XRD) is a non-destructive method used for identifying a material in a powder or thin film form for establishing the purities of their phases. The p-XRD studies were done using PANalytical X’Pert Pro theta-theta diffractometer (435 mm diameter, Malvern, UK). The data were obtained using detector scans with a grazing incidence angle of 3° and a scan range of 5° to 85° with a 0.03° step and a time step of 8 s/step. Then, the sample's diffraction patterns were compared to the ICDD index pattern. The strong powder X-ray diffraction (p-XRD) method may be used to identify crystalline materials. This approach may also be used to identify the distinct phases inside a material in conjunction with measurements of structural parameters such as phase composition, defect structures, strain state, preferred orientation, epitaxy, and grain size. Three fundamental components comprise an X-ray diffractometer: an X-ray tube, a sample container, and an X-ray detector. Within the X-ray tube, a cathode ray tube acts as a source of electrons that are accelerated using anode target materials (Cu, Fe, Mo, Cr). Distinctive X-ray spectra are formed when electrons have enough energy to disrupt the target materials inner shell electrons. Copper is the most common target material for single-crystal diffraction, with CuKα radiation of 1.5418. Collimated X-rays are directed towards the sample. By the bremsstrahlung effect, electrons collide with the target and produce X-rays, which are subsequently directed toward the sample. XRD diffraction measurements of crystalline materials are shown in Figure 2.1 where d is the distance between two parallel planes and λ is the wavelength and θ is the diffraction angles. X-rays diffracted by the layers of atoms comply Bragg’s law:

\[ n\lambda = 2dsin\theta \]  

(2.1)

This equation demonstrates how the angle of incidence may be calculated using the difference in path between the reflected rays by successive planes inside the lattice. Figure 2.1 illustrates how the prepared material may be identified by comparing the intensities and locations of diffraction peaks to those of known crystalline materials in the database. Additionally, the equation enable the identity and quantity of distinct sample, as well as the estimation of the particle size average through the widening of the p-XRD pattern line.

**Figure 2.1** x-ray Schematic representation of Bragg Diffraction

2
2.4 UV/Vis spectroscopy

UV-Vis-NIR (UV/Vis/NIR) absorbance spectroscopy is used to determine a material's optical band gap. Analyses may be performed on samples suspended in a solution or mounted on a clear substrate. The optical absorbance of a sample is measured by the amount of monochromatic light that passes through it (transmittance) across a range of wavelengths. Without the sample present, a reference sample of the carrier fluid or substrate is taken and its transmittance is subtracted from the sample measurement. Typically, one or more light sources are employed to span the wavelength range from ultraviolet (UV) to near infrared (NIR), with a scanning monochromator allowing for the passage of just one wavelength at a time. In the present work, optical absorbance spectra were utilised to determine the band gap of materials, and these absorbance spectra were recorded using an Agilent Cary 60 UV−vis spectrophotometer at wavelength ranging from 200–1000 nanometres. Band gap is usually calculated from the absorbance spectra by the analysis of UV-Visible spectroscopy data using the following equations. According to Beer-Lambert Law

\[ I = I_0 e^{-\alpha t} \]  

Where \( \alpha \) is absorption coefficient, \( t \) is the thickness, \( I \) and \( I_0 \) are intensities of the light after and before transmission through the material. By simplifying the equation into standard units, we get

\[ \log \left( \frac{I}{I_0} \right) = \log e^{-\alpha t} \]  

\[ \log \left( \frac{I}{I_0} \right) = -0.4343 \alpha t \]  

\[ \log \left( \frac{I_0}{I} \right) = 0.4343 \alpha t \]  

Where \( A = \log \left( \frac{I_0}{I} \right) \)

\[ \alpha = \left( \frac{2.3026}{t} \right) A \]  

Taking \( t=1 \text{cm} \),

\[ \alpha = 2.3026 A \text{ cm}^{-1} \]  

As we know that \( E = h \nu = \frac{1240}{\lambda} \)

\[ \alpha h \nu = \frac{1240}{\lambda} \times (2.3026)A \]

\[ \alpha h \nu = 2861 \times \frac{A}{\lambda} \]  

Here \( A \) is absorbance and \( \lambda \) is wavelength (nm)

Finally, the bandgap energy of the material was calculated from the following Tauc equation;

\[ (\alpha h \nu)^n = A(h \nu - E_g) \]  

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, \( n = 2 \) and \( \frac{1}{2} \) for allowed direct and allowed indirect transitions, respectively. Plots of the \( (\alpha h \nu)^n \) versus \( h \nu \) showed a linear behaviour for \( n = 2 \), which confirmed the direct transition in all
the samples see figure 2.2 below of the determination of optical band gap from the UV-visible absorption spectra using the Tauc Plot method. The average band gap was estimated from the intercept of linear portion of the \((\alpha h\nu)^n\) vs. \(h\nu\) plots on \(h\nu\) axis see Figure 2.3 b

![Figure 2.2 Tauc plot method to determine optical band gap from UV-visible absorption spectra.](image)

### 2.5 Raman spectroscopy

Raman spectroscopy is a valuable, simple, non-destructive approach that uses the interaction between light and the substance to obtain insight into its properties. Raman spectroscopy offers information about frequency modes and vibrations that can be used to deduce information about crystal lattices. Raman measurements also reveal the precise exact vibrations of a molecule, referred to as a molecular fingerprint, which is used for the identification of a chemical. A Raman spectrometer is comprised of the following components: a laser source, sample illumination and collection system, wavelength selector, detector, and data processing system. It is fundamentally based on the inelastic scattering of light by matter. When a sample is irradiated by an intense laser beam with a specific frequency in the UV Visible range and the light absorbed by the particles, a large number of photons are dispersed at a similar energy to the incoming photons Rayleigh scattering is the term used to describe that. Raman scattering occurs when a few of these photons scatter at a frequency different from that of the incoming photon. Stokes scattering occurs when the energy difference between the incident and scattered photons is greater than the energy difference between the incident and scattered photons. However, certain molecules activate in an excited state level and then relax to a lower energy level. The term anti-Stokes refers to this scattering (Figure 2.3). Because of the frequency of the light dispersed by the molecule, the structural features of molecular bonds may be changed. These characteristics may offer information on the electrical and vibrational properties of a semiconductor, including their stain, microstructure, quality of the crystals, the composition of the alloys, and their sensitivity to the free carrier density.
2.6 Scanning electron microscopy (SEM)

SEM produces three-dimensional (3D) pictures in the nanoscale resolution, allowing for the analysis of film and nanostructure formation. The SEM method employs a concentrated electron beam to scan the material and provide readily interpretable. According on the sample's composition and features, several vacuum settings are employed to study specimens by SEM, including high and medium vacuum, low vacuum, wet circumstances and at a different of temperatures and cryogenic. SEM works on the principle of scanning an electron beam over a specimen to generate a signal from secondary or reflected electrons. The specimen chamber and optical system must be kept at high vacuum of $10^{-3}$ to $10^{-4}$ Pa. When electron enter the specimen scattering occurs and electrons lose their energy and ultimately get absorbed in specimen. The scattering range is dependent on many factors which include, atomic number of elements, electron energy, density of specimen and its orientation. These electrons produce secondary electrons from the specimen’s constituent atoms valence shell. The energy of these electrons is small as compared to bombarded electrons and are easy to absorb by detectors. Secondary electrons generated are surface sensitive and are only generated from the top most surface. To detect these electrons emitted from specimen, secondary detector is used using scintillator. High voltage of about 10kV is used to attract the secondary electrons towards scintillator to generate light, this light is further detected by photo-multiplier-tube. This light is further converted into electrons as an amplified signal. To improve the resolution of the generated signal, secondary detector (through the lens detector) is placed right above the objective lens controlled by magnetic field. The shape, crystal orientation and chemical contents of the nanocrystals determined the intensity of the generated signals. The surface morphology and composition of samples may be determined using the secondary electrons. The number of secondary electrons generated is proportional to the angle at which the beam strikes the specimen's surface, i.e. the topography.
The resolution and contrast generation of image by SEM is dependent on the high-performance objective lens and electron gun.

The SEM generates a variety of signals, when interact with atom of the samples (figure 2.4) including specimen current, backscattered electrons (BSE), distinctive X-rays, transmitted electrons, light cathode-luminescence (CL), and secondary electrons (SE), the latter of which is regarded standard equipment in all SEMs. At or near the sample surface, the signals produced by electron beam interacts with atoms of the sample. The micrographs generated have a great depth of field due to the incredibly ultra-small size of electron beam.

![Figure 2.4 The interaction between electron and sample](image)

The output signal is magnified by changing width of electron probe for example, the screen of 10 cm represents 1 mm electron probe results in the magnification 100 times and so on. The standard scan dimensions of SEM are 12 cm horizontal and 10 cm vertical. The depth of focus is also dependent on magnification of SEM. Scanning electron microscopy (SEM) imaging in this work was performed using an FEI Quanta 650 Field Emission GUN (FEG)-SEM at an accelerating voltage of 10 - 20 kV.

### 2.7 Energy Dispersive X-ray spectroscopy (EDX)

Energy dispersive X-ray spectroscopy (EDS, EDX, or EDXRF) is an effective technique for identifying and quantifying components in micron-sized samples. It is a chemical characterisation technique that utilises an electron microscope, scanning electron microscopy (SEM), or transmission electron microscope (TEM) to determine the elemental analysis and elemental mapping of a material. By sending a beam of high-energy electrons at the sample, it may be run on EDX. When combined with the spectra generated by the characteristic X-rays, the BSE output data may give useful information on the distribution of different elements in the sample. Elastic scattering causes the beam electrons to be reflected off the sample, and the strength of the BSE signal is highly proportional to the atomic number of the specimen (Z). Characteristic X-rays are used to determine the amount of elements present in a sample as well as to determine its composition. These distinctive X-rays are produced when an electron beam removes an electron from the sample's inner shell, causing a
higher-energy electron to fill the shell and release energy.\textsuperscript{6} One incident electron may take an electron from an atom's inner shell, leaving a hole that will be filled by another electron from a higher energy shell. The difference in energy is measured by a spectrometer at a certain wavelength. EDX makes use of the fact that each element has a distinct electronic structure, which results in a distinct sequence of peaks when it interacts with electromagnetic radiation. The peaks X-ray fluorescence fingerprints identify the components exisent in the material. The primary limits of EDX include the inability to discriminate between ionic and non-ionic species, as well as the inability to quantify isotopic species or elements with atomic numbers less than carbon (Z<5).\textsuperscript{7} Energy dispersive X-ray (EDX) analysis was performed using an FEI Quanta 650 Field Emission GUN (FEG)-SEM equipped with an Oxford Instruments Xmax 50 Silicon Drift Detector with an accelerating voltage of 10 - 20 kV.

\textbf{2.8 SQUID MAGNETOMETRY}

A magnetic properties measuring system (MPMS) is a very sensitive magnetometer that is based on a superconducting quantum interference device cooled with liquid helium (SQUID). The sample is magnetised inside a cavity encircled by a superconducting magnet, and the sample response is determined by measuring the magnetic flux generated by the sample as it passes through a detecting coil, which produces a current proportionate to the sample's magnetic moment. Magnetic susceptibility (sample reaction to an applied field with fluctuating temperature) and molar magnetisation (sample response to a varying field at a constant temperature) are the two most often conducted measurements on chemical samples. Magnetic measurements were carried out using a Quantum Design MPMS-XL SQUID magnetometer equipped with a 7T magnet. Field cooled and zero - field cooled magnetisation curves applied magnetic field were obtained across a temperature ranging from 5 to 300 and a field strength of 100 Oe.
2.9 References


Chapter 3. Testing the Efficacy of the Synthesis of Iron Antimony Sulfide powders from Single Source Precursors

3.1 Introduction

Antimony chalcogenides (Sb$_2$S$_3$) is a (V-VI) semiconductor materials that has attracted much attention recently due to their unique semiconducting and optical properties.$^1$ Stibnite (Sb$_2$S$_3$) crystallizes in the orthorhombic system is high earth abundance and low toxicity$^2$ and has a direct bandgap of 1.5 - 2.5 eV that covers the visible and near-infrared region of the electromagnetic spectrum.$^3,4$ Some recent applications of Sb$_2$S$_3$ are in solar energy conversion,$^5$ television cameras,$^6$ microwave devices,$^7$ and switching devices.$^8$ Similarly iron sulfide compounds, Fe$_x$S$_y$ is a cheap, nontoxic earth abundant metal chalcogenide and demonstrate a wide range of magnetic and electrical properties depending upon the stoichiometric ratio between iron and sulfur.$^9$ Magnetic iron chalcogenides nanocrystals are important because of their use in magnetic data storage devices and as magnetic resonance imaging (MRI) contrast agents.$^{10,11,12}$ Berthierite (FeSb$_2$S$_4$) is an iron antimony sulfide mineral with interesting magnetic properties.$^{13}$ This work tested the efficacy of single source precursors approach toward the synthesis of Fe-Sb-S system. Antimony and iron diethylidithiocarbamate complexes of the form Sb[S$_2$CN(Et$_2$)]$_3$ (1) and Fe[S$_2$CN(Et$_2$)]$_3$ (2) were synthesised, characterised, and used as single-source precursors for the preparation of Sb$_2$S$_3$, Fe$_x$S$_y$, and mixed iron antimony sulfide Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ (0 ≥ x ≥ 1) powders using the solvent-less thermolysis method at different temperatures ranging from 300 to 475 °C. The effect of different mole fractions of the iron precursor was evaluated on morphology, shape, and optical and magnetic properties of Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ (0 ≥ x ≥ 1). The obtained powders were characterized by X-ray diffraction (XRD), Raman spectroscopy scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, magnetometer measurement, and UV/vis/NIR spectroscopy. The results demonstrated that the crystalline structure, morphology, and elemental composition of the samples changed with the mole fraction of the precursor. There was significant phase separation between Sb and Fe sulfides noted from EDX spectroscopic mapping, yet an optoelectronic study monitoring the direct band gap energy of antimony sulfide shows that the band gap energy increases as a function of Fe content, which suggests limited alloying is possible from the single source route. The work presented in this chapter is taken from published manuscript “Testing the Efficacy of the Synthesis of Iron Antimony Sulfide Powders from Single Source Precursors” which was published (Inorganics 2021, 9, 61).$^{14}$

3.2 Author contribution

Experiments were designed by Fadiyah Makin and Dr David Lewis. Fadiyah synthesised the dithiocarbamate precursors and characterised them via elemental analysis, IR, and TGA as detailed in the manuscript. Fadiyah
conducted the experimental work of the synthesis of $\text{Sb}_{2(1-x)}\text{Fe}_{2x}\text{S}_3$ ($0 \geq x \geq 1$) powders. Fadiyah performed characterisation for all samples using XRD, SEM, EDX, Raman and UVvis spectroscopy. Dalal Alzahrani and Floriana Tuna conducted the magnetic measurement for the samples. David J. Lewis and Firoz Alam provided useful discussions, and edited the manuscript.

3.3 Citation


3.4 References


3.5 Manuscript 1: Testing the Efficacy of the Synthesis of Iron Antimony Sulfide powders from Single Source Precursors

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3.5.1 Simple Summary

The phase diagram of the Fe-Sb-S system predicts that phase separation should occur at synthesis temperatures below 540 °C. In this paper we test the efficacy of alloying Fe into Sb₂S₃ using a molecular precursor approach which may be able to produce Fe-Sb-S alloys with a single pure phase. We find that whilst we do see a large degree of phase separation as predicted, we also find that there is some evidence that incorporation of Fe into the Sb₂S₃ host lattice occurs from this approach which could be a way to produce new magnetic materials.

3.5.2 Abstract

The antimony-iron sulfide system in general does not produce alloys below 540 °C from traditional solid-state methods. However, single source precursors have been known to produce unexpected products that arise from kinetically trapped polymorphs. In this paper, we test the efficacy of this approach toward the Fe-Sb-S system. Antimony and iron diethyldithiocarbamate complexes of the form Sb[S₂CN(Et₂)]₃ (1) and Fe[S₂CN(Et₂)]₃ (2) were synthesised, characterised, and used as single-source precursors for the preparation of Sb₂S₃, FeₓSᵧ, and mixed iron antimony sulfide Sb₂(1−x)Fe₂xS₃ (0 ≥ x ≥ 1) powders using the solvent-less thermolysis method at different temperatures ranging from 300 to 475 C. The effect of different mole fractions of the iron precursor was evaluated on morphology, shape, and optical and magnetic properties of Sb₂(1−x)Fe₂xS₃ (0 ≥ x ≥ 1). The obtained powders were characterized by X-ray diffraction (XRD), Raman spectroscopy scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, magnetometer measurement, and UV/vis/NIR spectroscopy. The results demonstrated that the crystalline structure, morphology, and elemental composition of the samples changed with the mole fraction of the precursor. There was significant phase separation between Sb and Fe sulfides noted from EDX spectroscopic mapping, yet an optoelectronic study monitoring the direct band gap energy of antimony sulfide shows that the band gap energy increases as a function of Fe content, which suggests limited alloying is possible from the single source route.
3.5.3 Introduction

In the past few decades, semiconductor nanocrystals have gained considerable interest in electronics, energy, and catalysis owing to their non-linear optical, magnetic, thermoelectric, and ferroelectric properties.\textsuperscript{1,2,3} The advantages of semiconducting nanostructures include a large absorption coefficient, a tunable energy band gap (Eg) due to the quantum size effect, and multiple exciton generation (MEG) by a single high energy photon (hv > 2Eg).\textsuperscript{4,5} Most of the established single junction photovoltaic technologies face numerous challenges for examples use of toxic elements, long-term stability, cost of raw materials and power conversion efficiency limitations, these all are most relevant considerations must be taken into account in order to look towards an era of terawatt solar photovoltaic power generation. Keeping the limitations of these mature technology in mind there is an urgent need to look for emerging photovoltaic solar cell absorbers including chalcogenides (sulphides, selenides, tellurides).\textsuperscript{6} Binary chalcogenide semiconductors including antimony and iron chalcogenides have attracted much attention due to their potential photovoltaic applications.\textsuperscript{7,8,9} Stibnite (Sb$_2$S$_3$) crystallizes in the orthorhombic system and has a direct bandgap of 1.5 - 2.5 eV that covers the visible and near-infrared region of the electromagnetic spectrum.\textsuperscript{10,11} Some recent applications of Sb$_2$S$_3$ are in solar energy conversion,\textsuperscript{12} television cameras,\textsuperscript{13} microwave devices,\textsuperscript{14} and switching devices.\textsuperscript{15} Recently, low dimensional absorber systems have attracted great attention because of their simple and earth abundant composition and improved performance for example quasi-1D antimony- based chalcogenide solar cells are nontoxic, stable and have achieved respectable power-conversion efficiencies (PCEs ) of 7% - 10%.\textsuperscript{16} In photovoltaic devices, stibnite Sb$_2$S$_3$ is a promising candidate thanks to its respectable power-conversion efficiencies (PCEs), which are a result of its bandgap commensurate in energy with solar flux and large absorption coefficients, as well as having beneficial features such as the earth abundance of its constituent elements and stability with low toxicity.\textsuperscript{17,18,19,20}
Sb$_2$S$_3$ thin films are employed as absorbing materials and semiconductors with a smaller bandgap in CdS/ Sb$_2$S$_3$ heterojunctions. Moreover, they are also used in Grätzel solar cells as a light sensitizer. Magnetic iron chalcogenides nanocrystals are important because of their use in magnetic data storage devices and as magnetic resonance imaging (MRI) contrast agents. Berthierite (FeSb$_2$S$_4$) is an iron antimony sulfide mineral with interesting magnetic properties.

A large number of methods are reported for the preparation of metal chalcogenides such as wet-chemical synthesis (hydrothermal, ion-exchange, hot injection, and self-assembly), chemical vapour deposition (CVD) based epitaxial growth, thermolysis, and solid-phase chemical synthesis. Multi-component methods have some inherent disadvantages of changing composition which varies from batch to batch, leading to poor reproducibility. Besides, multi-component precursor synthesis methods require a longer time, higher temperature, and high cost. Single source precursors (SSPs) offer specific benefits of stability, volatility, precise composition with fewer defects, and stoichiometry. SSPs based synthesis methods are the preferred choice over multi-component source methods for the preparation of binary, ternary, and quaternary metal chalcogenide and thin films. This method is potentially beneficial over others because of its simplicity, high purity, and its ability to yield high-quality materials with better control over composition. Recently, the use of metal dithiocarbamates for the synthesis of metal sulfides is being investigated due to their low decomposition temperature, clean decomposition, ease of synthesis, and their solubility in many organic solvents.

Iron and antimony dithiocarbamates single-source precursors have previously been used for the preparation of pure binary sulfides. Moreover, ternary and quaternary sulfides are also synthesized using metal dithiocarbamates complexes. For example, flower-like of Sb$_2$Bi,S$_3$ (x =0.4,1.0) nanostructures are synthesized using both antimony diethylldithiocarbamate [Sb(DDTC)$_3$] and bismuth diethylldithiocarbamate [Bi(DDTC)$_3$] by solvothermal method. Similarly, ternary copper-antimony sulfide nanocrystals are prepared using copper diethylldithiocarbamate trihydrate (Cu(DDTC)$_2$) and antimony diethylldithiocarbamate trihydrate (Sb(DDTC)$_3$) using a facile one-pot thermo-decomposition dual-precursor strategy.
Solvent-less thermolysis is a low-cost and simple solid-state method that involves the decomposition of precursors under thermal stress. Metal chalcogenides with different morphologies such as cubic nanoparticles,\textsuperscript{38} nano disks\textsuperscript{39}, and nanorods are prepared using the pyrolysis method.\textsuperscript{40} Compared to other methods, the solvent-less method has several advantages such as being solvent-free, cost-effective, environment-friendly, high yield, and easy control of reaction parameters.\textsuperscript{41} It has also been shown that by this type of route unexpected products can be isolated for example the production of various polymorphs of the W-Mo-S system\textsuperscript{42} that are kinetically locked in because the decomposition of precursors is rapid compared to the timescales required for ions to move through the lattice at low temperatures. The antimony-iron-sulfide system is interesting in this respect as below ca. 540 °C the phases are separate.\textsuperscript{43} However, if the use of precursors could circumvent phase separation then we may be able to unlock new antimony sulfides with bespoke properties e.g. iron-doping for magnetic materials. This work presents the attempted synthesis of Sb-Fe-S systems using different precursor stoichiometries using a mixture of metal dithiocarbamates (Sb[S\textsubscript{2}C\textsubscript{2}Et\textsubscript{2}]\textsubscript{3} and Fe[S\textsubscript{2}C\textsubscript{2}Et\textsubscript{2}]\textsubscript{3}) by the solvent-less thermolysis method at 450 °C. Sb\textsubscript{2(1-x)}Fe\textsubscript{2x}S\textsubscript{3} (x = 0, 0.2, 0.4, 0.6, 0.8 and 1) samples prepared are characterized by powder X-ray diffraction (p-XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) technique, Raman spectroscopy, and UV-Vis-NIR spectroscopy and SQUID magnetometry.

\textbf{3.5.4 Experimental}

\textbf{3.5.4.1 Chemicals}

Sodium diethyldithiocarbamate trihydrate ((C\textsubscript{2}H\textsubscript{5})\textsubscript{2}NCS\textsubscript{2}Na·3H\textsubscript{2}O, ≥ 99.0 %), antimony trichloride (SbCl\textsubscript{3}, ≥ 99.5 %), iron(III) chloride anhydrous (FeCl\textsubscript{3}, ≥ 99.99%), methanol (CH\textsubscript{3}OH, ≥ 99.8%), absolute ethanol (CH\textsubscript{3}CH\textsubscript{2}OH, ≥ 99.5 %), chloroform (CHCl\textsubscript{3}, ≥ 99%), isopropyl alcohol ((CH\textsubscript{3})\textsubscript{2}CHOH, ≥99.7%) were purchased from Sigma-Aldrich and used without further purification. The synthesis of all precursors was carried out in the air and no special handling was required.
3.5.4.2 Instrumentation

Elemental analysis (EA) was carried out in the micro-analytical laboratory at the Department of Chemistry, University of Manchester. TGA data was obtained using Perkin Elmer TGA 4000 in the temperature of 30 to 800 °C with a heating rate of 10 °C min\(^{-1}\) under N\(_2\). The XRD patterns were recorded using PANalytical X’Pert Pro theta-theta diffractometer (435 mm diameter). The data was collected using detector scans at a grazing incidence angle of 3° were undertaken with a scan range from 5° to 85° with 0.03° step and 8 s/step. SEM imaging was performed using FEI 200 Quanta 3D SEM for imaging and EDX analysis using an accelerating voltage of 20 kV. Magnetic data was measured using a MPMS XL SQUID magnetometer prepared with a 7 T magnet.

3.5.4.3 Synthesis of antimony (III) diethyldithiocarbamate, [Sb(S\(_2\)CN(Et)\(_2\))]\(_3\) (1)

Synthesis of precursor (1) was adapted from the method reported in literature.\(^{37, 44, 45}\) Briefly, sodium diethyldithiocarbamate trihydrate (6.76 g, 30 mmol) was dissolved in 100 mL of methanol and stirred. A solution of antimony (III) chloride (2.26 g, 10 mmol) was prepared in 25 mL of methanol and added dropwise to the sodium salt solution with constant stirring. The reaction mixture was further stirred for 30 minutes at room temperature. A yellow precipitate was obtained, which was filtered and washed several times using deionized water and finally with methanol. The product was dried overnight at room temperature in an open-air, resulting in a clear yellow solid. Yield: 4.3 g (86%); Elemental analysis found: C, 31.35 %; H, 5.19 %; N, 7.25%; S, 33.22 %; Calc. C, 31.81 %; H, 5.34 %; N, 7.42 %; S,33.90 %.IR (solid, \(\nu_{\text{max}}/\text{cm}^{-1}\)): 2966–2867\(\nu(\text{N–H})\); 1485 \(\nu(\text{C–N})\); 980 \(\nu(\text{C–S})\).

3.5.4.4 Synthesis of iron (III) diethyldithiocarbamate, Fe [S\(_2\)CNEt\(_2\)]\(_3\) (2)

For the synthesis of precursor (2) sodium diethyldithiocarbamate trihydrate (5g, 22.2 mmol) was dissolved in 100 mL of methanol and stirred, followed by the addition of iron (III) chloride anhydrous (1.19 g, 7.3 mmol) solution in 25 mL of methanol dropwise with constant stirring.
for 30 minutes. The resulting black precipitate was filtered and dried at room temperature. Yield: 3.4 g (92%); Elemental analysis found: C, 35.61%; H, 6.01%; N, 8.25%; S, 38.34% Calc. C, 36.01%; H, 6.05%; N, 8.40%; S, 38.37%. IR (solid, νmax/cm⁻¹): 2973–2866 ν(N–H); 1490 ν(C–N); 993 ν(C–S).

3.5.4.5 Synthesis of Sb₂S₃ powder by solvent-less thermolysis method

Solvent-less thermolysis was used for the synthesis of Sb₂S₃ using single-source precursors (1). A measured amount (0.40 mmol) of the precursors were placed into a ceramic boat inside a tube furnace and annealed at 300 °C, 400 °C, 425 °C, 450°C, and 475 °C, respectively for one hour under nitrogen flow, resulting in a black coloured residue. Samples were collected after cooling to room temperature for characterization.

3.5.4.6 Synthesis of Fe–Sb–S system by solvent-less thermolysis method

The antimony-iron sulfide (Sb₂(1–x)FeₓS₃) system was prepared by solvent-less thermolysis method using a mixture of precursors (1) and (2) with various molar ratios as shown in Table S1. The complexes were dissolved in 10 mL of chloroform to form a homogeneous mixture. Subsequently, the solvent was evaporated and a complex mixture was obtained. The uniform mixture was then placed into a ceramic boat for heating inside a tube furnace at 450 °C for 1 hour under nitrogen. Finally, the obtained black product was cooled to room temperature and stored in a vacuum for characterization.

3.5.5 Results and Discussion

3.5.5.1 Thermogravimetric analysis (TGA)

The thermal decomposition behaviour of the precursors was studied using TGA under nitrogen at a temperature ranging from 30 to 600 °C. TGA of the complexes Sb[S₂CNEt₂]₃ (1) and Fe[S₂CNEt₂]₃ (2) indicated single step decomposition with a rapid weight loss between 275-340 °C and 260-340 °C, respectively. Complex (1) showed a sharp loss (74%) in the first step
followed by gradual loss after 450 °C correspond to the loss of further sulfur atoms. The percentage residue of complex (1) was 23% which was close to the calculated value for Sb$_2$S$_3$ (29%). On the other hand, the weight loss percentage for complex (2) was 17% which is in good agreement with the calculated value of 17.5% for FeS. Compared to complex (2), the lower percentage for precursor (1) might be due to the loss of sulfur atoms at higher temperatures. The TGA results of two complexes indicated that both precursors decompose to their metal sulfide at a similar range of temperatures. The TGA results and the theoretical value of weight loss for the residues obtained from precursors are shown in Figure 3.1.

![Thermogravimetric analysis (TGA) of Sb[S$_2$CNEt$_2$]$_3$ and Fe[S$_2$CNEt$_2$]$_3$ complexes. The black dotted line refers to the weight loss to the formation of Sb$_2$S$_3$ and the red dotted line refers to the values of weight loss to produce FeS.](image)

Figure 3.1
Following the successful synthesis of binary antimony and iron sulfide powders from their respective metal dithiocarbamates (see figure S3.1 and S3.2 for analysis of these by powder XRD), both precursors were then investigated for their ability to synthesize Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ system. TGA results indicated that these complexes decomposed to their corresponding metal sulfide in a similar temperature range. Furthermore, both metals (iron and antimony) carried similar charges (+3). Accordingly, a mixture of these complexes was applied for the attempted synthesis of the Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ systems at different molar ratios of Fe.

3.5.5.2 X-Ray Diffraction (XRD)

Figure 3.2 illustrates the XRD patterns of Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ powder where x is the molar fraction of Fe synthesized by the solvent-less thermolysis method at 450 °C using a mixture of precursors (1) and (2). The XRD peaks for the prepared samples indicated the pure orthorhombic phase of Sb$_2$S$_3$ at x = 0 with lattice of a = 11.313 ± 0.034 Å, b = 3.833 ± 0.42 Å, and c = 11.225 ± 0.054 Å, which were in agreement with the reported values in the literature (ICDD: 01-073-0393), and pure hexagonal pyrrhotite Fe$_{1.05}$S$_{0.95}$ at x = 1 with lattice parameters of a = 3.4303 ± 0.036 Å, and c = 5.6802 ± 0.047 Å, which were also in agreement with the reported literature (ICDD:01-075-0600). A mole fraction of iron x = 0.2 resulted in diffraction peaks similar to Sb$_2$S$_3$ with some evidence of a small shift to a larger angle, implying the contraction of the lattice for the antimony peaks. Increasing the molar fraction to x = 0.4 resulted in a small reduction in the peak intensity (Figure 3.2). The peaks at 22°, 25°, 28°, 36°, 37°, 40°, 46°, 54°, 60°, 61°, and 63° shifted to higher angles with less intensity as the x value increased to x = 0.4, 0.6, and 0.8, representing the iron addition into the Sb$_2$S$_3$ samples. P-XRD analysis showed concentration-dependent phase changes at different concentrations of Fe (x = 0.2, 0.4, 0.6, and 0.8) and the majority of crystalline materials matched the pattern of orthorhombic Sb$_2$S$_3$ with Fe$_{1.05}$S$_{0.95}$. This indicates, as expected, some degree of phase separation as per the phase diagram, but also some evidence that the approach is successful in doping in some iron into the antimony sulfide structure. The substitution of Fe in Sb$_2$S$_3$ results the phase change which directly effects the physical attributes particularly the optical band-
gap. This result is expected and consistent with previous reports in similar kind of elemental doping.

**Figure 3.2** Powder X-ray diffraction (P-XRD) patterns of Sb$_2$(1-x)Fe$_2$xS$_3$ (0 ≤ x ≥ 1) produced by solvent-less thermolysis at 450 °C with variation in Fe/(Fe+Sb) molar ratio x = 0, x = 0.2, x = 0.4, x = 0.6, x= 0.8 and x = 1 with a standard pattern of Sb$_2$S$_3$ (bottom) and Fe$_{1.05}$S$_{0.95}$ (top).

3.5.5.3 Energy Dispersive X-Ray Spectroscopy

The atomic percentages of antimony, iron and sulfur in the Sb$_2$(1-x)Fe$_2$xS$_3$ (0 ≤ x ≤ 1) were measured using EDX spectroscopy and are presented as Figure S3. 3 and summarised in Table
S3. 2. The sample prepared at x= 0 showed a composition with an atomic percentage of Sb:S as (38:62) which is close to the expected stoichiometry for Sb$_2$S$_3$. Likewise, for x=1 (FeS), no additional peaks except Fe and S were observed in the spectrum. The atomic ratio of Fe to S was 45:55 which was close to the expected stoichiometry of iron sulfide determined from the XRD of Fe$_{1.05}$S$_{0.95}$. The EDX spectra of Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ with x = 0.2, 0.4, 0.6 and 0.8 displayed the characteristic peaks of antimony, iron and sulfur (Figure S3). The atomic percentages of antimony, iron, and sulfur at x=0.2 were measured and all the compositions were found in good agreement with the stoichiometric ratio calculated from the feed rate (Table S3. 2). Increasing the molar fraction to x=0.4 resulted in a higher elemental composition of iron and antimony. This might be due to the reason that EDX analysis uses a very small area of the samples which had less amount of sulfur. At x = 0.6 and 0.8, the amount of antimony was slightly higher and the amount of sulfur was lower which revealed that the prepared materials were sulfur deficient. A linear relationship between the amount of iron in the precursor feed and the amount of iron found in the Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ samples determined by the EDX analysis is shown in Figure 3.3.
Figure 3.3 Linear relationship between the amount of iron in the precursors and the amount of iron in \(\text{Sb}_{2(1-x)}\)Fe\(_{2x}\)S\(_3\) systems determined by energy dispersive X-ray (EDX) measurement.

3.5.5.4 Scanning Electron Microscopy

The SEM images of the \(\text{Sb}_{2(1-x)}\)Fe\(_{2x}\)S\(_3\) systems synthesized using 0, 0.2, 0.4, 0.6 0.8, and 1-mole fraction of Fe are presented in Figure 3.4. SEM Images of pure \(\text{Sb}_2\)S\(_3\) (x=0) revealed rod-like structures (Figure 3.4a). Previously, Xie et al prepared nanostructures with similar morphology from antimony diethyldithiocarbamate precursor by hydrothermal method.\(^{35}\) The morphology changed to a mixture of thicker rod and sheet clusters at x = 0.2, 0.4, and 0.6 as shown in Figures 3.4b and 3.4c. Further increase in the molar fraction of Fe to x = 0.8 showed sheet-like crystallites structure (Figure 3.4d). Besides, the morphology of pure iron sulfide at x=1 showed flower-like structures (Figure 3.4f). EDX elemental mapping of the \(\text{Sb}_{2(1-x)}\)Fe\(_{2x}\)S\(_3\)
system is presented in Figure 3.5 to show the spatial distribution of elements in the system. It can be seen that at this length scale sulfur was evenly distributed throughout the sample while iron and antimony were unevenly distributed throughout the entire sample. Again, this is not entirely unexpected for these samples based on their phase diagram. Interestingly in regions with high antimony content, there is also a low amount of iron content, suggesting that some iron is incorporated into the antimony sulfide structure which is commensurate with the peak shifts observed in the p-XRD patterns (vide supra). This suggests that the single source precursor route can produce stable doped materials, albeit as a mixture of products, but still can circumvent the product expected on the reported phase diagram. 43

Figure 3.4 SEM images of Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ powder prepared by melt method for 1h at 450 °C using different mole fractions of iron (a) x= 0 (b) x = 0.2 (c) x = 0.4 (d) x = 0.6 (e) x= 0.8 and (f) x = 1.
Figure 3.5 EDX elemental mapping of S ka, Sb La and Fe Kα for Sb₂(1-x)Fe₂xS₃ prepared by melt method for 1h at 450 °C using different mole fractions of iron (a) x= 0.2 (b) x = 0.4 (c) x = 0.6 and (d) x = 0.8.

3.5.5.5 Raman spectroscopy

Raman spectroscopy was used to study the Sb₂(1-x)Fe₂xS₃ (0 ≤ x ≤ 1) samples prepared (Figure 3.6). Pure Sb₂S₃ (x=0) sample showed dominant peaks at 53, 69, 98, 145, 184, 249 cm⁻¹ and three low-intensity peaks at 272, 366, and 445 cm⁻¹ (x=0) which are in agreement with the Raman analysis reported for the pure Sb₂S₃.⁴⁷ Similarly, the Raman spectrum of the pure FeS indicated peaks at 122, 155, 175, 224 and 325 cm⁻¹ which are in agreement with the Raman analysis reported for the iron sulfide.⁴⁸ For the Sb₂(1-x)Fe₂xS₃ (x= 0.2, 0.4, 0.6, and 0.8) the peaks
shifted continuously toward higher wavenumber with increasing iron content in the precursor, again suggesting doping is possible using metal dithiocarbamate precursors.

![Raman spectra of Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ samples](image)

**Figure 3.6** Raman spectra of Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ ($0 \leq x \leq 1$) samples prepared by melt method from mixture of antimony and iron diethyldithiocarbamate at 450 °C with different mole fractions of Fe.

### 3.5.5.6 Optical properties

For optical bandgap measurements, solutions of Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ ($0 \leq x \geq 1$) powder was prepared in methanol, and spectra were recorded in the wavelength range of 300–900 nm. The bandgap energy of the Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ ($0 \leq x \geq 1$) was calculated using the following equation:

$$(a\nu)^n = A(\nu - E_g),$$
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, $n = 2$ and $\frac{1}{2}$ for allowed direct and allowed indirect transitions, respectively. Plots of the $(\alpha h\nu)^n$ versus $h\nu$ showed a linear behavior for $n = 2$, which confirmed the direct transition in all the samples. Figure S3. 4 (Supporting Information) presents the absorption and the Tauc plot to determine the band gaps for all $\text{Sb}_2(1-x)\text{Fe}_2x\text{S}_3$ samples. For binary $\text{FeS}$ and $\text{Sb}_2\text{S}_3$ compositions, the direct band gaps were 3.92 and 2.71 eV, respectively. The obtained bandgaps were in agreement with the reported values for these materials. The bandgap for the mixed samples $\text{Sb}_2(1-x)\text{Fe}_2x\text{S}_3$ were 3.39, 3.47, 3.57 and 3.66 eV for $x = 0.2$, 0.4, 0.6 and 0.8, respectively, values which lie between pure $\text{FeS}$ and $\text{Sb}_2\text{S}_3$. Figure 3.7 represents the composition dependence of the bandgap of the $\text{Sb}_2(1-x)\text{Fe}_2x\text{S}_3$ samples, demonstrating that the bandgap of $\text{Sb}_2(1-x)\text{Fe}_2x\text{S}_3$ increased from 2.71 to 3.92 eV with increasing iron concentration. This gradual change in the bandgap is due to a small amount of iron being doped into the $\text{Sb}_2\text{S}_3$, which again suggests that the metal dithiocarbamate precursor route is able to produce materials that would not be predicted using a traditional phase diagram.
3.5.5.7 Magnetic properties

Variable temperature magnetisation measurements on Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ powder containing different amounts of paramagnetic Fe ($x = 0.2$, 0.4, 0.6, 0.8 and 1), were performed in both zero-field cooled (ZFC) and field-cooled (FC) conditions, to better characterise the systems. Data were collected under an applied magnetic field of 100 Oe are presented in Figure 3.8a. The most pronounced split between the ZFC and FC magnetisation curves was observed for the sample with the highest Fe content ($x = 1$), thought irreversibility was observed in all

![Graph showing variation of band gap with iron mole fraction](image)

**Figure 3.7** Variation of the direct band gaps for Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ ($0 \leq x \leq 1$) samples prepared at different mole fraction $x = 0.2$, 0.4, 0.6, and 0.8.
samples. This may indicate that the insertion of anisotropic Fe ions results in large nanoparticle anisotropy and possible ferromagnetic behaviour. Data are presented in Figure 3.8b.

**Figure 3.8** Plots of magnetization vs temperature for Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ (a) $x=1$ (b) $0.2 \leq x \leq 0.8$, measured in zero-field-cooled (ZFC) and field-cooled (FC) regimes, with 100 Oe applied field.

Measurements of magnetic hysteresis at 5 K (Figure 3.9a) and 300 K (Figure 3.9b) report open hysteresis loops in all cases. The coercivity and saturation of the magnetization increase with increasing the amount of the iron in the sample, but a full saturation of the magnetisation is not reached even at 7 T applied field. This could be the result of a too large anisotropy or occurrence of ferrimagnetic rather than ferromagnetic ordering. More information about the coercive field ($H_c$), remnant magnetization ($M_r$) and maximum magnetisation values at 5 and 300 K, as deduced from the data in Figure 3.9, are listed in Table 3.1.
Figure 3.9 Hysteresis loops at (a) 5 K, and (b) 300 K, for Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ (0.2 ≤ x ≤ 1). The inset is a zoom of the region around zero field.
Table 3. 1 Coercive field, maximum magnetization at 7 T, and remnant magnetization values at 300 and 5 K, based on Fig. 9 for $\text{Sb}_2(1-x)\text{Fe}_2x\text{S}_3$ ($0.2 \leq x \leq 1$).

<table>
<thead>
<tr>
<th>Sample</th>
<th>T(K)</th>
<th>$H_c$(Oe)</th>
<th>$M_r$(emu/g)</th>
<th>$M_{\text{max}}$(emu/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>($x = 0.2$)</td>
<td>5</td>
<td>2220.60</td>
<td>0.028</td>
<td>0.35</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>867.85</td>
<td>0.014</td>
<td>0.147</td>
</tr>
<tr>
<td>($x = 0.4$)</td>
<td>5</td>
<td>575.04</td>
<td>0.006</td>
<td>0.48</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>352.04</td>
<td>0.002</td>
<td>0.26</td>
</tr>
<tr>
<td>($x = 0.6$)</td>
<td>5</td>
<td>852.40</td>
<td>0.016</td>
<td>0.89</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>376.64</td>
<td>0.0059</td>
<td>0.65</td>
</tr>
<tr>
<td>($x = 0.8$)</td>
<td>5</td>
<td>1327.64</td>
<td>0.034</td>
<td>1.24</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>396.41</td>
<td>0.0063</td>
<td>0.95</td>
</tr>
<tr>
<td>($x = 1$)</td>
<td>5</td>
<td>3110.58</td>
<td>0.22</td>
<td>3.12</td>
</tr>
<tr>
<td></td>
<td>300</td>
<td>2374.44</td>
<td>0.12</td>
<td>2.24</td>
</tr>
</tbody>
</table>

3.5.6 Conclusion

In conclusion the incorporation of Fe into antimony sulfide led to changes in X-ray powder patterns, Raman spectra and band gap energies. The phase diagram of the Sb-Fe-S system predicts phase separated solid products in all cases and at all Fe-Sb ratios below ca. 540 °C using traditional solid-state synthesis. In this paper we tested the hypothesis that precursors could circumvent this due to their ability to rapidly form products. Sb-Fe-S powders were synthesized by the solvent-less thermolysis of metal diethylidithiocarbamate single-source precursors at a different molar ratio of iron at 450°C. TGA of two complexes indicated that the precursors decomposed to their corresponding metal sulfides at a similar range of temperatures. Furthermore, p-XRD analysis of synthesised materials revealed that a mixture of two phases including orthorhombic $\text{Sb}_2\text{S}_3$ and hexagonal pyrrhotite from the phase diagram. In optical properties, band gap is observed to increase with increasing Fe content and measured using UV-vis. The bandgap for the mixed samples $\text{Sb}_2(1-x)\text{Fe}_2x\text{S}_3$ were 3.39, 3.47, 3.57 and 3.66 eV.
for x = 0.2, 0.4, 0.6 and 0.8, respectively, values which lie between pure FeS and Sb$_2$S$_3$. In magnetic properties, temperature dependent (both zero-field cooled (ZFC) and field-cooled (FC) conditions) magnetisation measurements were performed on Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ powders for Fe content x = 0.2, 0.4, 0.6, 0.8 and 1. The resulting structures confirms the ferromagnetic nature. The Raman spectroscopy confirms that the peaks shifted to higher wavelengths with increasing Fe content and thus indicates that doping is possible using metal dithiocarbamate precursors. EDX mapping showed the co-localisation of both Sb and Fe alongside the phase separated binary materials. We conclude that the molecular precursor approach therefore may have some merit in producing novel materials in this system, but it must be acknowledged that the synthetic conditions would have to be optimised to produce phase pure materials.

3.5.7 Acknowledgements

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3.5.8 References


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3.5.9 Supporting information

**Table S3. 1.** Composition used for the synthesis of Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ system by solvent-less method

<table>
<thead>
<tr>
<th>Mole fraction</th>
<th>Fe[S$_2$CNEt$_2$]$_3$</th>
<th>Sb[S$_2$CNEt$_2$]$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe]/[Fe]+[Sb]</td>
<td>0 mmol</td>
<td>0.40 mmol</td>
</tr>
<tr>
<td>0</td>
<td>0.40 mmol</td>
<td>1.6 mmol</td>
</tr>
<tr>
<td>0.2</td>
<td>0.40 mmol</td>
<td>1.60 mmol</td>
</tr>
<tr>
<td>0.4</td>
<td>0.40 mmol</td>
<td>0.60 mmol</td>
</tr>
<tr>
<td>0.6</td>
<td>0.40 mmol</td>
<td>0.26 mmol</td>
</tr>
<tr>
<td>0.8</td>
<td>0.40 mmol</td>
<td>0. 10 mmol</td>
</tr>
<tr>
<td>1</td>
<td>0.40 mmol</td>
<td>0 mmol</td>
</tr>
</tbody>
</table>

**Binary systems: Sb$_2$S$_3$ and Fe$_x$S$_y$**

The thermal decomposition of precursor (1) and (2) synthesised at temperature 300, 400, 425, 450 and 475 for 1h resulted in a black residue which was analysed by P-XRD. P-XRD patterns of the nanocrystals resulted from Sb[S$_2$CN(Et$_2$)]$_3$ (1) at 400, 425, 450 and 475°C are illustrated in Figure S1. The analysis revealed that the crystalline phase produced corresponded to orthorhombic stibnite (Sb$_2$S$_3$, ICDD: 01-073-0393) with lattice parameters $a=11.313$ Å, $b=3.833$ Å, and $c=11.225$ Å. As shown in Figure S1, the intensities of peaks were similar in all cases with a slight increase in some of the peaks upon increase in the growth temperature.
P-XRD patterns of the nanoparticles resulting from decomposition of [Fe(S<sub>2</sub>CN(Et)<sub>2</sub>)]<sub>3</sub> (2) at 300, 400, 450 and 475 °C are illustrated in Figure S2. The diffraction peaks corresponded to a hexagonal pyrrhotite iron sulfide (Fe<sub>0.95</sub>S<sub>1.05</sub>, ICDD 01-075-0600) with lattice parameters a = 3.4303 Å, b = 3.4303 Å, and c = 5.6802 Å with major diffraction peaks corresponding to (100), (101), (102), (110) planes. There were no significant differences in the intensities of peaks of all four samples.

Figure S 3.1  P-XRD patterns of Sb<sub>2</sub>S<sub>3</sub> nanoparticles at (a) 300, (b) 400, (c) 425, (d) 450 and (e) 475 °C deposited from decomposition of Sb(S<sub>2</sub>CN(Et)<sub>2</sub>)<sub>3</sub> using melt method for 1h. All peaks corresponded to standard pattern of stibnite (ICDD 01-073-0393).
Figure S 3. 2 P-XRD patterns of FeS nanoparticles at (a) 300 °C, (b) 400 °C (c) 450 °C and (d) 475 °C from decomposition of Fe(S$_2$CN(Et$_2$))$_3$ using melt method for 1h. All peaks corresponded to standard pattern of pyrrhotite (ICDD 01-075-0600)
Table S3. 2 The content of Fe, Sb and S in $\text{Sb}_2(1-x)\text{Fe}_2x\text{S}_3$ prepared by melt method at 450°C ($x = 0, 0.2, 0.4, 0.6, 0.8$ and $1$ molar fraction of iron) calculated from the feed rate and found by EDX measurement.

<table>
<thead>
<tr>
<th>Mole Fraction</th>
<th>Elemental Composition Required (Atomic %)</th>
<th>Stoichiometry Required</th>
<th>Elemental Composition Found by EDX (atomic %)</th>
<th>Stoichiometry Found By EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe</td>
<td>Sb</td>
<td>S</td>
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</tr>
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<td>Sb$_2$S$_3$</td>
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<tr>
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<td>0.6</td>
<td>24</td>
<td>16</td>
<td>60</td>
<td>Fe$<em>{1.2}$Sb$</em>{0.8}$S$_3$</td>
</tr>
<tr>
<td>0.8</td>
<td>32</td>
<td>8</td>
<td>60</td>
<td>Fe$<em>{1.6}$Sb$</em>{0.4}$S$_3$</td>
</tr>
<tr>
<td>1</td>
<td>40</td>
<td>0</td>
<td>60</td>
<td>Fe$_2$S$_3$</td>
</tr>
</tbody>
</table>

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Figure S 3.3 The EDX spectra of Sb$_{2(1-x)}$Fe$_{2x}$S$_3$ samples prepared by melt method at 450 °C at various Iron mole fraction (a) x = 0, (b) x = 0.2, (c) x = 0.4, (d) x = 0.6, (e) x = 0.8 and (f) x = 1.
Figure S 3.4 Absorption spectra of $\text{Sb}_{2(1-x)}\text{Fe}_{2x}\text{S}_3$ and inset the Tauc plot of $\text{Sb}_{2(1-x)}\text{Fe}_{2x}\text{S}_3$ samples prepared by melt method at 450 °C at various Iron mole fraction $x = 0.2, 0.4, 0.6,$ and 0.8.
Chapter 4. Synthesis of particulate and thin film ternary copper antimony sulfide phases via solventless thermolysis and AACVD of metal diethyldithiocarbamate single-source precursors

4.1 Introduction

Ternary copper antimony sulfide has been presented as a low-cost, earth-abundant, and non-toxic photovoltaic material. Additionally, ternary copper antimony sulphide exhibits large absorption coefficients (greater than $10^5 \text{ cm}^{-1}$) in a variety of phases, with a suitable band gap for photovoltaic applications. Furthermore, copper antimony sulfide exists in multiple different phases, (Cu-Sb-S) including Cu$_3$SbS$_3$ (skinnerite), CuSbS$_2$ (chalcostibite), C$_{12}$Sb$_4$S$_{13}$ (tetrahedrite), and Cu$_3$SbS$_4$ (fematinite). All of these materials have band gaps between 1.1 – 1.9 eV, with high absorption coefficients ($>10^5 \text{ cm}^{-1}$), making them great candidates for solar energy harvesting. However, phase-pure Cu-Sb-S material (such as tetrahedrite) is difficult to manufacture, needing many weeks and high temperatures for multiple melting and annealing stages. Chalcostibite (CuSbS$_2$) has been offered as a possible alternative for CuInS$_2$ owing to its comparable optical characteristics and antimony's natural abundance in comparison to indium. Tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$) is another significant phase since it is not only an excellent candidate for solar absorbance in photovoltaic systems, but also for thermal energy harvesting through the Seebeck effect in thermoelectric devices. In this work, the thermal decomposition of copper and antimony diethyldithiocarbamate single source precursors resulted in the formation of distinct binary and ternary Cu-Sb-S phases. This was accomplished using solventless thermolysis and aerosol-assisted chemical vapour deposition, respectively. When the ratio of Cu:Sb precursors was varied, distinct phases were generated. Without the presence of a Sb precursor, solventless thermolysis with a low Cu ratio generated chalcostibite (CuSbS$_2$) and digenite (Cu$_{1.8}$S). The use of AACVD to deposit thin films resulted in the formation of fematinite (Cu$_3$SbS$_4$) with a low Cu ratio and chalcocite (Cu$_2$S) without the presence of a Sb precursor. Both procedures produced stibnite (Sb$_2$S$_3$) devoid of Cu and tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$) with a high Cu:Sb ratio. The work presented in this chapter taken from a published
4.2 Author contribution

Experiments were designed by Fadiyah Makin and Dr David Lewis. Fadiyah synthesised the dithiocarbamate precursors and characterised them via elemental analysis, IR, and TGA as detailed in the manuscript. Fadiyah conducted the experimental work of the synthesis of (CuSbS\(_2\)), (Cu\(_3\)SbS\(_4\)) and (Cu\(_{12}\)Sb\(_2\)S\(_{13}\)) powders and thin film. Fadiyah performed characterisation for all samples using XRD, SEM, EDX, Raman and UVvis spectroscopy. David J. Lewis and Mark Buckingham provided useful discussions, and edited the manuscript.

4.3 Citation

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4.4 References


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4.5 Manuscript 2: Synthesis of particulate and thin film ternary copper antimony sulfide phases via solventless thermolysis and AACVD of metal diethyldithiocarbamate single-source precursors

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4.5.1 Abstract

Copper antimony sulfide (Cu-Sb-S) has recently been proposed as an attractive alternative photovoltaic material due to the earth-abundant and non-toxic nature of the elements, high absorption coefficients and band gaps commensurate with efficient harvesting of solar photonic flux across multiple phases of Cu-Sb-S. These materials are therefore highly desirable if they can be synthesised with sustainable and scalable deposition techniques. In this paper, we demonstrate two facile, low-temperature and inexpensive techniques (solventless thermolysis and aerosol-assisted chemical vapor deposition (AACVD)) for the preparation of binary digenite (Cu$_{1.8}$S), chalcocite (Cu$_2$S) and stibnite (Sb$_2$S$_3$) and several phases of ternary copper-antimony-sulfide (Cu$_{2x}$Sb$_{2(1-x)}$S$_y$, where $0 \leq x \leq 1$). It was found that by utilising these different techniques and varying the ratio of Cu : Sb, pure phases of ternary chalcostibite (CuSbS$_2$), fematinite (Cu$_3$SbS$_4$) and tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$) can be achieved. Two single-source precursors were investigated for this purpose, namely the diethyldithiocarbamate (DTC) complexes of copper and antimony Cu(DTC)$_2$ and Sb(DTC)$_3$. These were decomposed both individually (to produce binary materials) and combined (to produce ternary materials) at different ratios. From the solventless thermolysis and AACVD methods, either particulate or thin film material was formed, respectively. These materials were then characterised by powder XRD, SEM, EDX and Raman spectroscopies to determine the crystalline phase, material morphology and uniformity of elemental composition. This analysis demonstrated that as the Cu-content increases, the phase of the ternary material changes from chalcostibite (CuSbS$_2$) and fematinite (Cu$_3$SbS$_4$) at a low Cu : Sb ratio to tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$) at a high Cu : Sb ratio.

4.5.2. Introduction

The world is currently facing a serious energy crisis from high consumption of non-renewable fossil fuels. Therefore, there is currently a huge drive towards developing green routes to produce sustainable energy from renewable sources such as solar energy.\textsuperscript{13} Photovoltaic (PV) devices have the potential to be low-cost and sustainable with high solar to electrical energy conversion efficiencies.\textsuperscript{14,15} However, this is highly dependent on the abundance and cost of the initial materials and the scalability of the deposition technique.
Numerous metal chalcogenide materials such as copper selenide (CuSe), cadmium selenide (CdSe), copper indium sulfide/selenide (CIS/Se), copper tin telluride (CuSnTe), copper indium gallium sulfide/selenide (CIGS/Se), copper zinc tin sulfide (Cu₂ZnSnS₄) (CZTS), and copper iron tin sulfide (Cu₂FeSnS₄) have received attention as solar absorbers in photovoltaic cells in recent years.⁴⁻⁹ Semiconducting copper and cadmium chalcogenides have played a significant role in developing high-efficiency solar cells. Copper indium gallium selenide (CuInGaSe) and cadmium telluride (CdTe) thin film solar cells have demonstrated efficiencies of 21.5% and 21.7%, respectively.²²,²³ However, these materials have several disadvantages, such as low elemental abundance,²⁴ high cost, and toxicity of elements such as Cd and Te.²⁵ These disadvantages have significantly hindered the widespread deployment of these materials as photovoltaic devices.

Ternary copper antimony sulfide has recently been proposed as an alternative PV material, due to the low-cost, earth-abundant, and non-toxic nature of the constituent elements.¹ Ternary copper antimony sulfide also yields high absorption coefficients (over 10⁵ cm⁻¹) in several phases,² with a suitable band gap for photovoltaic applications.³,⁴ However, there are several distinct phases of copper antimony sulfide, (Cu-Sb-S) including Cu₃SbS₃ (skinnerite), CuSbS₂ (chalcostibite), C₁₂Sb₄S₁₃ (tetrahedrite), and Cu₃SbS₄ (fematinite).⁵ These materials all possess band gap energies between 1.1 – 1.9 eV, with high absorption coefficients (>10⁵ cm⁻¹),² and are thus excellent candidates for solar energy harvesting.⁶⁻¹⁰ However, phase-pure material of Cu-Sb-S (such as tetrahedrite) is difficult to achieve and has previously been reported as requiring several weeks and high temperatures for various melting and annealing steps.²,¹¹,¹² Chalcostibite (CuSbS₂) in particular has been proposed as a candidate for the replacement of CuInS₂, due to equivalent optical properties and the natural abundance of antimony when compared to indium.² Tetrahedrite (Cu₁₂Sb₄S₁₃) is another important phase as this material is not only a good candidate for solar absorbance in photovoltaic devices,² but also as a candidate for thermal energy harvesting as a thermoelectric device via the Seebeck effect.²

The use of single-source precursors for the preparation of binary and ternary metal chalcogenides is of growing importance.²,²⁶⁻²⁹ This method is potentially beneficial because of the simplicity, high purity, and tunable size of the produced materials.³⁰ Copper and antimony dithiocarbamate (DTC) complexes are frequently used for binary and ternary metal sulfide thin
film preparation due to their ease of synthesis, clean decomposition at low temperature, and solubility of these complexes in many organic solvents. Ternary copper-antimony sulfide nanocrystals have been previously prepared using single-source precursors of antimony diethylidithiocarbamate (Sb(DTC)\textsubscript{3}) and copper diethylidithiocarbamate (Cu(DTC)\textsubscript{2}). The produced copper antimony sulfide nanocrystals exhibit different compositions, band gaps, and morphologies including rhombic Cu\textsubscript{3}SbS\textsubscript{3}, rectangular CuSbS\textsubscript{2} nanosheets, and trigonal-pyramidal Cu\textsubscript{12}Sb\textsubscript{3}S\textsubscript{13} nanocrystals, which have shown promising potential for photovoltaic applications. Zou et. al., synthesized chalcostibite CuSbS\textsubscript{2} nanocrystals using a colloidal route with dodecanethiol as ligands, which observed a direct band gap energy of 1.59 eV, and were further demonstrated for photovoltaic applications. Regulacio et. al. used copper and antimony diethylidithiocarbamate precursors for the synthesis of high-purity tetrahedrite (Cu\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13}) nanostructures using solvothermal decomposition.

Numerous methods have been developed for the deposition of particulate, nanomaterial and thin film copper antimony sulfides, such as the solvothermal, chemical bath deposition, spin coating, spray pyrolysis, thermal evaporation, and pulsed laser ablation. Solventless thermolysis involves decomposition of a precursor under thermal stress. This method is both facile and cheap and is inherently more sustainable that most other methods due to the absence of requiring solvent. Solventless thermolysis also produces high yields for the synthesis of desired materials. Different morphologies of metal chalcogenides can be prepared using this method such as nanorods, nanodisks, and cubic nanoparticles. However, difficulty in controlling the size of particles in the presence of capping agents has limited progress in designing these nanomaterials.

In the present study, two facile, scalable, and cost-effective methods for the preparation of phase pure binary Sb\textsubscript{2}S\textsubscript{3}, Cu\textsubscript{2}S and Cu\textsubscript{1.8}S, and three distinct phases of ternary copper antimony sulfide (CuSbS\textsubscript{2}, Cu\textsubscript{3}SbS\textsubscript{4}, and Cu\textsubscript{12}Sb\textsubscript{3}S\textsubscript{13}) can be prepared as either particulates (using solventless thermolysis) or thin films (using AACVD). These materials are prepared from single-source precursors of copper and antimony diethylidithiocarbamates (Cu(DTC)\textsubscript{2} and Sb(DTC)\textsubscript{3}) mixed at different molar ratios of Cu : Sb. The work presented here reports two
simple and scalable routes towards several pure phases of ternary Cu-Sb-S, which are highly relevant for both photovoltaic and thermoelectric applications.

4.5.3 Experimental

4.5.3.1 Chemicals

All chemicals were purchased from Sigma Aldrich and used without further purification, unless specified. Sodium diethyldithiocarbamate trihydrate (\((\text{C}_2\text{H}_5)_2\text{NCS}_2\text{Na} \cdot 3\text{H}_2\text{O}, \geq 99.0\%\)), antimony trichloride (\(\text{SbCl}_3, \geq 99.5\%\)), anhydrous copper(II) chloride (\(\text{CuCl}_2 \geq 98.0\%\)), methanol (\(\text{CH}_3\text{OH}, \geq 99.8\%\)), absolute ethanol (\(\text{CH}_3\text{CH}_2\text{OH}, \geq 99.5\%\)), chloroform (\(\text{CHCl}_3, \geq 99\%\)) and isopropyl alcohol (\((\text{CH}_3)_2\text{CHOH}, \geq 99.7\%\)). Synthesis of the precursors was performed in air and no special handling or inert atmosphere was required.

4.5.3.2 Instrumentation

Elemental analysis (EA) was performed in the micro-analytical laboratory of the University of Manchester. Thermogravimetric analysis (TGA) was conducted using a Perkin Elmer TGA 4000, in a temperature range of 30 to 600 °C and a ramp rate of 10 °C min\(^{-1}\) under a nitrogen atmosphere. Powder XRD patterns were recorded using an XRD5-PANaytical X-Pert Pro theta-theta diffractometer (435 mm diameter). The data was collected using detector scans at a grazing incidence angle of 3° and were undertaken with a scan range of 5° to 85° with a 0.03° step at 8 s step\(^{-1}\). Scanning electron microscopy (SEM) imaging was performed using an FEI Quanta 650 Field Emission GUN (FEG)-SEM equipped with an Oxford Instruments Xmax 50 Silicon Drift Detector (for EDX microanalysis) with an accelerating voltage of –0 - 20 kV. Raman spectra were recorded using a Renishaw 1000 Micro- Raman spectrometer, equipped with a 50x objective, with argon ion laser (514.5 nm, 25% powder).

4.5.3.3 Synthesis of Copper diethyldithiocarbamate, \(\text{Cu(DTC)}_2(1)\)

The synthesis of copper diethyldithiocarbamate (\(\text{Cu(DTC)}_2\)) was achieved by adapting a previously reported procedure.\(^{35}\) Sodium diethyldithiocarbamate trihydrate (10g, 44 mmol)
was dissolved in 100 mL of methanol and stirred until fully dissolved. A separate solution of copper (II) chloride (2.89 g, 22 mmol) was prepared in 25 mL of methanol. The copper solution was then added dropwise to the diethyldithiocarbamate solution under constant stirring for 30 minutes. A black precipitate was formed, which was filtered, and washed three times with room temperature deionized water and methanol and dried overnight under atmospheric laboratory conditions. The yield obtained was 74%, which observed the elemental composition of: C, 32.90%; H, 5.52%; N, 7.69%; S, 30.05%. Which is in agreement with the expected: C, 33.37%; H, 5.61%; N, 7.79%; but not in good agreement with S, 35.56%. This could be due to some reduction of the Cu(ii) to Cu(i), in line with previous reports and our observations of chalcocite (Cu$_2$S, Figure 8) and digenite (Cu$_{1.8}$S, Figure 4). The chemical structure of the precursor is illustrated in Figure 4.1(a).

4.5.3.4 Synthesis of Antimony diethyldithiocarbamate, Sb(DTC)$_3$ (2)

The synthesis of antimony diethyldithiocarbamate (Sb(DTC)$_3$) was achieved by adapting a previously reported procedure. Sodium diethyldithiocarbamate trihydrate (6.76 g, 30 mmol) was dissolved in 100 mL of methanol and stirred until fully dissolved. In a separate solution, antimony (III) chloride (2.26 g, 10 mmol) was dissolved in 25 mL of methanol. The prepared antimony chloride solution was then added dropwise to the diethyldithiocarbamate solution under constant stirring. Once fully added, the reaction mixture was further stirred for 30 minutes at room temperature. After this time, a yellow precipitate was filtered and washed several times with deionized water and methanol at room temperature. The product (yellow solid) was dried overnight at room temperature in atmospheric laboratory conditions. A yield of 86% was obtained with the following elemental composition: C, 31.35%; H, 5.19%; N, 7.25%; S, 33.22%. Which is in excellent agreement with the expected: C, 31.81%; H, 5.34%; N, 7.42%; S, 33.90%. The chemical structure of the precursor is illustrated in Figure 4.1(b).
Figure 4.1 Figure showing the chemical structures of the two single-source precursors utilised in this report. These are (a) copper diethylthiocarbamate (Cu(DTC)$_2$) and (b) antimony diethylthiocarbamate (Sb(DTC)$_3$).

4.5.3.5 Preparation of binary Cu$_x$S$_y$ and Sb$_2$S$_3$ powders by solventless thermolysis

Solventless thermolysis was used for the synthesis of particulate Cu$_x$S$_y$ and Sb$_2$S$_3$ using the single-source precursors Cu(DTC)$_2$ and Sb(DTC)$_3$, respectively. A measured amount (0.55 mmol) of precursor was placed into a ceramic boat inside a tube furnace and annealed at either 300, 400, 425, 450, or 475 °C for 1 h, under a nitrogen atmosphere. The obtained black product was cooled at room temperature and collected for characterization.

4.5.3.6 Preparation of copper-antimony-sulfide (Cu-Sb-S) powders by solventless thermolysis

Copper-antimony sulfide Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ was prepared by solventless thermolysis using a mixture of both precursors (Cu(DTC)$_2$ and Sb(DTC)$_3$) at different molar ratios, where $x$ = either 0, 0.2, 0.4, 0.6, 0.8 or 1 (the respective mol fractions, and absolute input amount (in mmol) are
displayed in Table S1). The mixture was dissolved in 10 mL of chloroform to form a homogeneous solution. The solvent was then evaporated under kneading using a pestle and mortar. The obtained mixture was then placed into a ceramic boat and heated in a tube furnace at 450 °C for 1 h under a nitrogen atmosphere. The obtained black product was cooled at room temperature and collected for characterization.

4.5.3.7 Preparation of copper-antimony-sulfide (Cu-Sb-S) thin films by AACVD

Prior to deposition, glass slides of the dimensions 1 cm x 2.5 cm were thoroughly cleaned by consecutively washing with deionized water (DI) and acetone for 10 minutes each, under ultrasonic conditions. The glass slides were then dried in the oven before loading inside a reactor tube for deposition. The deposition of copper antimony sulfide thin films was carried out using the aerosol-assisted chemical vapor deposition (AACVD) technique. The different molar fractions of Cu(DTC)$_2$ and Sb(DTC)$_3$ were dissolved in 20 mL of tetrahydrofuran (THF) and transferred to a two-necked round bottom flask. The flask outlet was connected to the reactor tube via rubber tubing, and argon gas was flowed into the inlet. The reactor tube was placed in a carbolite tube furnace and heated to 450 °C for one hour. The aerosol was generated by placing the reaction flask that contained the precursor solution on an ultrasonic aerosol generator. The argon flow (160-180 sccm) transported the aerosol to the hot wall reaction chamber where thermal decomposition took place to form a thin film on the substrates. The films obtained were then characterized by p-XRD, EDX, SEM, Raman, and UV-Vis spectroscopies.

4.5.4 Results and discussion

4.4.4.1 Solventless thermolysis of Cu(DTC)$_2$ and Sb(DTC)$_3$ to generate binary Cu$_x$S$_y$ and Sb$_2$S$_3$ systems

The aim of this research is to generate target phases of Cu-Sb-S substrates through simple, cost-effective routes. Namely, investigating both solventless thermolysis and AACVD
deposition techniques to decompose single-source precursors, producing both binary and
ternary metal chalcogenides. Initially, the two single-source precursors (Cu(DTC)₂ and
Sb(DTC)₃) were investigated individually for their thermal decomposition behaviour.

Thermogravimetric analysis (TGA) on the two single source precursors demonstrated
that both these precursors decompose in the temperature range 240 – 340 °C. The Cu(DTC)₂
precursor observed a single, rapid decomposition with no further loss in mass with increasing
temperature. The Sb(DTC)₃ precursor also observed a single, rapid decomposition, but was
followed by a more gradual decomposition at higher temperature, which is attributed to further
loss of elemental sulfur. The TGA results are shown in Figure S4. 1 and indicates that the
two precursors decompose to their respective metal sulfides within a similar temperature range,
this makes them ideal candidates to explore further to produce particulate binary metal
chalcogenides.

Therefore, thermal decomposition (via solvent-less thermolysis) of the two precursors
was performed to generate the respective binary particulate metal chalcogenide material. This
was undertaken at a range of temperatures for 1 h. The crystallinity of the resultant particulate
material was analysed by powder X-ray diffraction (p-XRD). The resultant p-XRD patterns of
the particulate material generated from Sb(DTC)₃ at 300, 400, 425, 450, and 475 °C are shown
in Figure S4. 2. This analysis revealed that the produced material was crystalline and
corresponded to orthorhombic stibnite (Sb₂S₃, ICDD: 01-073-0393) with lattice parameters a
= 11.313± 0.042 Å, b = 3.833±0.043 Å, and c = 11.225± 0.051 Å.

Analysis of the particulate product of the Cu(DTC)₂ precursor, decomposed at 300, 350,
400, and 450 °C was also undertaken. The resulting p-XRD diffraction patterns of these
particulate materials are shown in Figure S4.3. Again, this analysis also showed that the
resulting material was crystalline, with the major diffraction peaks corresponding to
rhombohedral digenite (Cu₁.₈S, ICDD 00-023-0962) with minor peaks in the pattern
corresponding to impurities of monoclinic chalcocite (Cu₂S, ICDD 00-033-0490, indicated by
a * on the p-XRD spectra, Figure S3), which is particularly prevalent for reactions performed
at lower temperatures. At higher decomposition temperatures (450 °C), there is no observable
Cu₂S present, producing phase pure Cu₁.₈S. The observed lattice parameters are a = 3.930±
0.046 Å, \( b = 3.930 \pm 0.046 \) Å, and \( c = 48.650 \pm 0.057 \) Å, with the major diffraction peaks corresponding to the (015), (018), (101), (110), planes (as shown on Figure S4. 3). The morphology and elemental composition of these binary \( \text{Cu}_{1.8}S \) and \( \text{Sb}_2S_3 \) particulate materials were further investigated by SEM and EDX analysis, and are discussed later, together with the ternary \( \text{Cu}_2\text{Sb}_{2(1-x)}S_y \) systems.

4.5.4.2 Synthesis of ternary \( \text{Cu}_{2x}\text{Sb}_{2(1-x)}S_y \) \((0 \leq x \leq 1)\) powder by solventless thermolysis

Following the success of producing particulate binary \( \text{Cu}_{1.8}S \) and \( \text{Sb}_2S_3 \) from their respective single-source precursors, the precursors were then investigated for their ability to synthesise more complex ternary metal sulfides. The TGA analysis demonstrated that both precursors decompose to their corresponding metal sulfides in a similar temperature range. Both precursors are soluble in chloroform, toluene, and other organic solvents. Therefore, we concluded that these complexes are good candidates for decomposition in tandem to generate more complicated ternary metal sulfides,\(^{27}\) at lower temperatures and faster time than typically employed for this synthesis (650 °C\(^{11}\) and 3 weeks\(^{12}\)).

These two precursors were therefore investigated towards the preparation of ternary copper-antimony-sulfide (Cu-Sb-S) material at various molar ratios of Cu : Sb. The temperature selected for this investigation was 450 °C, as this temperature produced the phase purest material in the \( \text{Cu(DTC)}_2 \) decomposition (Figure S4. 3). Therefore, solutions containing both precursors (\( \text{Cu(DTC)}_2 \) and \( \text{Sb(DTC)}_3 \)) of various ratios (Table S4. 1) were used to generate particulate \( \text{Cu}_{2x}\text{Sb}_{2(1-x)}S_y \) material, where the mol fraction (x) used was 0 (\( i.e. \) only \( \text{Sb}_2S_3 \)), 0.2, 0.4, 0.6, 0.8 and 1 (\( i.e. \) only \( \text{Cu}_{1.8}S \)).

4.5.4.3 SEM and EDX analysis of particulate \( \text{Cu}_{1.8}S \), \( \text{Sb}_2S_3 \), and \( \text{Cu}_{2x}\text{Sb}_{2(1-x)}S_y \) generated by solventless thermolysis

Initially, SEM and EDX spectroscopies were used to study the morphology and elemental composition of the generated particulate \( \text{Cu}_{2x}\text{Sb}_{2(1-x)}S_y \) material, at various values of
Representative SEM images of the six Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems, where x = 0, 0.2, 0.4, 0.6, 0.8 and 1 are shown in Figure 4. 2. SEM analysis of pure Sb$_2$S$_3$ (x = 0) revealed micro-rod structures (Figure 4. 2(a)), which are consistent with previously reported particulate Sb$_2$S$_3$, prepared using hydrothermal decomposition of an antimony diethyldithiocarbamate precursor. As the Cu content of the systems increased, the morphology changed to a mixture of shorter-length micro-rods and agglomerated clusters at x = 0.2, as shown in Figure 4. 2(b). As the Cu content increased to x = 0.4, again both rods and clusters are present, as shown in Figure 4. 2(c). Increasing the molar fraction of Cu to x = 0.6 and x = 0.8 showed no rod-character and only cluster-character (Figure 4. 2(d) and 4. 2(e)). Finally, the morphology of pure Cu$_{1.8}$S, where x = 1, showed even further (and smaller scale) clustering, resembling a floret-like morphology (Figure 4. 2(f)).

**Figure 4. 2** Representative SEM images of particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ prepared by solventless thermolysis at 450 °C for 1 h where x = (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8 and (f) 1. These were recorded at 15 k eV using secondary electron SEM.
These six particulate samples were then assessed for elemental composition by EDX spectroscopy. The Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems where $x = 0.2, 0.4, 0.6,$ and $0.8$ showed the characteristic peaks of copper, antimony, and sulfur (Figure S4). Figure S4. 5 shows both the expected elemental composition and the observed experimental composition for both Cu and Sb, based on the EDX analysis, the data is also tabulated in Table S4. 2. As shown in Figure S4. 5, the linear relationship between the expected and observed Cu and Sb mol% of the various synthesised particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems are in good agreement, with both observing a $>98\%$ fit). The one outlier is the Cu and Sb composition in the $x = 0.6$ system, which is deficient in Cu and rich in Sb (Table S4. 2).

4.5.4.4 EDX spectroscopic mapping of Cu$_{2x}$Sb$_{2(1-x)}$S$_y$

EDX elemental mapping was performed on the four Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems where $0 < x < 1$. This was not performed where $x = either 0 or 1$, as pXRD analysis above already demonstrated no contamination of Sb in the $x = 1$ system or Cu in the $x = 0$ system. The resultant element maps are shown in Figure 4. 3, which show the spatial distribution of Cu, Sb and S. From this analysis it is clear that the Cu and Sb are distributed together, which suggests the presence of ternary metal sulfide material, rather than two separate phases of Cu$_x$S$_y$ and Sb$_x$S$_y$. The only notable aspect of this analysis is the presence of apparent Cu-rich areas in the material where $x = 0.2$ (Figure 4. 3(a)). However, despite some localised clustering of Cu, there is still a general distribution across the entire area, suggesting the presence of Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ material.

This analysis yields useful insight into the generated particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ material, but does not indicate whether these structures are crystalline, or the phase or absolute composition of these particulate systems. To investigate this further, powder X-ray diffraction was employed on all six synthesised Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems.
Figure 4.3 EDX elemental mapping analysis of the various particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems prepared by solventless thermolysis at 450 °C for 1 h, where $x = (a) \ 0.2, (b) \ 0.4, (c) \ 0.6$ and (d) 0.8. Elemental mapping is also shown for (green) sulfur (Kα), (blue) copper (Kα) and (red) antimony (Lα). These were recorded at 15 k eV using secondary electron SEM. All scale bars present correspond to 10 μm.

4.5.4.5 Powder X-ray diffraction analysis of Cu$_{2x}$Sb$_{2(1-x)}$S$_y$

With the SEM analysis showing a change in morphology with increasing Cu character in the particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems, and the EDX elemental mapping analysis encouragingly showing the presence of both Cu and Sb localised together, these six particulate
systems were investigated by powder XRD. This was performed to determine both the crystallinity and the phase of the various Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems.

The p-XRD spectra of the six particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems are shown in Figure 4. As previously discussed, the XRD analysis for the sample where $x = 0$ exhibited pure orthorhombic phase stibnite (Sb$_2$S$_3$), and the XRD analysis for the sample where $x = 1$ exhibited pure rhombohedral digenite (Cu$_{1.8}$S). Next, the samples where $0 < x < 1$ were analysed. For the sample where $x = 0.2$, XRD analysis showed diffraction peaks consistent with ternary chalcostibite (CuSbS$_2$), with impurities of Sb$_2$S$_3$, in which it has been found that amount of Sb is higher than expected. Increasing the mole fraction to $x = 0.4$ resulted in the formation of pure orthorhombic chalcostibite (CuSbS$_2$, ICDD: 00-044-1417) (Figure 4. 4(b)). Upon further increasing the molar ratio of Cu to $x = 0.6$, a new phase of ternary copper antimony sulfide was observed; tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$, ICDD: 01-074-0270), with a lattice parameter of $a = 11.423 \pm 0.062$ Å, $b = 14.174 \pm 0.075$ Å, and $c = 3.765 \pm 0.038$ Å, with some impurities of Cu$_{1.8}$S. Previous reports have demonstrated that it is difficult to avoid a small number of impurities in the synthesis of tetrahedrite,$^{55,56}$ particularly when using copper and antimony xanthate (dithiocarbonate) precursors.$^2$ The presence of these impurities also account for the slight discrepancy in the EDX elemental composition analysis. Finally, increasing the molar ratio of Cu to $x = 0.8$ resulted in the generation of predominately pure phase cubic tetrahedrite (Cu$_{12}$Sb$_4$S$_3$, ICDD: 01-074-0270), as shown by the XRD pattern in Figure 4.4(c).
Figure 4.4 Plots showing the p-XRD analysis of Cu\textsubscript{2x}Sb\textsubscript{2(1-x)}S\textsubscript{y} produced by solventless thermolysis at 450 °C, where the mole fraction of Cu : Sb (x) was altered as in (a) x = 0, 0.2, 0.4, 0.6, 0.8 and 1, where x = 0 produced pure Sb\textsubscript{2}S\textsubscript{3} (ICDD: 01-073-0393, stick pattern on bottom) and x = 1 produced pure Cu\textsubscript{1.8}S (ICDD 00-023-0962, stick pattern on top). Also shown are the individual p-XRD patterns for (b) x = 0.4, showing pure chalcostibite (CuSbS\textsubscript{2}, ICDD: 00-044-1417) and (c) x = 0.6 and 0.8, showing pure tetrahedrite Cu\textsubscript{12}Sb\textsubscript{4}S\textsubscript{13} (ICDD: 01-074-0270).

4.5.4.6 Raman Spectroscopy of the Cu\textsubscript{2x}Sb\textsubscript{2(1-x)}S\textsubscript{y} systems

Raman spectroscopy was used to further study the particulate binary Cu\textsubscript{1.8}S and Sb\textsubscript{2}S\textsubscript{3} and ternary Cu\textsubscript{2x}Sb\textsubscript{2(1-x)}S\textsubscript{y} systems (as shown in Figure 4.5). The three systems where x = 0, 0.2 and 1 are shown in Figure S4. 6. For the system where x = 0.4, Raman spectroscopy further confirms the presence of pure chalcostibite (CuSbS\textsubscript{2}), with a sharp peak at 332 cm\textsuperscript{-1}, and lower intensity peak at 250 cm\textsuperscript{-1}.\textsuperscript{2} The p-XRD analysis indicates that the x = 0.6 and 0.8 systems were both tetrahedrite, of varying purities (Figure 4.4). The Raman spectra of these systems both
observed a sharp peak at 350 cm\(^{-1}\), corresponding to cubic tetrahedrite \(\text{Cu}_{12}\text{Sb}_4\text{S}_{13}\).\(^2\) In the \(x = 0.6\) system, a further peak at 250 cm\(^{-1}\) is also observed, which corresponds to Cu-S bonding (from the \(\text{Cu}_{1.8}\text{S}\) impurity).\(^{57, -59}\) This peak reduces in intensity as the mole fraction of Cu increases. These results correlate excellently with those previously reported for chalcostibite and tetrahedrite, obtained by solventless thermolysis of xanthate precursors of Cu and Sb.\(^2\)

![Figure 4.5 Raman spectra of the particulate \(\text{Cu}_2\text{Sb}_{2(1-x)}\text{S}_y\) systems where \(x = (a) 0.4, (b) 0.6\) and (c) 0.8. Indicating the presence of chalostibite (\(\text{CuSbS}_2\)) and tetrahedrite (\(\text{Cu}_{12}\text{Sb}_4\text{S}_{13}\)), respectively.](image)

**4.5.5 AACVD of \(\text{Cu}_2\text{Sb}_{2(1-x)}\text{S}_y\) (0 ≤ \(x\) ≤ 1) thin film systems**

The successful utilization of solventless thermolysis of the \(\text{Cu}_2\text{Sb}_{2(1-x)}\text{S}_y\) material is performed. The resulting materials are ranging between \(x=1\) results \(\text{Cu}_{1.8}\text{S}\) and \(x=0\) results \(\text{Sb}_2\text{S}_3\). The further mixing of Cu: Sb ratio results \(\text{CuSbS}_2\) and \(\text{Cu}_{12}\text{Sb}_4\text{S}_{13}\). In next step, thin films of these materials developed to interpret physical characteristics. The technique used for this purpose is aerosol-assisted chemical vapor deposition (AACVD). It is well known that AACVD is a ubiquitous approach and widely employed method of generating low cost thin films of metal chalcogenide materials from both metal dithiocarbamate and metal xanthate single-source precursors.\(^{26, 60-62}\) This technique was therefore utilised here to deposit both binary and ternary metal sulfides.
Deposition of the two precursors, to produce Sb$_2$S$_3$, Cu$_9$S$_5$ and Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ by AACVD was undertaken onto a glass slide under hot wall conditions using an adapted method described previously. The aerosol was generated by an ultrasonic humidifier and transported by flowing argon. Deposition of the films was carried out for 1 h at 450 °C, which generated black films with good surface coverage, as in Figure S4. 7. Initially, the morphology and elemental composition analysis was conducted on these six sample films by SEM and EDX analysis.

4.5.5.1 SEM, EDX and Elemental mapping analysis of the Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ thin films

The surface morphology of binary and ternary copper antimony sulfide thin films were initially investigated by SEM analysis. Figure 6 shows representative SEM images of the six investigated films. When $x = 0$ and 0.2, the SEM images portrays a rod-shaped structure (Figure 6(a & b)). On further increasing the doping content up to $x = 0.4$, the structural morphology changed to spherical particles from rods. This transformation is observed to increase with increasing Cu content see Figure 6 (c-e). This is consistent with the work reported by Chalapathi et. al. in which they found thin films of Cu$_3$SbS$_4$, generated by chemical bath deposition have a spherical crystal morphology. In another study, Van Ebden et. al. has also reported spherical nanoparticles of tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$). Therefore, our morphological analysis is in good agreement with the prior literature, despite being different from the particulate material generated by solventless thermolysis (Figure 4. 2). Finally, when $x = 1$ (i.e. only Cu is present), flake-like sheets were observed (Figure 4.6(f)), which is consistent with a previous report of AACVD decomposition of a Bis[N,N-dipropyl-N-(1-naphthoyl)thiourea]copper(II) precursor. We expect that the physical strength of thin films is increase linearly, by increasing Cu content in the structure. This is consistent with literature report i.e. by occurring transformation from rod like to grain size structures have generally shown more strength in thin films.
Figure 4.6 Representative SEM images of Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ thin film synthesised by the hot-wall AACVD at 450 °C using various values of x, where x = (a) 0, (b) 0.2, (c) 0.4, (d) 0.6, (e) 0.8 and (f) 1. These were recorded at 15 k eV using secondary electron SEM.

Following the morphological investigation of the thin film Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ samples, elemental composition analysis was then investigated through EDX analysis and is summarised in Table S4.3 (the spectra are shown in Figure S4.8). As expected, for the binary systems where x = 0 only Sb and S were present in the expected ratio (ca. 45:55), and x = 1 only Cu and S were present, also in the expected ratio (ca. 65:35).

For the ternary systems where 0 < x < 1, a composition of both Sb and Cu were present, alongside S. But in case of 0.2 concentration, the system was found to be Sb-rich and S-deficient, which could again be due to the presence of Sb$_2$S$_3$ as impurities. The amount of Sb is found slightly higher than expected which is consistent with p-XRD results. The ternary systems where x = 0.4, 0.6 and 0.8 all observed the expected composition (Table S4.3). Comparison of the EDX analysed expected vs observed Cu and Sb content again found a linear correlation.
(Figure S4. 9), equal to the particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ samples generated by solventless thermolysis. The comparison of expected to observed (both >95% fit) demonstrate the excellent agreement of the observed Cu and Sb to the expected when considering the phases of the Cu-Sb-S produced (see pXRD analysis below).

Having investigated the surface morphology of the deposited thin films, the various Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ thin films were investigated for elemental mapping on the samples where 0 < x < 1. This analysis again demonstrates a uniform distribution of all constituent elements (Cu, Sb and S) within the films (Figure 4. 7). For x= 0.2 concentration, the surface of the film is found to be Sb-rich and S-deficient, which could again be due to the presence of impurities of Sb$_2$S$_3$. Again, in thin film structures, the amount of Sb is found slightly higher than expected which is consistent with p-XRD results. Thus materials deposited by AACVD also demonstrate Cu-rich areas in the film where x = 0.2 but the content of Sb impurity is high as a result rod structures deforms to clusters (Figure 4. 7(a)). It can be observed that the presence of Cu-rich areas are also Sb-deficient relative the rest of the material. This analysis indicates that the two binary Cu-S and Sb-S phases were deposited separately, rather than depositing any ternary Cu-Sb-S material. This outcome is supported by the p-XRD analysis (vide infra) which could not accurately determine any distinct ternary phase. In the x = 0.4 thin film, there also appears to be Sb-rich areas (the larger particles in Figure 7(b)). This is due to the presence of Sb$_2$S$_3$ impurities as also shown by the pXRD pattern (Figure 8).
Figure 4. Figure showing both SEM (column 1) and elemental analysis maps (column 2, 3 and 4) for the four Cu$_2$xSb$_2$(1-x)S$_y$ systems where (a) x = 0.2, (b) x = 0.4, (c) x = 0.6 and (d) x = 0.8. These films were deposited by AACVD and decomposed at 450 °C. Elemental mapping is also shown for (green) sulfur (Kα), (blue) copper (Kα) and (red) antimony (Lα). These were recorded at 15 k eV using secondary electron SEM.

4.5.5.2 Powder XRD analysis of the Cu$_2$xSb$_2$(1-x)S$_y$ thin films

The SEM, EDX and elemental mapping analysis of the various Cu$_2$xSb$_2$(1-x)S$_y$ thin films showed that the expected ternary materials contained both Cu and Sb localised together. However, the morphology of these materials was different to those obtained through solventless thermolysis,
therefore the thin films were further examined under p-XRD analysis to clearly draw picture of compositional phase of each material.

It is found that, all deposited thin films for concentration $x < 1$ observed sharp peaks in the p-XRD patterns, indicating uniform crystallinity throughout the film. The deposited film where $x = 0$ (i.e. Sb only) again showed an orthorhombic structure of Sb$_2$S$_3$ (ICDD: 01-071-2432) with respective lattice parameters of $a = 11.2902 \pm 0.024$, $b = 3.6953 \pm 0.052$ Å and $c = 11.1398 \pm 0.038$ Å; $\alpha = \beta = \gamma = 90^\circ$), equivalent to the same material generated through solventless thermolysis. As the concentration of Cu increased at $x = 0.2$, the p-XRD pattern also showed chalcostibite (CuSbS$_2$) with impurities of orthorhombic Sb$_2$S$_3$. At $x = 0.4$, impurities of Sb$_2$S$_3$ is observed (see * in Figure 8(b)), but majority of peaks portrayed tetragonal fematinite (Cu$_3$SbS$_4$, ICDD: 01-071-0555) phase having lattice parameters $a = 5.3740 \pm 0.042$ Å, $b = 5.3754 \pm 0.042$ Å & $c = 10.5340 \pm 0.064$ Å (Figure 8(b)). Notably, this is a different phase of copper-antimony-sulfide to that obtained from the solventless thermolysis deposition at the same mole ratio of Cu : Sb. The phase comparison of resulting materials at $x = 0.2$ and 0.4 systems is drawn with phase diagram for Cu-Sb-S at 500 °C deposited by either AACVD to solventless thermolysis was compared. It has been reported that the thermodynamic product at the two Cu:Sb:S ratios where $x = 0.2$ and 0.4 (assuming 100% reduction of Cu(ii) to Cu(i)) are chalcosibite (CuSbS$_2$). Therefore, the formation of stibnite (Sb$_2$S$_3$) and fematinite (Cu$_3$SbS$_4$) demonstrates that AACVD deposition can form the kinetic product, whereas solventless thermolysis is prone to form the thermodynamic product. This dichotomy is also further demonstrated as solventless thermolysis forms the thermodynamically favourable digenite (Cu$_{1.8}$S) and AACVD deposits the kinetic chalcocite (Cu$_2$S). At concentration $x = 0.6$ and 0.8, the phase again changes to phase pure cubic tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$ ICDD: 01-088-0283) with lattice parameters calculated as $(a = b = c = 10.2853 \pm 0.072$ Å) (Figure 8(c)), which is entirely consistent with the particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ material obtained from solventless thermolysis. Analysis of the $x = 1$ thin film observed both sharp peaks (indicating crystallinity) alongside a broad, single peak which indicates some amorphous character within the film. The sharp, crystalline peaks of this spectra indicate cubic Cu$_2$S (ICDD: 01-084-1770) was formed, with lattice parameters equal to $a = b = c = 5.4539 \pm 0.054$.
Å. This is again different to the equivalent solventless thermolysis deposition which observed Cu\(_{1.8}\)S, indicating less sulfur loss is observed using AACVD and that AACVD is prone to deposit a kinetic, rather than the thermodynamically favourable phase.\(^{66}\)

**Figure 4.7** Plots showing the powder-XRD patterns for (a) all deposited Cu\(_{2x}\)Sb\(_{2(1-x)}\)S\(_y\) thin films of \(x = 0, 0.2, 0.4, 0.6, 0.8\) and 1. Also shown are the individual patterns for (b) \(x = 0.4\) fematinite (Cu\(_3\)Sb\(_4\), ICDD: 01-071-0555) and (c) \(x = 0.6\) and \(x = 0.8\) tetrahedrite (Cu\(_{12}\)Sb\(_4\)S\(_{13}\), ICDD:01-088-0283). These spectra were recorded on the AACVD thin films, deposited at 450 °C.
4.5.5.3 Raman spectroscopy of the Cu$_{2x}$Sb$_2$(1-x)S$_y$ thin films

Following the successful characterisation of the phases of the AACVD deposited Cu$_{2x}$Sb$_2$(1-x)S$_y$ thin films. The films were again analysed by Raman spectroscopy. The Raman spectra for the films where $x = 0, 0.2$ and $1$ are shown in Figure S 4.10. For the thin film deposited when $x = 0.4$, the peaks in the Raman spectrum appear at 253, 273, 317 and 343 cm$^{-1}$ (Figure 4. 9(a)), which correspond to tetragonal famatinite Cu$_3$SbS$_4$, confirming the p-XRD characterisation. As $x$ was increased to 0.6 and 0.8, the Raman peak was shifted to 352 cm$^{-1}$, which correspond to cubic tetrahedrite Cu$_{12}$Sb$_4$S$_{13}$ (Figure 4. 9(b)). A further peak at 323 cm$^{-1}$ was observed in the $x = 0.8$ thin film, also indicating pure cubic tetrahedrite Cu$_{12}$Sb$_4$S$_{13}$ (Figure 4. 9(c)). These results are all in good agreement with the previous literature investigating various phases of copper-antimony-sulfur.$^2$

![Raman spectra recorded for the AACVD-deposited thin films of Cu$_{2x}$Sb$_2$(1-x)S$_y$ where x = (a) 0.4 (b) 0.6 and (c) 0.8. Indicating the presence of (a) famatinite (Cu$_3$SbS$_4$) and (b) and (c) tetrahedrite (Cu$_{12}$Sb$_4$S$_{13}$).](image)

**Figure 4. 8**

4.5.6 Conclusions

In this study, various binary and ternary Cu-Sb-S phases were produced by the thermal decomposition of both copper and antimony diethylidithiocarbamate single source precursors. This was achieved as both particulates and thin films through solventless thermolysis, or aerosol-assisted chemical vapor deposition, respectively. Utilising different methods of
deposition resulted in the generation of different phases when altering the ratio of Cu : Sb precursors. Under solventless thermolysis using a low Cu ratio produced chalcostibite (CuSbS₂), and digenite (Cu₁.₈S) with no Sb precursor present. Using AACVD to deposit thin films resulted in fematinite (Cu₃SbS₄) under a low Cu ratio and chalcocite (Cu₂S) with no Sb precursor present. Both methods were found to produce stibnite (Sb₂S₃) with no Cu present and tetrahedrite (Cu₁₂Sb₄S₁₃) with a high ratio of Cu : Sb.

The morphology of these produced materials was characterised by SEM and the elemental composition of these materials was determined through EDX analysis and EDX-mapping. These analyses demonstrated that the morphology of the materials change from a rod-like structure at low Cu content to more particulate material with increasing Cu content. Elemental mapping demonstrated that Cu and Sb were present in the same local environments, indicating the successful synthesis of ternary metal sulfides, which was confirmed by powder XRD and Raman spectroscopy.

This report demonstrates that both deposition methods (solventless thermolysis and AACVD) provide a facile, low-temperature and efficient synthetic approach towards the preparation of phase pure binary and ternary metal sulfides from single-source diethylidithiocarbamate precursors. The synthesised phase-pure ternary copper antimony sulfide materials CuSbS₂, Cu₃SbS₄ and Cu₁₂Sb₄S₁₃ are all targets relevant for photovoltaic applications, and it is likely this approach is universal towards the synthesis of ternary metal chalcogenides.

### 4.5.7 Author contributions

F.M undertook the experiments and initially drafted the manuscript. F.A was responsible for laboratory supervision, collection of the characterisation data and general data interpretation. M.A.B was responsible for some data analysis and manuscript preparation. D.J.L was responsible for conceptualisation and overall supervision.
4.5.8 Acknowledgments

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4.5.9 Conflicts of interest

There are no conflicts of interest to declare

4.5.10 References


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4.5.11 Supplementary information

Contents:

Table S4.1: Composition used for synthesis of Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ powders and thin films

Figure S4.1: Thermogravimetric analysis of the Cu(DTC)$_2$ and Sb(DTC)$_3$ precursors.

Figure S4.2: P-XRD patterns of particulate Sb(DTC)$_3$

Figure S4.3: P-XRD patterns of particulate Cu(DTC)$_2$

Figure S4.4: The EDX spectra of Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ samples prepared by solventless thermolysis

Figure S4.5: The amount of copper expected and the amount of copper in Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems synthesized by solventless thermolysis.

Figure S4.6: Raman spectra of the particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems where $x = (a)$ 0, (b) 0.2 and (c) 1.

Figure S4.7: Photographs of the thin film Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems deposited by AACVD

Figure S4.8: The EDX spectra of Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ thin films prepared by AACVD.

Figure S4.9: The amount of copper expected and the amount of copper in Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ thin films synthesized by the AACVD method.

Figure S4.10: Raman spectra recorded for the AACVD-deposited thin films of Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ where $x = (a)$ 0 (b) 0.2 and (c) 1.
Table of data of various mole fraction Cu : Sb precursors used in the synthesis of ternary 
$Cu_{2x}Sb_{2(1-x)}S_y$

Table S 4. Composition used for the synthesis of $Cu_{2x}Sb_{2(1-x)}S_y$ system by the solventless thermolysis and AACVD methods

<table>
<thead>
<tr>
<th>Mole fraction [Cu]/[Cu]+[Sb]</th>
<th>Cu[DTC]$_2$</th>
<th>Sb[DTC]$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0 mmol</td>
<td>0.55 mmol</td>
</tr>
<tr>
<td>0.2</td>
<td>0.55 mmol</td>
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</tr>
<tr>
<td>0.4</td>
<td>0.55 mmol</td>
<td>0.80 mmol</td>
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<td>0.6</td>
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<td>0.35 mmol</td>
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<td>0.8</td>
<td>0.55 mmol</td>
<td>0.13 mmol</td>
</tr>
<tr>
<td>1</td>
<td>0.55 mmol</td>
<td>0 mmol</td>
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</table>

TGA analysis of the individual Cu(DTC)$_2$ and Sb(DTC)$_3$ precursors

The final residual mass of the Cu(DTC)$_2$ precursor was observed to be 13%, which is significantly less than the expected value of 22% for Cu$_2$S, or 20% for Cu$_9$S$_5$. In this case no further loss was observed at higher temperature (Figure S1). The Sb(DTC)$_3$ precursor also observed a single, rapid decomposition, followed by a more gradual decomposition resulting in a product ca. 25% of the initial mass, which is also significantly lower than the expected 30% for Sb$_2$S$_3$. Beyond 425 °C, a gradual loss of further mass is observed, which can be attributed to further loss of elemental sulfur.$^1$ The TGA results indicate that the two precursors decompose to their respective metal sulfides within a similar temperature range, this makes them ideal candidates to explore further to produce particulate binary metal chalcogenides.

![Figure S 4. 1 Plot showing the TGA decomposition analysis of the Cu(DTC)$_2$ and Sb(DTC)$_3$ and precursors.](image)
Powder XRD diffraction patterns for solventless decomposition of Sb(DTC)$_3$ at various temperature

**Figure S 4.** Plot showing the p-XRD patterns of particulate Sb(DTC)$_3$ decomposition products, where the decomposition temperature was (a) 300 °C, (b) 400 °C, (c) 425 °C, (d) 450 °C and (e) 475 °C, decomposed by solvent-less thermolysis for 1 h. All peaks corresponded to standard pattern of stibnite Sb$_2$S$_3$ (ICDD 01-073-0393)
Powder XRD diffraction patterns for solventless decomposition of Cu(DTC)$_2$ at various temperature

Figure S 4.3 Plot showing the p-XRD patterns of particulate Cu(DTC)$_2$ decomposition products, at decomposition temperatures of (a) 300 °C, (b) 350 °C (c) 400 °C and (d) 450 °C, decomposed by solvent-less thermolysis for 1 h. Peaks correspond to digenite (Cu$_9$S$_5$) ICDD 00-023-0962. Minor phase monoclinic chalcocite (Cu$_2$S) ICDD 01-072-1071 have been marked with an * in part (a), which are still present in (b) and (c).
Elemental analysis spectra of the particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ samples produced by solventless thermolysis

**Figure S 4.4** The EDX spectra of Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ samples prepared by solventless thermolysis at 450 °C at various mole fractions where (a) x = 0, (b) x = 0.2, (c) x = 0.4, (d) x = 0.6, (e) x = 0.8 and (f) x = 1.
Expected Cu and Sb content vs observed Cu and Sb content in the particulate ternary Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems produced by solventless thermolysis

**Figure S 4.5** Linear relationship between the amount of copper expected and the amount of copper in the particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems synthesized by solventless thermolysis at 450 °C, obtained from EDX analysis.
Table S 4. The content of Cu, Sb and S in Cu$_{2x}$Sb$_{2(1-x)}$S$_2$ prepared by solventless thermolysis at 450°C for 0 \( \leq x \leq 1 \), as calculated from the theoretical values and found by EDX analysis.

<table>
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<th>Mole Fraction</th>
<th>Elemental Composition Expected (Atomic %)</th>
<th>Stoichiometry expected</th>
<th>Elemental Composition Found by EDX (atomic %)</th>
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<td></td>
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<td>67</td>
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<td>33</td>
<td>Cu$_2$S</td>
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</table>
Raman spectroscopy for particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ samples where $x = 0, 0.2$ and $1$ from solventless thermolysis

**Figure S 4.6** Raman spectra of the particulate Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ systems where $x = (a) 0$, (b) 0.2 and (c)1.
Photographs of the AACVD thin films of $\text{Cu}_{2x}\text{Sb}_{2(1-x)}\text{S}_y$

**Figure S 4.** Figure showing photographs of the AACVD deposited thin films of $\text{Cu}_{2x}\text{Sb}_{2(1-x)}\text{S}_y$, where the particular $x$ values are shown.
Elemental analysis of the thin film $\text{Cu}_{2x}\text{Sb}_{2(1-x)}\text{S}_y$ samples produced by AACVD

Figure S 4.8 The EDX spectra of $\text{Cu}_{2x}\text{Sb}_{2(1-x)}\text{S}_y$ thin films prepared by AACVD at 450 °C at various Iron mole fraction (a) $x = 0$, (b) $x = 0.2$, (c) $x = 0.4$, (d) $x = 0.6$, (e) $x = 0.8$ and (f) $x = 1$. 
Expected Cu content vs observed Cu content in the ternary Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ thin films deposited by AACVD

**Figure S 4.** Linear relationship between the amount of copper expected and the amount of copper in Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ thin films synthesized by the AACVD method at 450°C from EDX analysis.
Table S 4. The content of Cu, Sb and S in Cu$_{2x}$Sb$_{2(1-x)}$S$_3$ thin film prepared by AACVD method at 450°C (x = 0, 0.2, 0.4, 0.6, 0.8 and 1 molar fraction of copper) calculated from the theoretical values and found by EDX analysis.

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Raman spectra of thin film Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ samples where $x = 0$, 0.2 and 1, deposited by AACVD.

Figure S 4. Raman spectra recorded for the AACVD-deposited thin films of Cu$_{2x}$Sb$_{2(1-x)}$S$_y$ where $x = (a)$ 0 (b) 0.2 and (c) 1.
References

Chapter 5. Synthesis of Co$_{2x}$Sb$_2$(1-x)S$_3$ nanoparticles and thin films via solvent less thermolysis of metal diethyldithiocarbamates and AACVD method

5.1 Introduction

Sulfide-based nanomaterials have generated considerable attention because to their unique properties, which include high conductivity, low cost, minimal toxicity, and excellent thermal stability.\(^1\) Its characteristics enable it to be employed in a wide variety of applications; it has the potential to be used in supercapacitors, batteries, dye-sensitized solar cells, drug delivery, and electrocatalysis.\(^2\) Stibnite (Sb$_2$S$_3$) is high earth abundance and non toxic \(^3\) it has a direct bandgap of 1.5 - 2.5 eV. Some recent applications of Sb$_2$S$_3$ are in solar energy conversion,\(^4\) television cameras,\(^5\) microwave devices,\(^6\) and switching devices.\(^7\) Cobalt sulfides are inexpensive, abundant, and have low toxicity. They also have an appropriate bandgap (1.2–1.9 eV) with great electrical conductivity for high-efficiency solar cell applications.\(^8\) Ternary cobalt antimony sulfides (costibite CoSbS) have been fabricated using a variety of methods such as, vapor phase technique \(^9\) vacuum melting \(^10\) and ball-milling.\(^11\) All these methods exhibit varying degrees of efficiency, having numerous limitations as well. Solvent-less pyrolysis is a simple, low-cost, green, and high yield method to synthesize ternary metal sulfides in a solid-state.\(^12\) Another significant advantage of the solventless pyrolysis method is that sulfides with different morphologies and sizes can be synthesized.\(^13\) The aerosol-assisted chemical vapor deposition (AACVD) method is widely used for the preparation of metal sulfide thin films with uniform thickness, high purity, and good adhesion.\(^14\) AACVD is a low-cost and easily controllable method, that usually works in an ambient environment.\(^15\) More recently, metal sulfides are prepared by employing single-source precursors using AACVD to achieve high purity, uniform thickness, and simplicity in synthesis.\(^16\) In this research cobalt antimony sulfide Co$_{2x}$Sb$_2$(1-x)S$_3$ nanoparticles and thin films are prepared by solventless thermal pyrolysis of single-source precursors and AACVD method at 450°C. Cobalt diethyldithiocarbamate trihydrate (Co(Ddtc)$_2$) and antimony diethyldithiocarbamate trihydrate (Sb(Ddtc)$_3$) is used as single-source precursors. The as-prepared Co$_{2x}$Sb$_2$(1-x)S$_3$ (x =
0, 0.2, 0.4, 0.6, 0.8, and 1) samples are characterized for structure and morphology investigation and their optical and magnetic properties are evaluated.

5.2 Author contribution

Experiments were designed by Fadiyah Makin and Dr David Lewis. Fadiyah synthesised the dithiocarbamate precursors and characterised them via elemental analysis, and TGA as detailed in the manuscript. Fadiyah conducted the experimental work of the synthesis of $\text{Co}_{2x}\text{Sb}_{2(1-x)}\text{S}_3$ ($0 \geq x \geq 1$) powders. Fadiyah performed characterisation for all samples using XRD, SEM, EDX and UVvis spectroscopy. Dalal Alzahrani and Flouriana Tuna conducted the magnetic measurement for the samples. David J. Lewis and Firoz Alam provided useful discussions, and edited the manuscript.

5.3 References


14 M. D. Khan and N. Revaprasadu, Progress in single source precursors for layered 2D metal chalcogenide thin films and nanomaterials, *SPR Nanosci.*, 2019, **5**, 86–120.

5.4 Manuscript 3. Synthesis of Sb$_{2(1-x)}$Co$_{2x}$S$_3$ nanoparticles and thin films via Thermolysis of metal diethyldithiocarbamates and AACVD method

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5.4.1 Abstract

Here, we report the synthesis and characterization of antimony and cobalt diethyldithiocarbamate complexes of Sb\([S_2CN(Et_2)]_3\) (1) and Co\([S_2CN(Et_2)]_2\) (2) and used as single-source precursors for the production of ternary antimony cobalt sulfides \([Sb_{2(1-x)}Co_{2x}S_3\) (0 ≤ x ≥ 1)] nanoparticles and thin films using solventless thermal pyrolysis and aerosol assisted chemical vapour deposition (AACVD), respectively. Both nanoparticles and thin films were prepared at 450 °C by varying the molar concentration of Co and Sb. In the system. The samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, magnetometer measurement, and UV-Vis absorption spectroscopy. XRD results show that different molar ratios of cobalt and antimony diethyldithiocarbamate resulted in single-phase Sb\(_{2(1-x)}Co_{2x}S_3\) nanoparticles and thin films. SEM images revealed a change in the morphology of the prepared samples as the amount of cobalt increased in the complexes. EDX results were consistent with the ratio obtained from the feed concentrations. The crystal structure, morphology, magnetic and optical properties were significantly varied as a function of the Co content, indicating that limited alloying through the single source approach is conceivable.

5.4.2 Introduction

The demand of energy efficient materials has increased significantly since past two decades as a result of rising industrialisation and other economic activity. Researchers are consistently reporting their novel efforts in discovering new materials to be used as alternate efficient renewable energy sources.\(^1\) Among most commonly known sources to transform energy, photovoltaics (PV) has evolved as a simple, cheap, efficient and environment friendly technique of generating renewable source of energy.\(^4,5\) Additionally, the availability of a variety of solar cells, such as organic/inorganic interface, nanohybrids and semiconducting nanomaterials, has contributed momentously in the rapidly grown field.\(^6,7\) Significant number of compounds have reported efficient solar cell materials like perovskites,\(^8,9\) full-half Heuslers\(^10,11\) and Spinels.\(^12\) Similarly, semiconducting metal-metal sulfides have been intensively
explored and developed via low cost-effective methods especially for large scale production and have shown promising potential for creating more efficient solar cells. Due to their low band gap energy, binary metal sulphides such as zinc sulfide, nickel sulfide, bismuth sulfide, lead sulfide, cadmium sulfides, and cobalt sulfide have been extensively used for the photovoltaics applications. Among all aforementioned sulfides, binary cobalt sulfides have greater electrical conductivity and solar cell application potential. The fundamental reason behind this is that Cobalt sulfides are inexpensive, can be fabricated from abundantly available resources of minerals and have low toxicity (Pb free materials) as compare to other highly efficient solar cell materials. Furthermore, most imperative part in eloquent attraction of the materials is the bandgap (1.2–1.9 eV) which is suitable range and ideally operatable conditions for high-efficient solar cell applications.

In past few years there has been seen a surge of interest in ternary metal sulfides (TMS) to be used in photovoltaics, particularly in the development of high-efficiency solar cells. The well-known materials in TMS family are CoIn$_2$S$_4$, NiCo$_2$S$_4$, CuCo$_2$S$_4$, Cd$_{1-x}$Co$_x$S, and CoNi$_2$S$_4$ in photovoltaic applications. The best part in developing these materials is the synthesize method in which slight modifications via doping drastically enhances the physical attributes of the compounds. These materials have broad dimension of advanced applications not only in photovoltaics but also to be used in as novel magnetic materials. Such as Zn based TMS Zn$_{1-x}$TM$_x$S (TM = Fe, Co and Ni) has been reported as ferromagnetic materials with spin-polarized band gaps in both spin channels, which makes them very much suitable for magnetically active spintronic devices.

Ternary cobalt sulfides such as CoSbS, CoSbSn, CuCo$_2$S$_4$, Co$_3$S$_4$, CuCo$_2$S$_4$ and NiCo$_2$S$_4$ are synthesized by a variety of methods including thermal evaporation, spray pyrolysis, spin coating, solvothermal method, pulsed laser ablation, and chemical bath deposition. Costbite (CoSbS) is an important compound which have shown very developed electronic applications. The compound has not only been studied in pristine form, it is specifically being studied under several metal doping. For example, Zi lu et al have studied the effect of Ni in costbite and found enhanced optical and charge transport properties. Du Q et al have recently reported simple method to fabricate low temperature thermos power applications. There are
thin film fabrication of doped structures are also available. Frumarova, B. et al. \(^{33}\) have studied thin films of samarium (Sm) doped in Sb\(_2\)S\(_3\). They found that Sm doping has improved optical conductivity and structural stability with increasing Sm content. In another study by Frumarova, B. et al. \(^{27}\) the optical transparency is studied with chalcogenide glasses doped with Pr and Yb. The lumincence of resulting film is observed to increase with doping content of Yb. These properties are mainly observed in Sb\(_2\)S\(_3\) structures under different metal or rare earth doping. There are several techniques reported in literature utilized to fabricate CoSbS type structures namely vapor phase technique \(^{34}\) vacuum melting approach \(^{30}, 35\) solid state reaction \(^{36}, 37, 38\) and ball-milling. \(^{39}\) All these methods have inherited merits and de-merits which depends on choice of application. Solvent-less pyrolysis is a simple, low-cost, green, and high yield method to synthesize ternary metal sulfides in a solid state. \(^{40}\) Another significant advantage of the solventless pyrolysis method is that sulfides with different morphologies and sizes can be synthesized. \(^{41}\) The aerosol-assisted chemical vapor deposition (AACVD) method is widely used for the preparation of metal sulfide thin films with uniform thickness, high purity, and good adhesion. \(^{42}\) AACVD is a low-cost and easily controllable method, usually works in an ambient environment. \(^{43}\) More recently, metal sulfides are prepared by employing single-source precursors using AACVD to achieve high purity, uniform thickness, and simplicity in synthesis. \(^{44}\)

In literature, we have found that there are no reports available in Co doped Sb\(_2\)S\(_3\) thin films and nanoclusters. The similar compounds have shown very attractive applications in optoelectronics. Therefore, to fill the research gap we have studied in detail the effect of Co doped Sb\(_2\)S\(_3\) nano particles and thin films. The fabrication of cobalt antimony sulfide Sb\(_2\)(1-x)Co\(_x\)S\(_3\) nanoparticles and thin films are prepared by solventless thermal pyrolysis of single-source precursors and AACVD method at 450°C. Cobalt diethyldithiocarbamate trihydrate (Co(Ddtc)\(_2\)) and antimony diethyldithiocarbamate trihydrate (Sb(Ddtc)\(_3\)) is used as single-source precursors. Sb\(_2\)(1-x)Co\(_x\)S\(_3\) (x = 0, 0.2, 0.4, 0.6, 0.8, and 1) samples prepared are characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) technique, UV/vis/NIR spectroscopy and SQUID magnetometry. The results have shown excellent improvement in the resulting material which has shown potential ability to be used in advanced photovoltaics.
5.4.3 Experimental

5.4.3.1 Chemicals

The chemicals used in the fabrication process were Sodium diethyldithiocarbamate trihydrate (\((\text{C}_2\text{H}_5)_2\text{NCS}_2\text{Na} \cdot 3\text{H}_2\text{O}, \geq 99.0\%\)), antimony trichloride (\(\text{SbCl}_3, \geq 99.5\%\)), cobalt (II) chloride hexahydrate (\(\text{CoCl}_2 \cdot 6\text{H}_2\text{O} \geq 99.99\%\)), methanol (\(\text{CH}_3\text{OH}, \geq 99.8\%\)), absolute ethanol (\(\text{CH}_3\text{CH}_2\text{OH}, \geq 99.5\%\)), chloroform (\(\text{CHCl}_3, \geq 99\%\)) and isopropyl alcohol (\((\text{CH}_3)_2\text{CHOH}, \geq 99.7\%\)). All pure samples were purchased from Sigma-Aldrich and used with no further purification. The synthesis of all precursors was carried out in the air and no special handling was needed.

5.4.3.3 Synthesis of antimony (III) diethyldithiocarbamate, \([\text{Sb} (\text{S}_2\text{CN} (\text{Et})_2)_3]\) (1)

As described previously in chapter 3 and 4, sodium diethyldithiocarbamate trihydrate (6.76 g, 30 mmol) was dissolved in 100 mL of methanol with constant stirring. The solution of antimony (III) chloride (2.26 g, 10 mmol) was prepared in 25 mL methanol and added drop wise to the sodium salt solution with constant stirring. The resulting mixture was further stirred for 30 minutes at room temperature and pressure until yellow precipitates were obtained. These precipitates were filtered and washed several times by using deionized water and with methanol. The resulting sample of yellow precipitates were allowed to dry overnight at room temperature in an open air, which transformed as clear yellow solid. Yield: 4.3 g (86%); Elemental analysis, found: C, 31.35 %; H, 5.19 %; N, 7.25%; S, 33.22 %; Calc. C, 31.81 %; H, 5.34 %; N, 7.42 %; S, 33.90 %.
5.4.3.4 Synthesis of Cobalt (II) diethyldithiocarbamate, [Co (S$_2$CN(Et)$_2$)$_2$] (2)

The method used to prepare sample (2) is similar to the one used to prepare sample (1). Sodium diethyldithiocarbamate trihydrate (5 g, 20 mmol) was dissolved in 100 mL of methanol then, cobalt (II) chloride hex hydrated (2.38 g, 10 mmol) was dissolved in 25 ml of methanol and added dropwise to the sodium salt with a continuous stirring. The reaction mixture was stirred for about 30 minutes at room temperature. The green precipitate which formed was filtered and washed a number of times using deionized water and finally with methanol and left to dry overnight at room temperature in the open air, resulting in a clear green solid. Yield 3.7 g, (84%). Elemental analysis, found: C, 33.80%; H, 6.05%; N, 7.64%; S, 35.25%; Calc. C, 33.81%; H, 5.68%; N, 7.89%; S, 36.25%

5.4.3.5 Synthesis of Sb$_2$S$_3$ and CoS powders

Complexes (1) and (2) were used to produce Sb$_2$S$_3$, and CoS powders using solvent-less thermolysis (melt method). In briefly, 0.56 mmol of the complex (1) and (2) were located in a ceramic boat inside a tube furnace and melted at 300, 400, 425, 450, and 475 °C for 1 h under a flow of nitrogen gas, resulting in black coloured powders, which were collected for further characterization.

5.4.3.6 Synthesis of Sb-Co-S ternary powders

Antimony cobalt sulfide Sb$_{2(1-x)}$Co$_{2x}$S$_3$ powders were prepared by the solvent-less thermolysis (melt method) using a mixture of complexes (1) and (2) with different molar ratios as shown in Table S 5.1. The complexes were dissolved in 10 mL of chloroform to ensure the formation of a homogeneous mixture. Subsequently, the solvent was evaporated by kneading using a mortar and pestle and the solid mixture was then placed into a ceramic boat inside a furnace tube at 450 °C for 1 h under a nitrogen atmosphere. The obtained black powder was allowed to cool to room temperature and collected for characterization.
5.4.3.7 Antimony cobalt sulfide (Sb-Co-S) thin films

Aerosol assisted chemical vapor deposition (AACVD) was used to deposit cobalt antimony sulfide thin films on a cleaned glass substrate (1 cm x 2.5 cm) at 450 °C under a nitrogen atmosphere. AACVD has been used and reported for the deposition of similar systems. Different molar fractions of \([\text{Sb(S}_2\text{CN(Et)}_2\text{)}_3]\) and \([\text{Co(S}_2\text{CN(Et)}_2\text{)}_2]\) were dissolved in 20 ml of THF in a two-necked round-bottomed flask. One side of the flask was connected to the reactor tube via a piece of rubber tube and the other side was connected to an argon carrier gas which was controlled by a platon flow gauge. The reactor tube placed inside a carbolite tube furnace was heated to 450 °C. The aerosols were generated by placing the two-necked round-bottomed flask with the precursor solution on an ultrasonic humidifier. The flow of argon was kept in between 160-180 sccm helped to transport the steam of aerosols into reactor tube, where it gets decomposed and deposit uniformly over the substrates.

5.4.4 Results and discussion

5.4.4.1 Thermogravimetric analysis

An investigation of the thermal stability of precursors (1) and (2) was carried out using thermogravimetric analysis (TGA). The Fig. 5.1 shows TGA curves of antimony and cobalt complexes. The TGA curve for complex (1) indicates that it began decomposing at 240°C, losing 74% of its mass in the first rapid step and then gradually decreasing mass beyond 400°C, corresponding to the loss of sulfur in line with previous reported. But the TGA analysis of precursor (2) revealed a two-step breakdown. The first breakdown of 2% of its mass occurred at 170 °C, which was attributable to the sample's moisture content. At elevated temperature up to 390 °C, the second strong decomposition stage was observed with a weight loss of 71.08 percent due to ligand decomposition. This resulted in a total 23.30 % weight loss during annealing, which is consistent with the complex's theoretical CoS content of 25.59 %. On further increasing temperature above above 370 °C, no further weight loss was recorded, which indicates the stability in the structural phase of cobalt sulfide.
5.4.4.2 Solventless thermolysis of Sb\(\text{S}_2\text{CN(Et)}_2\text{)}_3\) and Co\(\text{S}_2\text{CN(Et)}_2\text{)}_2\) to generate binary systems: \(\text{Sb}_2\text{S}_3\) and CoS

Thermal decomposition of the precursors (1) and (2) synthesized at temperatures 300, 400, 425, 450, and 475\(^\circ\)C for 1h resulted in black powder residues. The powdered samples were analysed by XRD patterns, resulted from (1) see Fig. 5.1 SI. The structural phase formed indicates that the sample is composed of orthorhombic stibnite (\(\text{Sb}_2\text{S}_3\), ICDD: 01-073-0393) with lattice parameters \(a=11.313\pm0.043\) Å, \(b =3.833\pm0.043\) Å, and \(c=11.225\pm0.052\) Å. The peaks intensities were similar in all cases with a slight increase in intensity in some of the samples prepared at the higher temperatures.

The XRD patterns of the samples obtained from the decomposition of (2) at 300, 350, 400 and 450 °C are illustrated in Fig. 5.2 SI. The diffraction peaks correspond to the hexagonal jaipurite.
cobalt sulfide phase (CoS, ICDD 01-075-0605) as the major phase at all temperatures with lattice parameters $a = 3.257 \pm 0.043 \ \text{Å}$, $b = 3.257 \pm 0.043 \ \text{Å}$, and $c = 5.1430 \pm 0.052 \ \text{Å}$, corresponding to (100), (101), (102), (110), (200), and (201) planes. There was no significant difference in the peak intensities of all studied four samples.

5.4.4.3 Synthesis of ternary $\text{Sb}_2(1-x)\text{Co}_{2x}\text{S}_3$ ($0 \leq x \leq 1$) powder by solventless thermolysis

X-ray diffraction (XRD) patterns of $\text{Sb}_2(1-x)\text{Co}_{2x}\text{S}_3$ ($0 \leq x \geq 1$) at different Co/Co+Sb molar ratios (a) $x = 0$ (b) $x = 0.2$ (c) $x = 0.4$ (d) $x = 0.6$ (e) $x = 0.8$ and (f) $x = 1$ are shown in figure 5.2. The XRD peaks as mentioned before indicated the pure orthorhombic phase of $\text{Sb}_2\text{S}_3$ at $x = 0$ with lattice parameters of $a = 11.313 \pm 0.043 \ \text{Å}$, $b = 3.833 \pm 0.043 \ \text{Å}$, and $c = 11.225 \pm 0.052 \ \text{Å}$ which were in agreement with the standard powder pattern (ICDD: 01-073-0393). On the other hand, when Co concentration is full i.e. $x = 1$, pure hexagonal jaipurite phase of CoS was observed with lattice parameters of $a = 3.257 \pm 0.035 \ \text{Å}$, $b = 3.257 \pm 0.035 \ \text{Å}$, and $c = 5.1430 \pm 0.046 \ \text{Å}$ and diffraction peaks appear at (100), (101), (102), (110), (200) and (201) planes at angles $30.5^\circ$, $35.2^\circ$, $46.97^\circ$, $54.28^\circ$, $63.57^\circ$, and $66.5^\circ$, respectively which are found to be in agreement with the standard pattern (ICDD: 01-075-0605). When concentration of alloys $\text{Sb}_2(1-x)\text{Co}_{2x}\text{S}_3$ reach around $x = 0.2$ and 0.4 of cobalt, it can be seen from figure 3.2 that there was no significant change in the intensity plot of the alloys, the four patterns have a minor peak difference which appeared at $30^\circ$ and shifted to higher intensity with increase in the concentration of Co. The peak has significant shift as compared to the corresponding (100) plane for pure CoS. On further increasing the cobalt content to $x = 0.6$ and 0.8 molar fraction, the crystallographic data appears to match excellently with crystalline pattern of orthorhombic paracostibite CoSbS phase and pure hexagonal jaipurite phase of CoS, respectively. In general, it has been found that by increasing Co concentration in $\text{Sb}_2\text{S}_3$, the structural phase appears to change. The concentrations of Co at $x = 0.2$, 0.4, 0.6 have generally orthorhombic phase while concentration of 0.8 exhibit hexagonal phase. The results have shown that doping approach has significant effect on phase change which has effected the physical attributes of the studied materials.
Figure 5. 2 XRD patterns of Sb$_{2(1-x)}$Co$_{2x}$S$_3$ ($0 \leq x \leq 1$) produced by solventless thermolysis at 450 °C with different Co/Co+Sb molar ratio (a) $x = 0$ (b) $x = 0.2$ (c) $x = 0.4$ (d) $x = 0.6$ , (e) $x = 0.8$ and (f) $x = 1$ with a standard pattern of Sb$_2$S$_3$ (bottom) and CoS (top)

SEM images of Sb$_{2(1-x)}$Co$_{2x}$S$_3$ synthesized using $x = 0$, 0.2, 0.4, 0.6, 0.8, and 1-mole fraction of Co are presented in Figure 5. 3. SEM Images of pure Sb$_2$S$_3$ ($x=0$) shown rod-like structures (Figure 5. 3a). Before, Sheikhiabadi et al reported a sample with the same morphology of Sb$_2$S$_3$ via a hydrothermal method in an aqueous solution at 100 °C, using antimony chloride (SbCl$_3$) and thioglycolic acid. The structural morphology appear to change to a mix combination of small rod and sheet clusters when Co concentration is at $x = 0.2$, 0.4, 0.6, and 0.8 see Figure 5.3 (b, c, d and e). Moreover, the morphology of pure cobalt sulfide at $x=1$ has shown very small cluster structures like fumes (Figure 5.3 f). Thus, the
deficiency of Sb in replacement of Co has shown that rod like structure transforms to fume like cluster of CoS at higher concentration of Co.

Figure 5. 3 SEM images of \( \text{Sb}_2(1-x)\text{Co}_{2x}\text{S}_3 \) powder prepared by the melt method for 1 h at 450 °C using different mole fractions of cobalt (a) \( x = 0 \) (b) \( x = 0.2 \) (c) \( x = 0.4 \) (d) \( x = 0.6 \) (e) \( x = 0.8 \), and (f) \( x = 1 \).

Figure 5. 4 shows the EDX elemental mapping Co, Sb, and S present in the \( \text{Sb}_2(1-x)\text{Co}_{2x}\text{S}_3 \) system, which shows the elements spatial distribution. Except for cobalt, all of the sulfur and antimony in the sample were spread uniformly at \( x=0.2 \) and 0.4, as can be observed. It is clear from Figure 5. 4 (c, d) that all three elements Co, Sb, and S were uniformly distributed throughout this length scale as the cobalt concentration was raised to \( x=0.6 \) and 0.8.
EDX spectroscopy was used to measure the atomic percentages of antimony, cobalt, and sulfur in the Sb$_2$(1–x)Co$_2$xS$_3$ (0 ≤ x ≤ 1), as shown in Figure S 5.3 and Table 5.1. EDX spectra of Sb$_2$(1–x)Co$_2$xS$_3$ with x = 0.2-0.8 revealed the characteristic peaks of antimony, cobalt, and sulfur. The atomic percentages of antimony, cobalt, and sulfur at x = 0.2 were determined and all the compositions agreed well with the stoichiometric ratio calculated from the feed (Table 5.1). Increasing the molar fraction to x = 0.4 resulted in an excellent agreement with the stoichiometric ratio computed from the feed rate with a small sulfur loss. At x = 0.6 and 0.8, antimony and cobalt concentration was somewhat higher however the sulfur content was lower, suggesting that the prepared materials were low in sulfur. A linear relationship between the amount of cobalt in the precursor feed and the amount of cobalt in the Sb$_2$(1–x)Co$_2$xS$_3$ samples measured by the EDX analysis is shown in Figure 5.
Table 5. The content of Co, Sb, and S in Sb$_{2(1-x)}$Co$_{2x}$S$_3$ prepared by solventless method at 450°C ($x = 0.2, 0.4, 0.6$ and $0.8$ molar fraction of cobalt) calculated from the feed rate and found in EDX measurement.

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<td>16</td>
<td>24</td>
<td>60</td>
<td>Co$<em>{0.8}$Sb$</em>{1.2}$S$_3$</td>
</tr>
<tr>
<td>0.6</td>
<td>24</td>
<td>16</td>
<td>60</td>
<td>Co$<em>{1.2}$Sb$</em>{0.8}$S$_3$</td>
</tr>
<tr>
<td>0.8</td>
<td>32</td>
<td>8</td>
<td>60</td>
<td>Co$<em>{1.6}$Sb$</em>{0.4}$S$_3$</td>
</tr>
</tbody>
</table>

Figure 5. A linear relationship between the amount of cobalt in the precursors and the amount of cobalt in Sb$_{2(1-x)}$Co$_{2x}$S$_3$ systems, determined by energy-dispersive X-ray (EDX) measurements.

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5.4.4.4 Magnetic properties of Sb$_{(1-x)}$Co$_{2x}$S$_3$ powder

Sb$_{(1-x)}$Co$_{2x}$S$_3$ powder containing varying quantities of paramagnetic Co was studied under zero-field (ZF) and field-cooled (FC) settings. Figure 5.6 below shows the results of applied magnetic field of 100 Oe to the samples. It can be seen that there is a significant rise in magnetization for all studied samples below 10 K and the ZFC and FC has minor influence of magnetic irrepressibility. Interestingly magnetism in the samples is observed to increase with increase in Co concentration at extremely low temperature region. The rapid rise in magnetization is observed for Co$_2$S$_3$. The possible reason for this attribute is the anisotropic effect influenced by Co ions substitution in the samples which have undergone this ferromagnetic exchange. Rest of the studied particles Sb$_{(1-x)}$Co$_{2x}$S$_3$ (x = 0.2, 0.4, 0.6 and 0.8) have shown comparatively weak ferromagnetic behaviour.

![Graph showing magnetization vs temperature for Sb$_{(1-x)}$Co$_{2x}$S$_3$](image)

**Figure 5.6** Plots of magnetization vs temperature for Sb$_{(1-x)}$Co$_{2x}$S$_3$ (x = 0.2, 0.4, 0.6, 0.8 and 1) nanoparticles measured in ZFC and FC regimes.
Magnetic hysteresis measurements at 300 K (Fig. 5.7(a) and 2 K (Fig. 5.7(b) indicate that samples with a higher Co content had open hysteresis loops. Magnetization coercivity and saturation both increase considerably as the amount of cobalt in the sample increases, indicating a weak ferromagnetic ordering. Table 5.2 contains further information on the coercive field \( H_c \), remnant magnetization \( M_r \), and maximum magnetization values at 2 and 300 K deduced from the data in Figure 5.7.

**Figure 5.7**. Hysteresis loops at (a) 300 K, and (b) 2 K, for \( \text{Sb}_{2(1-x)}\text{Co}_{2x}\text{S}_3 \) \((0.2 \leq x \leq 1)\). The inset is a zoom of the region around the zero-field (more information in Table1).
Table 5. Coercive field, maximum magnetization at 7 T, and remnant magnetization values at 300 and 2 K, based on Fig. 7 for Sb$_{(1-x)}$Co$_x$S$_3$ (0.2 ≤ x ≤ 1).

<table>
<thead>
<tr>
<th>Sample</th>
<th>T(K)</th>
<th>$H_c$ (Oe) ± 0.5</th>
<th>$M_r$ (emu/g) ± 0.05</th>
<th>$M_{max}$ (emu/g) ± 0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb$_{(1-x)}$Co$_x$S$_3$ (x = 0.2)</td>
<td>300</td>
<td>1.45</td>
<td>0.00014</td>
<td>0.0052</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>9.50</td>
<td>0.00028</td>
<td>0.454</td>
</tr>
<tr>
<td>Sb$_{(1-x)}$Co$_x$S$_3$ (x = 0.4)</td>
<td>300</td>
<td>2.19</td>
<td>0.00017</td>
<td>0.033</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>24.2</td>
<td>0.00035</td>
<td>0.465</td>
</tr>
<tr>
<td>Sb$_{(1-x)}$Co$_x$S$_3$ (x = 0.6)</td>
<td>300</td>
<td>10.86</td>
<td>0.00041</td>
<td>0.154</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>26.2</td>
<td>0.00087</td>
<td>0.482</td>
</tr>
<tr>
<td>Sb$_{(1-x)}$Co$_x$S$_3$ (x = 0.8)</td>
<td>300</td>
<td>18.70</td>
<td>0.00045</td>
<td>0.174</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>28.1</td>
<td>0.0019</td>
<td>1.497</td>
</tr>
<tr>
<td>Sb$_{(1-x)}$Co$_x$S$_3$ (x = 1)</td>
<td>300</td>
<td>31.44</td>
<td>0.0031</td>
<td>0.642</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>123.2</td>
<td>0.0096</td>
<td>10.13</td>
</tr>
</tbody>
</table>

5.4.4.5 AACVD Synthesis of antimony cobalt sulfide Sb$_{(1-x)}$Co$_x$S$_3$ thin films

The concentration variation of Co and Sb diethyldithiocarbamate precursors is observed to harmonize the composition of deposited thin films Sb$_{(1-x)}$Co$_x$S$_3$. The CoSbS thin films were fabricated from the mixture of molar ratios of precursors (1) and (2) in tetrahydrofuran (THF) by using the AACVD technique at 450°C. The XRD analysis of thin films was used to investigate the crystalline structure of the deposited film see Fig.5.8 (a). Initially when x = 0, the XRD pattern of the film has shown orthorhombic phase of Sb$_2$S$_3$ matched excellently with the available experimental results of (ICDD: 01-071-2432). The obtained structural parameters...
of the film are $a = 11.2902 \pm 0.026$, $b = 3.6953 \pm 0.037$ Å, and $c = 11.1398 \pm 0.035 \pm 0.028$ Å; $\alpha = \beta = \gamma = 90^\circ$. By increasing Co concentrations to 0.2 and 0.4, the resulting structure is found to match with ternary orthorhombic costibite CoSbS phase which has matched excellently with standard ICDD pattern 00-022-1082 (see figure 5.8 (b)). On further increasing the Co concentration up to 0.6, the resulting structure formed is Paracostibite phase of orthorhombic CoSbS, which has shown consistency with (ICDD: 01-077-1542). The obtained lattice parameters of this phase are ($a = 5.9402 \pm 0.043$, $b = 5.7253 \pm 0.052$, and $c = 11.2898 \pm 0.042$ Å; $\alpha = \beta = \gamma = 90^\circ$). Lastly for Co concentration of 0.8, it is found that CoS peaks are dominant at angles 35.07, 46.87 and 54.4 degree. Thus, the resulting structure is pure hexagonal jaipurite CoS with lattice parameters of $a = 3.257 \pm 0.036$, $b = 3.257 \pm 0.036$, and $c = 5.1430 \pm 0.046$ Å.

**Figure 5.** 8 (a) XRD patterns of Sb$_{2(1-x)}$Co$_{2x}$S$_3$ ($0 \leq x \geq 1$) thin films produced by AACVD at 450 °C at different Co/Co+Sb molar ratio (a) $x = 0$ (b) $x = 0.2$ (c) $x = 0.4$ (d) $x = 0.6$, (e) $x = 0.8$ and (f) $x = 1$ with a standard pattern of Sb$_2$S$_3$ (bottom) and CoS (top) (b) P-XRD patterns of CoSbS thin films at (a) $x = 0.2$ and (b) $x = 0.4$ prepared by the AACVD method.
The surface morphology of antimony cobalt sulfide thin film deposited at different molar ratios of Co and Sb diethyldithiocarbamate precursors was investigated by SEM see Fig. 5. 9. At x = zero, SEM images shows the rod-like structures of pure Sb$_2$S$_3$ (Fig. 5.9 a). Previously, Murtaza et. al synthesized Sb$_2$S$_3$ by the AACVD methods with similar morphology using tris(thiobenzoato)antimony(III) 48. When x = 0.2, circular particles were observed as shown in Fig. 5.9b. Structural morphology further changed when x increases to 0.2 to 0.8 in to sheet like structure (Fig. 5.9c, 5.9d and 5.9e) and finally, CoS sulfide at x= 1 is formed which has shown spherical particles (Fig. 5.9f). The structure at x=1 has shown similar results reported by L.P. Mgabi et al. 48.

![SEM images of Sb$_{2(1-x)}$Co$_x$S$_3$ thin film synthesised by the AACVD method at 450 °C using different mole fractions of cobalt](image)

**Figure 5. 9** SEM images of Sb$_{2(1-x)}$Co$_x$S$_3$ thin film synthesised by the AACVD method at 450 °C using different mole fractions of cobalt (a) x= 0, (b) x = 0.2 inset CoSbS image at 1 micron (c) x = 0.4 (d) x = 0.6 (e) x= 0.8 and (f) x = 1.
EDX elemental mapping of $Sb_{2(1-x)}Co_{2x}S_3$ $(0 \leq x \geq 1)$ thin films are shown in Figure 5.10 and all the elements present in the samples are evenly dispersed, indicating the successful formation of thin films with uniform distribution of elements. The respective thin film of Sb Lα, Co Kα, and S Kα emissions spectra are in good agreement with the XRD results of pure ternary materials.

**Figure 5. 10** EDX elemental mapping of S Kα, Sb Lα and Co Kα for $Sb_{2(1-x)}Co_{2x}S_3$ thin film prepared by the AACVD method at 450 °C using different mole fractions of copper (a) $x=0.2$, and (b) $x=0.4$.

Antimony, cobalt, and sulfur were detected in the $Sb_{2(1-x)}Co_{2x}S_3$ $(0 \leq x \geq 1)$ at $x=0.2$ and 0.4 by EDX spectroscopy (Figure 4 SI and Table 3). At $x=0.2$, the elemental composition reported that the atomic percentages of Co, Sb, and S were (39.8:32.9:27.3), which was close to the expected stoichiometric proportions of $Sb_{2(1-x)}Co_{2x}S_3$ $(0 \leq x \geq 1)$. When $x$ was increased to 0.4, the EDX spectrum revealed a decrease in the elemental content of antimony and sulfur with a rise in the elemental content of cobalt in $Sb_{2(1-x)}Co_{2x}S_3$ $(0 \leq x \geq 1)$.
Table 5. Co, Sb, and S content in Sb$_{2(1-x)}$Co$_{2x}$S$_3$ (0 ≤ x ≥ 1) thin film prepared by AACVD method at 450°C (x = 0, 0.2 and 0.4 molar fraction of cobalt) calculated from the feed rate and found by EDX measurement.

<table>
<thead>
<tr>
<th>Mole Fraction (Co%)</th>
<th>Elemental Composition Expected (Atomic %)</th>
<th>Stoichiometry Required</th>
<th>Elemental Composition Found by EDX (atomic %)</th>
<th>Stoichiometry Found By EDX</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Co</td>
<td>Sb</td>
<td>S</td>
<td>Co</td>
</tr>
<tr>
<td>0.2</td>
<td>33.33</td>
<td>33.33</td>
<td>33.34</td>
<td>CoSbS</td>
</tr>
<tr>
<td>0.4</td>
<td>33.33</td>
<td>33.33</td>
<td>33.34</td>
<td>CoSbS</td>
</tr>
</tbody>
</table>

5.4.4.6 Optical properties of CoSbS

The optical properties of the materials are characterized by its UV-Vis absorption spectroscopy. It is among commonly used powerful tools to know the optically active regions of the material under visible spectrum. To find the optical band gap of pure ternary Sb$_{2(1-x)}$Co$_{2x}$S$_3$ (0 ≤ x ≥ 1) thin films, the samples were recorded for wavelength irradiated between 300–1000 nm. The bandgap energy of the Sb$_{2(1-x)}$Co$_{2x}$S$_3$ (0 ≤ x ≥ 1) when x= 0.2 and 0.4 was 1.75 and 1.76 eV respectively. The increase in the band gap with increase in concentration is evident from

$$(\alpha h\nu)^n = A(h\nu - E_g)$$
the literature. The small variation in the band gap is the result of small substitution of the Co content.

Figure 5. 11 The absorbance and the Tauc plot of (a) Sb$_{2(1-x)}$Co$_{2x}$S$_3$ (0 ≤ x ≥1) at x=0.2 and (b) Sb$_{2(1-x)}$Co$_{2x}$S$_3$ (0 ≤ x ≥1) at x=0.4 thin films prepared by AACVD method from the mixture of antimony and copper diethyldithiocarbamate at 450 °C with different mole fractions of Co.

5.4.5 Conclusion

In conclusion, we have studied in detail the structural, optical and magnetic properties of Sb$_{2(1-x)}$Co$_{2x}$S$_3$ nanoparticles and thin films produced via solventless thermolysis and AACVD utilizing single-source precursors. The TGA analysis revealed that the precursors decomposed into their respective metal sulfides within a similar temperature range. The phase diagram indicates initial samples as a mixture of two phases which includes orthorhombic Sb$_2$S$_3$ and hexagonal CoS at 450 °C, however the single orthorhombic phase of CoSbS is observed above this temperature. The EDX mapping revealed that Sb and Co co-localized with the phase-separated binary compounds. Which results in the formation of enhanced size, shape, structure, composition, magnetic, and optical properties of Sb$_{2(1-x)}$Co$_{2x}$S$_3$ nanoparticles and thin films. The UV-vis spectroscopy of the ternary CoSbS thin films revealed optical band gap falls in the range 1.75–1.76 eV, suitable for making devices operatable in IR region. The magnetic nature
of the material changes with the increase of cobalt in the materials. Thus, our results portray excellent applications of materials to be used in photovoltaic and magnetism.

5.4.6 References


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5.4.7 Supporting information

Contents:

**Figure S1:** P-XRD patterns of particulate Sb(S₂CN(Et)₂)₃

**Figure S2:** P-XRD patterns of particulate Co(S₂CN(Et)₂)₂

**Table S1:** Composition used for synthesis of Sb₂(1-x)Co₂xS₃ powder and thin film

**Figure S4:** The EDX spectra of Sb₂(1-x)Cu₂xS₃ samples prepared by solventless thermolysis

**Figure S5:** The EDX spectra of Sb₂(1-x)Co₂xS₃ thin films prepared by AACVD at 450 °C at various cobalt mole fraction (a) x = 0.2 and (b) x = 0.4.
Powder XRD diffraction patterns for solventless decomposition of Sb(S₂CNEt₂)₃ at various temperature

**Figure S 5.** Plot showing the p-XRD patterns of particulate Sb(S₂CN(Et)₂)₃ decomposition products, where the decomposition temperature was (a) 300 °C, (b) 400 °C, (c) 425 °C, (d) 450 °C and (e) 475 °C, decomposed by solvent-less thermolysis for 1h. All peaks corresponded to standard pattern of stibnite Sb₂S₃ (ICDD 01-073-0393)
Powder XRD diffraction patterns for solventless decomposition of Co(S₂CN(Et)₂)₂ at various temperature

Figure S 5. Plot showing the p-XRD patterns of particulate Co(S₂CN(Et)₂)₂ decomposition products, where the decomposition temperature was (a) 300 °C, (b) 350 °C (c) 400 °C and (d) 450 °C decomposed by solvent-less thermolysis for 1h. Peaks correspond to (ICDD:01-075-0605)
Table S 5. Composition used for the synthesis of Sb$_{2(1-x)}$Co$_{2x}$S$_3$ system by solventless and AACVD method

<table>
<thead>
<tr>
<th>Mole fraction [Co]/[Co]+[Sb]</th>
<th>Co[S$_2$CNEt$_2$]$_3$</th>
<th>Sb[S$_2$CNEt$_2$]$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0 mmol</td>
<td>0.56 mmol</td>
</tr>
<tr>
<td>0.2</td>
<td>0.56 mmol</td>
<td>2.2 mmol</td>
</tr>
<tr>
<td>0.4</td>
<td>0.56 mmol</td>
<td>0.84 mmol</td>
</tr>
<tr>
<td>0.6</td>
<td>0.56 mmol</td>
<td>0.37 mmol</td>
</tr>
<tr>
<td>0.8</td>
<td>0.56 mmol</td>
<td>0.14 mmol</td>
</tr>
<tr>
<td>1</td>
<td>0.56 mmol</td>
<td>0 mmol</td>
</tr>
</tbody>
</table>
**Figure S 5.** The EDX spectra of Sb$_{2(1-x)}$Co$_{2x}$S$_3$ samples prepared by solventless thermolysis at 450 °C at various cobalt mole fraction (a) x = 0.2, (b) x = 0.4, (c) x = 0.6 and (d) x = 0.8.
Figure S 5. 4 The EDX spectra of Sb$_{2(1-x)}$Co$_{2x}$S$_3$ thin films prepared by AACVD at 450 °C at various cobalt mole fraction (a) $x = 0.2$ and (b) $x = 0.4$. 
Chapter 6. Conclusion and future work:

Conclusion.

In this study it has been found that transition metal sulfide nanomaterials and corresponding thin films have attracted considerable attention because of special electrical, mechanical, optical and magnetic properties. All these aforementioned attributes are useful and essential ingredient for a wide range of applications such as solar cells, light emitting diodes, sensors and electronic devices. In this thesis, main work is on dithiocarbamate complexes of antimony (III), iron(III), copper(II) and cobalt (II) of the form \( M(S_2CNEt_2)n \) \( (M=Sb, Fe, Cu and Co) \), which were synthesised and characterised with respect to their structure, crystallography by elemental analysis. By performing, thermogravimetric analysis (TGA) the study of thermal properties of these complexes have been discussed. These metal complexes were used as molecular precursors for the formation of binary and ternary metal sulfide nanomaterials and respective thin films by the solvent less thermolysis and aerosol assisted chemical vapour depositions (AACVD) methods. All resulting nanoparticles and thin films of ternary \( Sb_2_{2-x}A_{2x}S_3 \) \( (A=Co, Cu and Fe; 0 \leq x \leq 1) \) are found to exhibit excellent tuned physical attributes, particularly useful in sensor applications near IR and mid IR regions. The crystallography, morphology, and magnetic characteristics of the compounds were extensively characterized by p-XRD, SEM-EDX, Raman UV, and SQUID magnetometry.

In the third chapter \( Sb_2_{2-x}Fe_{2x}S_3 \) \( (0 \leq x \leq 1) \) powders were synthesized by the solvent-less thermolysis of metal diethylidithiocarbamate single-source precursors at a different molar ratio of iron at 450°C. The TGA analysis of two complexes revealed that the precursors decomposed into their respective metal sulfides within a comparable temperature range. According to the phase diagram, the powder samples were synthesised as a combination of two phases containing orthorhombic \( Sb_2S_3 \) and hexagonal pyrrhotite. In optical properties, band gap is observed to increase with increasing Fe content and measured using UV-vis, The bandgap for the mixed samples \( Sb_2(1-x)Fe_{2x}S_3 \) were 3.39, 3.47, 3.57 and 3.66 eV for \( x = 0.2, 0.4, 0.6 \) and \( 0.8 \), respectively, values which lie between pure FeS and \( Sb_2S_3 \). In magnetic properties, temperature dependent (both zero-field cooled (ZFC) and field-cooled (FC) conditions) magnetisation
measurements were performed on Sb\(_{2(1-x)}\)Fe\(_{2x}\)S\(_3\) powders for Fe content x = 0.2, 0.4, 0.6, 0.8 and 1. The resulting structures confirms the ferromagnetic nature. The Raman spectroscopy confirms that the peaks shifted to higher intensity with increasing Fe content and thus indicates that doping is possible using metal dithiocarbamate precursors. EDX mapping revealed that Sb and Fe co-localized with the phase separated binary compounds. We conclude that although the molecular precursor technique may have some potential for developing new materials in this environment, but it must be recognised that the synthesis conditions would need to be optimised to yield pure phase of materials.

The fourth chapter, describes the formation of ternary Sb\(_{2-2x}\)Cu\(_{2x}\)S\(_3\) (0 ≤ x ≤ 1) solid solution in entire range with excellent stoichiometric control via solventless thermolysis using Sb (III) and Cu (II) diethylidithiocarbamate as molecular precursors. The structural investigation demonstrates that copper was successfully incorporated as a solid solution into the antimony sulfide. Thin films were also deposited on glass substrates using AACVD. A single-phase pure of both chalcostibite (CuSbS\(_2\)) and tetrahedrite (Cu\(_{12}\)Sb\(_4\)S\(_{13}\)) were obtained using the solvent less method. However, fematinite (Cu\(_3\)SbS\(_4\)) and tetrahedrite (Cu\(_{12}\)Sb\(_4\)S\(_{13}\)) thin films was deposited by the AACVD at 450 °C using the same concentration of the same precursors. The EDX results of nano particles produced indicates the higher concentration of Sb due to presence of Sb\(_2\)S\(_3\) impurity when x=0.2 concentration is enhanced. Same results are found for thin films formed. The Raman spectra for thin films developed, confirms the structural consistency of our XRD results. For concentrations x = 0.2, thin film deposited exhibited CuSbS\(_2\) phase while for x = 0.4, the peaks in the Raman spectrum appear at 253, 273, 317 and 343 cm\(^{-1}\), which correspond to tetragonal famatinite Cu\(_3\)SbS\(_4\), confirming the XRD characterisation. On further increasing the x content to 0.6 and 0.8, the Raman peak was shifted near 352 cm\(^{-1}\)and at 323 cm\(^{-1}\), respectively and forming pure cubic tetrahedrite Cu\(_{12}\)Sb\(_4\)S\(_{13}\)

The fifth chapter, describes the incorporation of cobalt into Sb\(_2\)S\(_3\) via reactive melt routes. Sb (III), and Co (II) complexes of diethylidithiocarbamate have been applied as molecular precursors for the synthesis of Sb\(_{2-2x}\)Co\(_{2x}\)S\(_3\) (0 ≤ x ≤ 1) solid materials. In addition to the solvent less synthesis, AACVD method was also used for the deposition of CoSbS thin films and the effect of the chemical composition on band gap of the thin films and magnetic properties of the
particles were investigated. The EDX mapping of the resulting structures revealed that Sb and Co co-localized with the phase-separated binary compounds. It is found that this co-localization has direct impact on enhancing size, shape, structural composition, magnetic ordering and optical attributes of Sb$_{2(1-x)}$Co$_{2x}$S$_3$ nanoparticles and thin films. In structural analysis, the obtained lattice parameters are consistent with available structures. While in optical properties, the band-gap is measured by UV-vis spectroscopy, which indicates the optical band gap of the thin films falls in the range 1.75~1.76 eV for x=0.2 and 0.4 respectively. The range is best suitable for making devices operable in IR region particularly solar cells. The magnetic properties indicate the nature of the material occurring magnetic fluctuation via doping, and found to increase linearly with concentration. On bases of our experimental results which have matched excellently with available literature. It is suggested that studied materials have shown potential ability to be used in novel magnetic and optical applications.

In general, diethyldithiocarbamate precursors have been shown to be effective in synthesizing pure crystalline phase of metal sulfide nanoparticles at relatively lower temperatures than reported in literature. Additionally, the chemicals used in synthesis were relatively non-toxic, abundantly available in nature, and inexpensive. By adjusting the reaction conditions, such as the concentration of the precursors, the temperature growth and the ratio of the doping, the direct cheap, with no toxicity or solvent thermolysis of the diethyldithiocarbamate precursors can yield nanoparticles and thin films having a different morphologies, particle size, optical and magnetic properties.

**Future work.**

Future work will concentrate on the synthesis of antimony sulfide, iron sulfide, copper sulfide and cobalt sulfide nanoparticles and thin films from dithiocarbamate precursor’s complexes using different methods such as colloidal routes to further investigate the importance of dithiocarbamate complexes as single source precursors. It will be useful to research the hot injection synthesis or the heating method of antimony sulfide, iron sulfide, copper sulfide and cobalt sulfide. This approach offers a number of benefits, including the solvent employed as a capping agent, which may aid in the formation of crystalline minerals.
Besides synthesis of single source precursors for antimony, iron, copper and cobalt telluride and selenide to compare the chemical, physical, optical and magnetic properties with those of their sulfide. These metal complexes may be combined in new ways to create novel phases and hence new characteristics when deposited in a ternary or quaternary system. Additionally, the work in Fe,Cu and Co alloys with the $\text{Sb}_2\text{S}_3$ nanoparticles and thin films can be characterised using more sophisticated techniques such as X-ray photoelectron spectroscopy (XPS). This can be used for understanding the host and guest elements interactions. Finally, Preparation of quaternary alloys of the composition Cu-Fe-Sb-S and Cu-Co-Sb-S and Co-Fe-Sb-S from diethylidithiocarbamate complex as single source precursors using solvent-less thermolysis and AACVD method to study the chemical, physical, optical and electrical properties for photovoltaic applications.