Synthesis of crystalline chalcogenide arsenates in surfactants via a low temperature route

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**SYNTHESIS OF CRYSTALLINE CHALCOGENIDE
ARSENATES IN SURFACTANTS VIA A LOW
TEMPERATURE ROUTE**

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ENGINEERING**

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“Ad astra per aspera.”

Jai Santhoshi Ma!

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ABSTRACT

The synthesis of novel materials drives forward the engine that is material science. The discovery of new materials is important not just from the standpoint of new applications, but is also important for the study of the fundamental forces that guide the reaction mechanism.

Ever since Flanigen et. al. first reported the synthesis of zeolite like open framework in 1982, this field has grown exponentially. Nearly 25 elements of the periodic table have open framework structures attributed to them. Metal – chalcogenides have been a very important part of this Solid State chemistry. They have a wide range of applications like ion conductivity, magnetism and non – linear optical response. The larger size of chalcogen atoms allows them to have larger coordination numbers, thus increasing the number of ways they can form open frameworks. This offers a very good opportunity to study the area of open frameworks from different reactions.

Solvent thermal synthesis has garnered much attention lately for its ability to produce diverse open framework topologies. By varying the reaction media and the structure directing agent, the desired properties expected of the final product can be finely tuned. Recently, using Ionic Liquids as reaction media, a number of new chalcogenide open frameworks have been reported. The high cost and limited commercial availability of Ionic Liquids has been a great obstacle to the exploitation of their properties as reaction media.

Surfactants have long been used to influence the structure of open frameworks. In this investigation, surfactants are used as reaction media, in place of Ionic Liquids. The advantages of this approach is the cheaper costs of the surfactants and their vast varieties available, like acidic, basic, neutral, ionic, etc. This offers great scope for many different interactions between the reagents and the surfactants to form novel open frameworks.

In this report, a series of chalcogenidoarsenates is used to demonstrate the excellent qualities of using Surfactants as reaction media. A homologous series of chalcogenidoarsenates is synthesised with dimensionalities varying from 0D clusters to 3D framework. The crystals exhibit semiconductor behaviour, with band gaps of 1.91eV to 2.46eV, which corresponds to the colour of the crystals. The crystals also exhibit magnetic properties, which are tested.

Thus, this method offers new possibilities in the field of open framework syntheses of crystalline materials with diverse range of structures and properties.

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CHAPTER 1 An Introduction

1.1 Background

Synthesis is the foundation on which the study of Chemistry is built. It is one of the frontier areas of research and a primary source of new substances to be studied. Different synthetic methodologies lead to materials with different properties. With today's requirement of materials with a complex collection of qualities to aid in their multi-functionality, the development of new synthetic techniques and processing of materials is an ever urgent need.

The approach to synthesis can be targeted or exploratory. Targeted synthesis deals with designing the final material with targeted properties and their optimisation. The study of solid state chemistry deals more with exploratory synthesis, which has resulted in the yield of many discoveries. Crystal growth is a particular area of synthesis which is very important; both for the discovery of new materials as well as the production of large crystals for property testing. However, synthesis which is assisted by a background in theory is still an emerging science, which nonetheless needs to be encouraged for better targeted synthesis.

A considerable progress has been made towards directed synthesis of materials in solid state chemistry. A few examples are simple isoelectronic elemental substitution, the intercalation of species into solids, the synthesis of coordinated structures etc^{1,2}. Concepts of compound formation can also be used to help tailor compounds to the desired properties, like the concept of phase homology. Diverse phases of a homologous series of compounds can be placed in a single context. Moreover, new phases can be predicted with a high degree of probability. This is because within a homologous series of compounds, the type of fundamental building units and the principles that define their combinations remain preserved.

1.2 Chalcogenides and Open Frameworks

High-tech applications demand great complexity and more importantly, multiple functionality and multiple materials. Here, there is scope for novel strategies for the development of new, complex products with multiple components and multi-functionality. Hierarchies of pore structures and multiple component assemblies are currently mostly found in natural materials which exhibit a high performance and serve multiple functionalities. Here, the material chemist has the opportunity to develop this field of synthetic chemistry to move closer to the complexity of structures and characteristics of materials found in nature.

Porous metal frameworks are crystalline solids which are assembled by connecting metal ions or clusters through coordination by molecular bridging^{3,4}. The integrity of the building blocks and properties are maintained so that a variable composition can be designed into the structure on a periodic scale⁵. The structures often contain solvent molecules within their framework, though it is possible in many cases to replace the solvent guests or remove them completely while not compromising their structure. In contrast to zeolites, metal frameworks are held together by weaker bonds which allows for solvent driven, controlled structural transformations during synthesis⁶.

Metal chalcogenides are an important aspect of solid state chemistry, not merely because of the range of their applications but also because of the role they have played in the development of new chemical synthetic concepts and methodologies. For instance, the report of metal intercalation into binary TiS highlighted the then novel approach of “soft chemistry”⁷. Through this low temperature method, compounds can be obtained whose structures are similar to that of the precursors.

This low temperature route has been used to synthesize inorganic metal-chalcogenide frameworks with organic molecules as templating agents. Notable is the synthesis of supertetrahedral cluster of metal chalcogenides, whose properties have been extensively studied for applications such as ionic conductivity⁸ and hydrogen production⁹.

1.3 High Temperature Solid State Synthesis

For a very long time, the only method available for the synthesis of new materials was the high temperature solid state route. Due to the low diffusion coefficient of solids, this route requires a high thermal activation. In this method, the reactants are measured out in a specific ratio, sealed in an evacuated container and heated to very high temperatures. The products are often multiphase and powdered. To produce sufficiently large crystals for single crystal diffraction studies, a lengthy annealing process is often required.

The high temperature method allows for thermodynamic control of the process, but is limited by the lack of more subtle control over the reaction and thus cannot be used to tailor the product properties. Despite being the oldest technique for synthesising solid state materials, it continues being an exploratory in nature and suffers from the inability of current principles of chemistry to fully understand the relation between composition, reaction and structure. This method remains empirical and success is still based on a serendipitous mixture of analogies, intuition and accumulated knowledge.

Synthesis from fluxes can be viewed as a slow cooling of a melt that can have a vastly different composition from the resulting phase of the crystal. This flux synthetic route is quite popular for crystal growth of oxides and chalcogenides. The flux is selected based on criteria such as solubility of reagents, low melting point and inertness. The ability to dissolve reagents allows for better reactivity and the low melting point means there is better kinetic control over the reaction. Flux is isolated from the final product in many ways such as chemical etching with various solutions or centrifuging at higher temperatures of the melt.

1.4 Low Temperature Solid State Synthesis

Low temperature methods for the synthesis of solid state compounds are becoming increasingly popular for mixed metal oxide and chalcogenide compounds. As the interface between solid state chemistry and nano technology widens, this method is gaining increased importance. They use an aqueous or non aqueous reaction media to facilitate nucleation and growth of crystals. The idea is that chemical methods like reduction or decomposition of molecular precursors creates a condition of supersaturation which can precipitate the metal particles with the organic ligands attached.

In contrast to high temperature solid state synthesis, these are low temperature solution reactions, which mean that solid-solid diffusion is not a limiting factor for the precipitation of crystals. Further, there is a more subtle level of control over the reaction; surface energy and the templating and surface directing agents which help to preserve the crystallinity of the product have a more profound effect here than in the traditional high temperature processes, where they may be neglected.

From the standpoint of a fundamental understanding of the chemistry, solution based low temperature synthesis offers a better perspective of how the properties of small molecular clusters translate into the bulk material. The progress towards this end has been slow because a structural correlation between the bulk and their molecular cluster derivatives is currently lacking. An approach that offers some clues is to oxidise these clusters and study the resulting elemental structures. The low temperature and better kinetic control over the reactions might result in metastable structures of the elements.

In conclusion, it has been demonstrated that materials obtained previously solely by high temperature routes can now be obtained by low temperature chemical methods. This method has already been proved in its ability to produce binary, ternary and quaternary compounds. Low temperature synthesis also allows for a greater degree of control over the reaction kinetics and hence a greater degree of accuracy in the targeted synthesis of a product.

1.5 Objective and Scope

This report presents the findings of an ongoing investigation into the use of Surfactants as reaction media for growing open framework chalcogenide. A family of Chalcogenidoarsenates is primarily considered in this investigation due to their varied structures and interesting properties like magnetism, conductivity and non – linear optical response.

The objective of this report is the synthesis and characterisation of 0D, 1D, 2D and 3D chalcogenidoarsenates, using the following surfactants as reaction media. – Polyethylene Glycol 400 (PEG 400), Polyvinyl Pyrrolidone (PVP) and 1–Hexadecyl–3–Methylimidazolium Chloride ([HMIM]Cl) (Fig. 1.1). The crystals obtained from the reactions are viewed and characterised to ascertain their properties.

(c)

Figure 1.1 : The Surfactants used in this investigation. (a) Polyethylene Glycol 400 (PEG 400), (b) Polyvinyl Pyrrolidone (PVP) and (c) 1-Hexadecyl-3-Methylimidazolium Chloride ([HMIM]Cl).

The report is structured as follows,

Chapter 1 provides a brief overview of the subject of this investigation. It outlines in brief the Objective and Scope of the report, as well as the Novelty and Motivation behind this work.

Chapter 2 provides a detailed review of various Literatures related to the subject of this investigation.

Chapter 3 lists the Experimental Methodology followed in this investigation to synthesise and characterise the crystals.

Chapter 4 outlines the principle behind the Experimental Methodology and discusses, briefly, the objective of the experiments conducted.

Chapter 5 provides the Data obtained during the investigation and offers a detailed Reasoning of the results.

Chapter 6 concludes the content of this investigation, while proffering a future course that this investigation might take.

1.6 Novelty and Motivation

New strategies for synthesizing open framework compounds are very important, both for applied technology and for the fundamental study of reaction chemistry. Since the advent of the low temperature solvent chemical method of synthesis, many new discoveries have been made – new materials have been synthesised and new phases of existing materials have been discovered too.

The choice of reaction media for solvent thermal reaction is very important. The reaction media ensures good solubility, reactivity and also exhibits structure directing properties, while remaining inert in the reaction. Of recent interest has been the use of Ionic Liquids as reaction media. They show very good solubility, and with a low melting point, they make a very good media for reaction. Also, the wide variety of Ionic Liquids make for an interesting study of the relationships between their use and the final product formed.

Surfactants have long been used to tailor the surface characteristics of nanocrystals. They have even been shown to control the size of the pores of mesoporous materials. They exhibit good solubility and have low melting points.

Ionic Liquids are prohibitively priced and are limited in availability, commercially. This is a huge obstacle for scaling up of syntheses.

In this investigation, the novel use of surfactants in place of ionic liquids or other solvents will be reported. Surfactants are available commercially in wide varieties as well as at a lower cost. This opens up new opportunities to study the reaction mechanisms and attempt to understand the relationships between the use of a specific type of surfactant and the properties of the resulting product formed.

CHAPTER 2 A Review of Literature Reports

2.1 Open Framework Materials

In 1982, Flanigen et. al. first reported the formation of a zeolite like aluminophosphate open framework compound¹⁰. Since then, the field of open framework materials has grown at a staggering pace, with open frameworks being reported for over 25 elements in the periodic table¹¹. Along with the aluminophosphates, soon other elements like gallium¹², vanadium¹³, tin¹⁴, indium¹⁵ etc. have been made into open frameworks. More recently these open framework materials have expanded to include nitrides¹⁶, phosphites¹⁷, oxofluorides¹⁸, sulphates¹⁹, sulphides²⁰, selenides²¹, arsenates²², halides²³ etc.

Post 1990, organic molecules were also introduced into the open frameworks to form hybrid structures. These contained organic ligands – normally oxygen or nitrogen donors – along with inorganic elements to form porous frameworks. Based on the dimensionality of the obtained frameworks, they are classified as, (i) Organic – Inorganic hybrid materials (1D and 2D), (ii) Coordination Polymers (0D) and (iii) Pure Organic Materials²⁴.

The idea of organic – inorganic hybrid materials was pioneered by Johnson and Jacobson and co – workers²⁵. These materials have organic ligands connecting layers of inorganic chains. In this class of materials, porous hybrid phosphates were formed using diphosphonates and dicarboxylates^{26,27}. Also, there have been reports of a family of oxalate – phosphates²⁸ and MOXI – n family (Molybdenum oxides, nitrogen donor ligands and various transition metal ions)²⁹.

0D Coordination Polymers have isolated metal clusters connected by mostly metal – ligand bonding to organic ligands³⁰. Yaghi and co – workers synthesised a family of zinc clusters linked by dicarboxylate ligands³¹. They reported that by changing the length and nature of the ligands used, pore sizes could be varied. This paved the way for the synthesis of porous 0D frameworks, by using design methodologies that have been developed by many other researches now. This synthesis methodology has the

advantage of having low costs, coupled with the potential to design various organic ligands and the versatility of the chemistry of metal ions. These materials have also found uses in methane and hydrogen storage³².

Figure 2.1 : Different dimensionalities in open-framework materials. (A) 3D inorganic framework. (B) 2D hybrid framework formed by inorganic layers pillared by organic ligands. (C) 1D hybrid framework with layers of inorganic chains linked to organic ligands. (D) 0D Coordination polymer, created by clusters of metal ions, connected to organic ligands. (E) Purely organic framework formed by organic molecules interlinked through non-covalent bonds such as hydrogen-bonds or $\pi - \pi$ interactions²⁴.

Organic frameworks are essentially organic ligands connected to each other through hydrogen bonding or $\pi - \pi$ interactions. Depending on the kind of interaction several open frameworks have been synthesised^{33,34}. The materials exhibit a channel like structure that is often unstable in the absence of solvent molecules in the structure. This is due to the inherent weak nature of supramolecular interactions. Some materials have been reported with strong, stable organic frameworks by Ibragimov et. al.³⁵ and Wuest and co – workers³⁶.

Open framework materials have shown a lot of scope in terms of potential uses. This is a direct consequence of the large variety of elements that can be used to constitute the framework. Several of their potential uses include sensing and separation of gases³⁷, catalysis³⁸, and physical properties such as ion conduction^{39,40}, electrical conductivity⁴¹, magnetic properties^{42,43} and optical properties⁴⁴, which enable these materials to be used as multifunctional materials.

2.2 Open Framework Chalcogenides

There has been a steady research on the improvement and synthesis of new crystalline materials due to their technological applications^{45,46}. Initially, this was sought by attempting to replace the Al^{3+} or the Si^{4+} cations of zeolites with species like Ga^{3+} , P^{5+} etc. this resulted in a large number of oxide materials, which are based off of phosphates and silicates. Since the early 1990s, researchers have attempted to replace the anionic species of the framework (O^{2-}) with other species like organic ligands⁴⁷ (such as amines, nitriles etc.) or with chalcogens like S^{2-} , Se^{2-} and Te^{2-} ^{48,49,50}.

Zeolites were mainly thought to have been constructed from small rings or small cages that are the secondary building units (SBUs). Open framework chalcogenides, however exhibit higher hierarchies in their structures. Feng et. al. have described a series of tetrahedral topologies designated T_n ⁵¹ (Table 2.1). These are similar to the ZnS cubic lattice. The number of anions in any T_n cluster is the number of cations in the subsequent cluster (T_{n+1}). Here n denoted the number of metal layers (Fig. 2.2)

n	Stoichiometry of T_n	Examples
1	MX_4	MS_4^{6-} (M – Mn, Fe, Cd)
2	M_4X_{10}	$Ge_4E_{10}^{4-}$ (E – S, Se), $M_4S_{10}^{8-}$ (M – In, Ga)
3	$M_{10}X_{20}$	$M_{10}S_{20}^{10-}$ (M – In, Ga)
4	$M_{20}X_{35}$	$M_4In_{16}S_{35}^{14-}$ (M – Mn, Fe, Co, Zn, Cd)
5	$M_{35}X_{56}$	$[Cu_5In_{30}S_{56}]^{17-}$, $[Zn_{13}In_{22}S_{56}]^{20-}$
6	$M_{56}X_{84}$	None
>7	M_xX_y $x = [n(n+1)(n+2)]/6$; $y = [n(n+1)(n+2)(n+3)]/6$	None

Table 2.1 : List of tetrahedral clusters⁵².

Figure 2.2 : Diagrams of T2, T3, T4 and T5 tetrahedral clusters. Anions and cations are denoted in red and yellow respectively. Metal ions are shown in blue⁵¹.

An important advantage of using chalcogenide atoms is their largeness, when compared to oxygen atoms. Sulphur, for example can exhibit a coordination number of 4 even for large atoms such as Cadmium and Indium. Oxygen, on the other hand can very rarely form tetrahedral coordination, owing to their smaller sizes⁵². Open framework chalcogenides are special, that both cations and anions are able to form tetrahedral coordination. Zeolites are usually described as a net of atoms; chalcogenide openframeworks can be described as a net of clusters with variations shown even within individual clusters⁵³. Thus, chalcogenide open frameworks can be tuned at two different scales, thereby providing more control over their characteristics.

2.3 Synthesis Methodology

The preparation of open framework Chalcogenide materials can follow one of several synthetic methodologies.

2.3.1 Hydrothermal Route

This route utilises water as a solvent, at autogenous pressures, mildly alkaline conditions and temperatures ranging from 100°C to 250°C. It was pioneered by R M Barrer^{54,55,56} and R M Milton⁵⁷ in the synthesis of zeolite like aluminophosphate microporous materials using reactive gels.. To direct the structure of the crystals, an amine or an ammonium salt is added to the mixture. The duration of the reaction may range from a few hours to a few weeks, depending on the reactants, the reaction temperature and the expected morphological considerations. This route for synthesis was later explored to synthesise other materials like gallophosphates, iron phosphates, cobalt phosphates, nickel phosphates, manganese phosphates and others⁵⁸. Some of the pioneering works by other researches in this field of synthesising zeolite like compounds and open framework materials is as shown (Table. 2.2).

Flannigen and Breck first presented a hypothesis for mechanism for the nucleation and growth of crystals via the hydrothermal route^{59,60}. This fitted the S – shaped curves obtained during growth studies against time. They hypothesised that the slower induction period followed by a sudden spurt of growth could be attributed to a successive ordering of the gel as the process of crystallisation proceeds, meaning that the growth of crystals takes place mostly in the solid phase⁶¹. Breck later provided a schematic explanation of the process (Fig. 2.3). He expected the gel structure to be depolymerised by the hydroxide ions which then re-arrange due to the presence of the hydrated cations present. The tetrahedral regroup to form the basic polyhedral units. These link together to form a zeolite structure⁶².

author(s)	year	title
Barrer	1966	Mineral synthesis by the hydrothermal technique
Barrer	1968	Synthesis of molecular sieve zeolites
Zhdanov	1971	Some problems of zeolite crystallization
Flanigen	1973	A review and new perspectives in zeolite crystallization
Breck	1974	The synthetic zeolites (Chapter 4 of book)
Robson	1978	Synthesising zeolites
Rollmann	1979	Templates in zeolite crystallization
Sand	1980	Zeolite synthesis and crystallization
Barrer	1981	Zeolites and their synthesis
Barrer	1982	Hydrothermal chemistry of zeolites (book)
Barrer	1983	Zeolite synthesis: some chemical aspects
Lok, Cannan, & Messina	1983	The role of organic molecules in molecular sieve synthesis
Lechert	1984	New routes in zeolite synthesis
Rollmann	1984	Synthesis of zeolites, an overview
Barrer	1985	Synthesis of zeolites
Thompson & Dyer	1985	Mathematical analyses of zeolite crystallization
Moretti, Contessa, & Padovan	1985	Zeolite synthesis in the presence of organic components
Bajpai	1986	Synthesis of mordenite type zeolite
Guth & Caullet	1986	Zeolite synthesis – status and future prospects
Jacobs & Martens	1987	Synthesis of high-silica aluminosilicate zeolites (book)
Lowe	1988	Synthesis mechanisms for zeolites and molecular sieves
Barrer	1988	Zeolite synthesis: an overview
Occelli & Robson (Eds)	1989	Zeolite synthesis (symposium proceedings)
Barrer	1989	Zeolites: their nucleation and growth
Keijsper & Post	1989	Precursors in zeolite synthesis – a critical review
Guth et al.	1989	Zeolite synthesis in the presence of fluoride ions
Bell	1989	Applications of NMR spectroscopy to the study of zeolite synthesis
McCormick & Bell	1989	The solution chemistry of zeolite precursors
Kessler	1989	Recent advances in zeolite synthesis
Di Renzo et al.	1989	Are the general laws of crystal growth applicable to zeolite synthesis?
Szostak	1989	Hydrothermal zeolite synthesis (Ch. 2 of book), Process of zeolite formation on a molecular level (Ch. 3)
Knight	1990	Are zeolite secondary building units really red herrings?
Guth et al.	1990	New mobilizing and templating agents in the synthesis of crystalline microporous solids
Zhdanov, Khvoshchev, & Feoktistova	1990 (1981)	Synthetic zeolites: crystallization (book)

Table 2.2 : Works by other researches in this field of synthesising open framework materials⁵⁸.

Figure 2.3 : Mechanism for the nucleation and growth of crystals via the hydrothermal route, hypothesised by Flannigen and Breck⁶¹.

2.3.2 Ionothermal Route

Since the precursors of zeolites are ionic, solvents tend to have the best performance when they are polar⁶³. Ionic liquids are solvents with a very high degree of polarity and a pre – organised solvent structure⁶⁴. Ionic liquids are defined as liquids that only contain ions, and which are liquids at temperatures under 100°C⁶⁵. A note of interest is their properties of high thermal stability, negligible vapour pressure and very high solvating abilities.

Walden synthesised the first ionic liquid with a melting point of 12°C in 1914⁶⁶. Since then several ionic liquids were synthesised, but couldn't be exploited for their solvating properties because of their sensitivity to air and moisture. However in 1992, Wilkes and Zaworotko reported the synthesis of water stable ionic liquids⁶⁷, which has provided renewed vigour to ionic liquid chemistry. Ionic liquids can have a wide variety of organic cations and inorganic or organic anions. Since there are so many of these, the potential combinations for ionic liquids are vast⁶⁸. However, in practice, only a few typical Ionic Liquids are usually used^{69,70}, particularly the ones containing imidazolium cations (Fig. 2.4).

Cooper et. al.⁷¹ first reported the synthesis of a zeolite using Ionic Liquids as both solvent and structure directing agent, in 2004⁷². This methodology was dubbed Ionothermal Synthesis. Since then, several openframework materials such as aluminosilicate zeolites, metal phosphates and organic – inorganic hybrid materials have been synthesised using Ionothermal synthesis. Binary metal – chalcogenides like Bi₂S₃, Sb₂S₃, ZnS and CdS have been reported by several groups like Jiang and Zhu⁷³ and Rao and co – workers⁷⁴. Recently Kanatzidis et. al. synthesised ternary chalcogenide crystal [Sb₇S₈Br₂](AlCl₄)₃ using ionic liquids⁷⁵.

Figure 2.4 : Some commonly used cations and anions in the synthesis of Ionic Liquids⁷⁰.

Ionic Liquids have many advantageous properties as solvents. Their most important character is their strong polarity. This makes them very suitable solvents for the inorganic reactants. And, since many of them are based on alkylimidazolium or pyridine cations, which are known templates, the ionic liquid can also act as a template⁷⁶. This means that the competition between template – framework and solvent – framework interactions is removed. This is the most significant difference

between Ionothermal and Hydrothermal / Solvent Thermal synthetic methodologies⁷⁷ (Fig. 2.5). However, this is not always the case, as a small fraction of Ionic Liquid cations may decompose to form smaller template agents and these may preferentially act as structure directing agents⁷⁸.

Figure 2.5 : Schematic representation of processes in **(a)** Hydrothermal / Solvent Thermal Reaction and **(b)** Ionothermal Reaction. In **(a)**, solvent – framework interactions dominate while in **(b)**, template – framework interactions dominate⁷⁶.

2.3.3 Solvent Thermal Route

Similar to the hydrothermal method, this route, instead, uses non – aqueous solvents to synthesise materials. Certain advantages of using non – aqueous solvents are the ability to synthesise anhydrous materials and also using milder temperature conditions, since many of the solvents used are organic and have lower reaction temperatures.. This is because the properties of the solvents like viscosity, solubility and diffusivity vary vastly at elevated temperatures, thus exhibiting different characteristics. This

enhances the reactivity of the reactants and enables a lower temperature reaction when compared to other solvents.

When forming zeolites the tendency of the solvents to form hydrogen bonds must also be taken into account. The purpose of a solvent is to efficiently transport reactants and not to react strongly with them. If these solvents form hydrogen bonds that are very strong, then the templating agent will fail to interact with the reactants and this will prevent the nucleation of the framework species. Therefore, solvents like glycol, glycerol, propanol and hexanol are preferred which tend to form hydrogen bonds of intermediate strength.

Numerous materials have been processed by researchers like Kanatzidis et. al. who used a mixture of methanol and water as a solvent.

CHAPTER 3 Experimental Methodology

3.1 Synthesis

3.1.1 [MnAs₃S₆][NH₄]

Crystals of [MnAs₃S₆][NH₄] (**Compound 1**) were synthesised by a solvent thermal route. Molar quantities of Manganese [Mn], Arsenic Sulphide [As₂S₃] and Sulphur [S] were mixed with Hydrazine Monohydrate [N₂H₄.H₂O] in the ratio 1:1:2.5:8. These were then mixed with 1g of the surfactant [HMIM]Cl (1-Hexadecyl 3-Methylimidazolium Chloride). The mixture was sealed in a 23ml Autoclave lined with teflon, and kept in an oven at 140°C, for 5 days. Red, block crystals of **compound 1** were obtained, which were then washed with Ethanol and Water. The crystals were stored in Ethanol to prevent decomposition.

3.1.2 [NH₄]₈[Mn₂As₄S₁₆]

Crystals of [NH₄]₈[Mn₂As₄S₁₆] (**Compound 2**) were also synthesised via a solvent thermal route. The same starting materials were used, but with 1g of Poly Vinyl Pyrrolidone (PVP) instead of [HMIM]Cl. After 5 days at 160°C, yellow block crystals of **compound 2** were obtained. These crystals were cleaned using Ethanol and Water and then stored in Ethanol to prevent decomposition.

3.1.3 [Mn(NH₃)₆][Mn₂As₂S₈(N₂H₄)₂]

Crystals of [Mn(NH₃)₆][Mn₂As₂S₈(N₂H₄)₂] (**Compound 3**) were also synthesised via a similar solvent thermal route. The same starting materials as for **compound 1** were used, but with 1g of Poly Ethylene Glycol – 400 (PEG – 400) instead of [HMIM]Cl. After 5 days at 110°C, light yellow crystals of **compound 3** were obtained. These

crystals were cleaned using Ethanol and Water and then stored in Ethanol to prevent decomposition.

3.1.4 [enH][Cu₃As₂S₅]

Crystals of [enH][Cu₃As₂S₅] (**Compound 4**) were synthesised by a solvent thermal route. Molar quantities of Arsenic Sulphide [As₂S₃], Copper Iodide [CuI] and Sulphur [S] were mixed with Ethylenediamine [NH₂-CH₂-CH₂-NH₂] in the ratio 0.5:1:2.5:8. These were then mixed with 1g of the surfactant Poly Ethylene Glycol – 400 (PEG – 400). The mixture was sealed in and kept in an oven at 160°C, for 5 days. Dark red, flake like crystals of **compound 4** were obtained, which were then washed with Ethanol and Water. The crystals were stored in Ethanol to prevent decomposition.

The chemicals used for the syntheses are analytical reagents and were obtained commercially, without further purification.

3.2 Characterisation

The crystals of [MnAs₃S₆][NH₄] were subjected to various characterisation techniques,

3.2.1 Visual Inspection and Elemental Analysis :

This was performed using an EDX equipped JEOL/JSM-6360A SEM. A good quality crystal was picked, under a microscope, cleaned and placed on a carbon tape. This was then placed on the sample holder of the SEM for visual as well as elemental analysis.

3.2.2 Single Crystal X-Ray :

The single crystal X-Ray diffraction study was carried out in a Bruker APEX II CCD diffractometer with a graphite monochromatised Mo-K α radiation. The structure was solved and refined using least squares cycle in SHELX. The non – hydrogen parameters were refined by anisotropic parameters. A good quality crystal was picked and cleaned and placed on the sample holder of the Bruker machine.

3.2.3 Powder X-Ray diffraction :

Powder X-Ray diffraction studies were carried out on powdered samples in a Bruker D8 Advance diffractometer with graphite monochromatised Cu-K α radiation. Good quality crystals were picked and powdered. About 10mg of the powdered sample was placed on the sample holder.

The experimental diffraction patterns were compared with a simulated pattern, obtained from the Single Crystal Diffraction data, using the DIAMOND Crystal and Molecular Structure Visualisation software.

3.2.4 Ultra Violet Spectroscopy :

Solid state UV – vis reflectance spectroscopy was done on powdered samples using a Model UV-2501 PC. The measurements were taken at room temperature, with a BaSO₄ plate used as standard (100% reflectance). The powdered sample was placed on a BaSO₄ plate for analysis.

3.2.5 Thermo – gravimetric Analysis :

TGA study was done on the powdered samples, using a TGA Q500 machine, under flowing nitrogen. 5mg of the powdered sample was placed on the pan and a gradual heating rate of 5°C per minute was used.

3.2.6 Magnetic Susceptibility Study :

Magnetic studies were performed on the powdered sample of **compound 1**. About 15mg of the powdered sample was subjected to magnetic susceptibility studies, using a MPMS Magnetometer in the temperature range of 5K to 300K.

CHAPTER 4 Theory of Experiment

4.1 X – Ray Spectroscopy

X Ray spectroscopy is a powerful method to determine the structure of solids as well as to glean other information about the phase of the solid specimen.

4.1.1 Principle

X – Ray studies work on the principle of Diffraction of X – Rays by the crystal specimen. X – Ray diffraction behaves like the reflections from planes of atoms. However, only at particular orientations of the crystal with respect to the source, are X – Rays reflected. That is because at those orientations, the condition for constructive interference of the X – Rays is satisfied. This condition occurs when Bragg Law is satisfied. Bragg Law for constructive interference of the diffracted X – Rays is given by the Bragg equation,

$$\lambda = 2d \sin \theta$$

where, λ is the wavelength of the incident X – Rays, d is the interplanar spacing and θ is the incident angle of the X – Rays.

Figure 4.1 : Bragg reflection of X – Ray of wavelength λ at incident angle θ , from a set of crystal planes with interplanar spacing d (Courtesy : <http://wgharris.ifas.ufl.edu>)

4.1.2 Working

X – Ray reflections take place when the λ , θ and d values satisfy the Bragg equation. Normally, X – Rays of known wavelengths are used and the angles at which reflections occur is determined experimentally. The d values are then computed using the Bragg equation. With this information, one can go about estimating the unit cell dimensions and the distribution of the atoms within the unit cell.

X – Ray diffraction studies are carried out in different ways, each with its specific objective,

- Single Crystal X – Ray Diffraction
- Powder X – Ray Diffraction

4.1.3 Single Crystal X - Ray Diffraction

Single-crystal X-ray Diffraction is a non-destructive analytical technique which provides detailed information about the lattice of crystalline substances, including the dimensions of their unit cells, bond-lengths, bond-angles and site-order. The data generated from the X-ray analysis is interpreted and refined to obtain the sample's crystal structure.

In the case of single crystal X-ray diffraction, the X-rays are incident on the object, which is a crystal and the diffraction pattern is formed in the form of dots, recorded by a detector. Based on the spatial arrangements collected, the electron densities are calculated resulting in a structure. The structure is then solved with molecular models to obtain the final single crystal structure.

The single crystal x-ray crystallography configuration consists of a set up similar to the traditional Laue set up, except that, it has 3-4 goniometers at various angles, which define the relationship of the crystal with the detector. This method of crystallography is a non-destructive technique and is of great use in determining mineral chemistry.

Figure 4.2 : A schematic of the Single crystal X-ray crystallography. (Courtesy:

<http://www.rigaku.com/>)

As in my case, the crystal was subjected to this method in order to know the precise crystal structure of the material. This is one of the most effective ways to understand the fundamental structure and its correlation with the crystals physical properties.

4.1.4 Powder X – Ray Diffraction

This method utilises the sample, in the form of a fine powder, to obtain data regarding the cell structure and phase information of the material. The finely ground powder contains a large number of very small crystallites at random orientations. This sample is placed in the path of a monochromatic beam of X – Rays. Reflections occur from the planes of those crystallites that satisfy the Bragg equation.

Since the crystallites are distributed randomly and can lie in all directions while still satisfying the Bragg equation, the reflections lie on the surface of cones whose semi apex angle is equal to the deflection angle 2θ .

Figure 4.3 : Cones produced by the Powder X – Ray diffraction (Courtesy : <http://pd.chem.ucl.ac.uk>).

The experiential setup used for Powder X – Ray Diffraction studies consists of a Debye – Scherrer camera, whose length is very small compared to its diameter. The powdered sample is mounted in the centre of the camera and is placed in the path of a

collimated, monochromatic beam of X – Rays. The sample is rotated to bring all possible planes into a diffracting condition and the cones are recorded using the camera.

Figure 4.4 : Experimental Debye – Scherrer setup for Powder X – Ray Diffraction (Courtesy : <http://www.advancedlab.org>).

Now, the collection of powder diffraction data is done by using automatic diffractometers. These use a CCD to record the angle and the intensity of the reflected beams which are then plotted as intensity against 2θ .

Figure 4.5 : Schematic of an automated Powder X – Ray diffractometer (Courtesy : <http://chemwiki.ucdavis.edu>).

Powder X – Ray Diffraction can be used to study the following,

- It can be used to detect the presence of a known compound or phase in a given sample.
- It can be used to gauge the size of the crystallite. As the size of the crystallite decreases, the width of the diffraction peak increases.

4.2 Thermogravimetric Analysis

Thermogravimetric Analysis is a thermal method of characterisation of a specimen, by measuring the weight change in a sample as a function of temperature. This data is used to determine the thermal stability of the material and also predict their composition. Information about the behaviour of the material can be gleaned as the specimen undergoes weight gain due to oxidation or a weight loss due to dehydration

or decomposition. The TGA also yields information about the moisture and volatile content in the material, thermal stability and the decomposition kinetics.

4.2.1 Principle

Thermogravimetric Analysis works on the principle of a balance. The balance consists, on one side, a pan containing the sample specimen and on the other side, additional weights to offset the mass of the apparatus. The pan is suspended in a furnace. The balance is brought to the zero position. The specimen is then heated at a predetermined rate. When the balance is shifted due to the changes in the sample, the balance is returned to the zero position by the application of current to the metering system. The amount of current applied is proportional to the weight loss or the weight gain of the sample.

4.2.2 Preparation of the Sample

The preparation of the sample for a TGA is an important step as it affects the resolution of weight change recorded by the instrument. This is due to the following reasons,

- There can be a differential heat transfer that causes a temperature difference between the surface of the specimen and its bulk.
- Due to the temperature difference, thermal reactions can more often occur on surface of the specimen than its bulk.

To minimise these effects, it is advisable to increase the surface area of the sample to the maximum possible. Powders, therefore are ideally suited to TGA.

4.2.3 Factors which affect TGA Data

The quality of the data obtained through TGA is affected by many factors, some of which are outlined as follows,

4.2.3.1 Mass of the Sample

- The thermal reaction occurring in the sample may cause the temperature of the sample to deviate from a linear function. Larger the mass of the sample, the longer is the heat transfer through the bulk of the sample and therefore greater the deviation from a linear temperature change.
- The thermal decomposition of the sample may cause the emission of gaseous product. The mass of the sample will govern the rate at which this gaseous product will diffuse through the void space around the degraded sample. With a larger sample mass, the gas will take longer to emanate from the sample and therefore the observed decomposition temperature will appear to be higher than the actual.
- In a sample with a low thermal conductivity, higher mass will cause larger temperature gradients between the surface of the sample and its bulk. This will result in differential decomposition of the sample, resulting in an increase in the observed decomposition temperature of the sample.

4.2.3.2 Rate of Heating

The rate of heating plays an important role in recording data for TGA. Heating rates determine the observation time for the recording of data. Shorter the observation time,

less movable are the molecules in the specimen. Therefore a higher heating rate allows the sample to stay at a temperature for a shorter time. This improves the accuracy of the reading at any given temperature.

The flip side of this is that thermal decomposition depends not only on the temperature but also on time. The shorter the sample is allowed to stay at a particular temperature, the less complete will the reaction at that temperature be. Due to this, the observed decomposition of the sample may be higher than it actually is. Therefore, depending on the rate of heating a sample may seem more stable or less stable than it really is. It is therefore important to state the rate of heating during the TGA while reporting the data.

4.2.3.3 Atmosphere of the Furnace

The TGA instrument may be operated under air or an inert atmosphere like Nitrogen or Argon gas. The use of any particular environment plays a significant role in the data observed. An oxygen rich atmosphere may accelerate the thermal degradation of the sample, while this is not so in an inert atmosphere like Nitrogen or Argon. This will cause the observed temperature of decomposition to vary depending on the type of furnace atmosphere used.

4.2.4 Applications of TGA

- The thermal stability of a material is a measure of the resistance offered by the material to permanent change due to heat. TGA can measure the onset of degradation by recording the change in weight of the sample. Using this, the temperature corresponding to the change in weight is the temperature of onset of decomposition of the material.

- Using TGA, the composition of a mixture of materials can be identified. If a sample is a mixture containing materials of different thermal stabilities, TGA can estimate the percentage composition of each material in the mixture by measuring the individual onsets of degradation of the components.

CHAPTER 5 A Discussion on the Results

5.1 Elemental Analysis

The elemental analyses of $[\text{MnAs}_3\text{S}_6][\text{NH}_4]$ (**Compound 1**), $[\text{NH}_4]_8[\text{Mn}_2\text{As}_4\text{S}_{16}]$ (**Compound 2**), $\text{Mn}(\text{NH}_3)_6[\text{Mn}_2\text{As}_2\text{S}_8(\text{N}_2\text{H}_4)_2]$ (**Compound 3**) and $[\text{enH}][\text{Cu}_3\text{As}_2\text{S}_5]$ (**Compound 4**) are as shown (Fig. 5.1, Fig. 5.2, Fig. 5.3 and Fig. 5.4).

Figure 5.1 : EDX spectrum of $[\text{MnAs}_3\text{S}_6][\text{NH}_4]$ (**Compound 1**). K α lines indicate the presence of the target elements.

Figure 5.2 : EDX spectrum of $[\text{NH}_4]_8[\text{Mn}_2\text{As}_4\text{S}_{16}]$ (**Compound 2**). K α lines indicate the presence of the target elements.

Figure 5.3 : EDX spectrum of $\text{Mn}(\text{NH}_3)_6][\text{Mn}_2\text{As}_2\text{S}_8(\text{N}_2\text{H}_4)_2]$ (**Compound 3**). $K\alpha$ lines indicate the presence of the target elements.

Figure 5.4 : EDX spectrum of $[\text{enH}][\text{Cu}_3\text{As}_2\text{S}_5]$ (**Compound 4**). $K\alpha$ lines indicate the presence of the target elements.

5.2 Single Crystal X-Ray Crystallography

Compound 1 conforms to a non centrosymmetric R3 space group. Mn atoms have an octahedral configuration and As atoms have a tetrahedral one. The atoms occupy seven unique sites in the lattice. The crystal is made of a semi-cuboidal $[\text{As}_3\text{S}_3\text{Mn}]$ hetero-metallic framework. These clusters are bridged by S atoms occupying the S2 sites such that each Mn atom bridges to an As atom of the adjacent cluster (Fig. 5.5).

In the $[\text{As}_3\text{S}_3\text{Mn}]$ semi-cube, the S atom at the S2 site is separated from the Mn and As atoms by $2.5183\text{\AA}$ and $2.1773\text{\AA}$ respectively. The Mn atom is $2.7238\text{\AA}$ away from the S atoms at S1 sites. The As-S1 bond length is in the range of $2.3203 - 2.3044\text{\AA}$.

Figure 5.5 : $[\text{As}_3\text{S}_6\text{Mn}]$ sub units of **Compound 1**.

The unit cell has a Z value of 3 and comprises of $(\text{As}_3\text{S}_6\text{Mn})^-$ anions and $(\text{NH}_4)^+$ cations. The $(\text{NH}_4)^+$ cations provide stability and are bonded by weak Van der Waal forces to S2 site bridging S atoms with a bond distance of $2.5355\text{\AA}$. The $[\text{As}_3\text{S}_3\text{Mn}]$ link to form a 3-D framework consisting channels which are populated by $(\text{NH}_4)^+$ cations. The $[\text{As}_3\text{S}_3\text{Mn}]$ cluster, along the c – axis shows hexagonal pseudo symmetry (Fig. 5.6).

Figure 5.6 : NH_4^+ ions are seen in the channels of the $[\text{As}_3\text{S}_6\text{Mn}]$ framework. The structure also shows a hexagonal pseudo symmetry from the C – Axis.

Empirical formula	$\text{As}_9 \text{H}_{12} \text{Mn}_3\text{N}_3\text{S}_{18}$
Formula weight	1470.23 g/mol
Temperature	93(2) K
Wavelength	0.71073 Å
Crystal system	Rhombohedral
Space group	R3
Unit cell dimensions	$a = 9.1872(4) \text{ Å} \quad \alpha = 90^\circ.$
	$b = 9.1872(4) \text{ Å} \quad \beta = 90^\circ.$
	$c = 10.8539(5) \text{ Å} \quad \gamma = 120^\circ.$
Volume	$793.38(6) \text{ Å}^3$
Z	3
Density (calculated)	3.077 g/cm^3
Absorption coefficient	11.686 mm^{-1}
Theta range for data collection	3.17 to 35.17° .
Completeness to theta = 35.17°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.013
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0204, wR2 = 0.0433$
R indices (all data)	$R1 = 0.0208, wR2 = 0.0434$

Table 5.1 : Single Crystal Data of **Compound 1**.

Compound 2 has a Monoclinic P2/n type structure. The Mn atoms have an octahedral configuration while the As atoms have a tetragonal one. As atoms occupy two unique sites in the crystal structure. The crystal consists of $[\text{As}_4\text{S}_{16}\text{Mn}_2]^{8-}$ hetero – metallic units which, in turn, consist of two oppositely facing semi cuboidal units formed by two common Mn atoms and a tetrahedral $[\text{AsS}_4]$ unit.

To complete the octahedral configuration of the Mn atoms, each Mn atom is again attached to another $[\text{AsS}_4]$ subunit. $(\text{NH}_4)^+$ cations, from the decomposition of N_2H_4 , are present in the channels and provide stability to the structure. Each cation is present in the space between the anionic clusters. The As-S bond length is in the range of 2.1433 – 2.1894 Å. The Mn-S bond lengths vary from 2.5863 – 2.7565 Å (Fig. 5.7).

The unit cell has a Z value of 4 and consists of $(\text{As}_2\text{S}_8\text{Mn})$ anions and (NH_4) cations. The $[\text{As}_4\text{S}_{16}\text{Mn}_2]$ sub units form a layered framework, with channels populated by the (NH_4) species.

Figure 5.7 : $[\text{As}_4\text{S}_{16}\text{Mn}_2]^{8-}$ sub units with NH_4^+ ions in the channels.

Empirical formula	As ₂ H ₁₆ MnN ₄ S ₈
Formula weight	533.43 g/mol
Temperature	103(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2/n
Unit cell dimensions	a = 9.2086(4) Å α = 90°.
	b = 8.8211(4) Å β = 96.047(2)°.
	c = 20.7793(10) Å γ = 90°.
Volume	1678.51(13) Å ³
Z	4
Density (calculated)	2.111 g/cm ³
Absorption coefficient	5.673 mm ⁻¹
Theta range for data collection	2.53 to 29.11°.
Completeness to theta = 29.11°	99.0 %
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F²	1.052
Final R indices [I>2sigma(I)]	R1 = 0.0210, wR2 = 0.0427
R indices (all data)	R1 = 0.0266, wR2 = 0.0440

Table 5.2 : Single Crystal Data of **Compound 2**.

Compound 3 crystallises in the C2/c space group. Mn atoms occupy two unique sites and have an octahedral configuration. The As atoms occupy one unique site and have a tetrahedral configuration. The crystal has a Z value of 4 and consists of anionic 1D chains of [Mn₂As₂S₈], which in turn consists of two oppositely facing semi cuboid units formed by two common atoms of Mn and a tetrahedral unit of [AsS₄] (Fig. 5.8). These units are linked together by shared [N₂H₄] molecules to form anionic [Mn₂As₂S₈(N₂H₄)₂]_n²ⁿ⁻ chains parallel to the b – axis (Fig. 5.9).

Mn1 ions are coordinated with four S atoms and two N atoms from two different hydrazine ligands. Mn 2 ions are coordinated with six NH₃ molecules to form [Mn(NH₃)₆]²⁺ complexes which act to balance the charge of the crystal and fill the space between the anionic units.

Figure 5.8 : (i) Tetranuclear $[\text{Mn}_2\text{As}_2\text{S}_8]$ double semicube unit with two pairs of $\text{H}_2\text{N}-\text{NH}_2$ molecules.

(ii) 1D anionic $[\text{Mn}_2\text{As}_2\text{S}_8(\text{N}_2\text{H}_4)]_n^{2n-}$ chain built of such subunits.

Figure 5.9 : View of packing of 1D anionic chains along B-Axis, separated by $[\text{Mn}(\text{NH}_3)_6]$ cations.

The As – S bond lengths vary from 2.1234 – 2.1899 Å. The Mn – S and Mn – N bond lengths are in the range of 2.6096 – 2.6699 Å and 2.55 – 2.296 Å respectively.

Empirical formula	H ₂₆ As ₂ Mn ₃ N ₁₀ S ₈
Formula weight	737.53 g/mol
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	a = 24.312(5) Å α = 90°.
	b = 7.930(16) Å β = 93.21(3)°.
	c = 12.412(3) Å γ = 90°.
Volume	2389.24(9) Å ³
Z	4
Density (calculated)	2.05024 g/cm ³
Absorption coefficient	5.017 mm ⁻¹
Theta range for data collection	2.53 to 29.11°.
Completeness to theta = 29.11°	99.0 %
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F²	1.001
Final R indices [I > 2σ(I)]	R1 = 0.0247, wR2 = 0.0626
R indices (all data)	R1 = 0.0277 wR2 = 0.0637

Table 5.3 : Single Crystal Data of **Compound 3**.

Compound 4 conforms to the P1 space group. Cu atoms occupy three unique sites and have a tetrahedral configuration. As atoms occupy two unique sites and have a tetrahedral configuration. The crystal has a Z value of 2.

As1 and As2 atoms are coordinated with three S atoms and one Cu atom to form [AsCuS₃] units. Cu1 and Cu2 atoms are coordinated with three S atoms and one As atom to form an inverted tetrahedral [CuAsS₃]. Each [AsCuS₃] is linked to a [CuAsS₃]

to form $[\text{AsCuS}_6]$ dimers. These dimers are arranged in an alternating fashion to form chains of $[\text{As}_2\text{Cu}_2\text{S}_{10}]$ (Fig. 5.10 i).

Each Cu3 atom is coordinated with four S atoms from adjacent $[\text{AsCuS}_6]$ dimers to form $[\text{CuS}_4]$ tetrahedral. Pairs of these tetrahedral are linked to each other by shares S atoms with a Cu – Cu bond length of 2.672 Å (Fig. 5.10 ii)

Figure 5.10 : (i) $[\text{CuAsS}_6]$ dimmers are connected by vertex sharing of S atoms to form $[\text{Cu}_2\text{As}_2\text{S}_{10}]$ ribbons parallel to A-Axis. (ii) $[\text{Cu}_2\text{As}_2\text{S}_{10}]$ units in adjacent ribbons are linked by interconnected pairs of $[\text{CuS}_4]$ tetrahedral.

Figure 5.11 : Anionic $[\text{Cu}_3\text{As}_2\text{S}_5]^{n-}$ layer, when viewed from the C-Axis.

The [As₂Cu₂S₁₀] ribbons are linked via Cu₃ – Cu₃ and As₂ – S₅ bonds to yield 2D anionic [Cu₃As₂S₅]_nⁿ⁻ layers (Fig. 5.11). The As – Cu bond length varies from 2.450 – 2.514 Å. The As – S and Cu – S bond lengths are in the range of 2.216 – 2.346 Å and 2.55 – 2.476 Å respectively.

Empirical formula	As ₂ Cu ₃ S ₅
Formula weight	500.84 g/mol
Temperature	296(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P1
Unit cell dimensions	a = 6.166(2) Å α = 78.12(6)°.
	b = 9.604(4) Å β = 77.98(6)°.
	c = 10.790(4) Å γ = 71.82(5)°.
Volume	586.89(4) Å ³
Z	2
Density (calculated)	2.83399 g/cm ³
Absorption coefficient	11.805 mm ⁻¹
Theta range for data collection	2.53 to 29.11°.
Completeness to theta = 29.11°	99.0 %
Refinement method	Full-matrix least-squares on F ²
Goodness-of-fit on F²	1.004
Final R indices [I > 2σ(I)]	R1 = 0.0850, wR2 = 0.4719
R indices (all data)	R1 = 0.1064, wR2 = 0.3104

Table 5.4 : Single Crystal Data of **Compound 4**.

5.3 Powder X-Ray Diffraction

The powdered samples are subjected to X-Ray diffraction studies. As is seen, the experimental plot and the simulated diffraction spectroscopy match (Fig. 5.12, Fig. 5.13, Fig. 5.14 and Fig. 5.15), thus indicating that the crystals are of the same phase as the crystal studied previously under the single crystal X-Ray.

Figure 5.12 : Simulated and Experimental Powder X-Ray pattern of **Compound 1**.

Figure 5.13 : Simulated and Experimental Powder X-Ray pattern of **Compound 2**.

Figure 5.14 : Simulated and Experimental Powder X-Ray pattern of **Compound 3**.

Figure 5.15 : Simulated and Experimental Powder X-Ray pattern of **Compound 4**.

5.4 UV-Vis Spectroscopy

Diffuse reflectance ultra violet spectroscopy was conducted on the powdered specimens. The absorption spectra was calculated with the help of Kubelka Munk Function,

$$\alpha/S = (1 - R)^2/2R$$

where, α is the absorption coefficient, S is the scattering coefficient and R is the reflectance.

The absorption edge or band edge is defined as the transition between the strong short-wavelength and the weak long-wavelength absorption in the spectrum of a semiconductor. The spectral position of this edge is determined by the energy separation between the valence and conduction bands of the material in question. Diffuse reflectance measurements provide a more appropriate means of measurement for powdered materials. The band gap of the materials can be estimated from the graph of Enregy vs. Kubelka Munk function. The band gap is the value obtained at the intersection of the absorption edge with the Energy of the incident light.

The band gap of **Compounds 1-4** was estimated to be 2.08eV (Fig. 5.15), 2.32eV (Fig. 5.16), 2.46eV (Fig. 5.17) and 1.91eV (Fig. 5.18) respectively, which corresponds to the colour of the crystals.

The compounds show steep absorption edges, which may be due to the charge transfer between the Sulphur based valence band and the transition metal based conduction band.

It is observed that, with change in Surfactant, there is a change in the observed band gap. This may be because of the effect the Surfactant has on the bonding between the valance band of Sulphur and the conduction bands of the transition metals.

There appears to be no correlation between the band gaps and the dimensionality of the compounds. However, it is seen that the synthetic precursor used has an effect on the band gap of the material. A point of further research may be to better study the surfactants to fine tune the band gaps of the resulting compounds.

Figure 5.16 : Diffuse Reflective UV Spectroscopy of **Compound 1**. Energy band gap estimated at 2.08eV.

Figure 5.17 : Diffuse Reflective UV Spectroscopy of **Compound 2**. Energy band gap estimated at 2.32eV.

Figure 5.18 : Diffuse Reflective UV Spectroscopy of **Compound 3**. Energy band gap estimated at 2.46eV

Figure 5.19 : Diffuse Reflective UV Spectroscopy of **Compound 4**. Energy band gap estimated at 1.91eV

5.5 Thermo Gravimetric Analysis

The TGA plot of **Compound 1** (Fig. 5.20) shows one loss in mass of 78%. This corresponds to a loss in formula unit of one NH_3 molecule, one S molecule and one unit of $[\text{AsS}]$.

Figure 5.20 : TGA curve of **Compound 1**.

The TGA plot of **Compound 2** (Fig. 5.21) shows two distinct losses in mass of 23% and 20%. These losses correspond to a loss in formula unit of eight molecules of NH_3 and three molecules of H_2S (23%). In the second stage, the loss corresponds to one molecule of As_2S_2 (20%).

Figure 5.21 : TGA curve of **Compound 2**.

The TGA plot of **Compound 3** (Fig. 5.22) shows one main weight loss of 65% which corresponds to the loss in formula weight of six molecules of NH_3 (13.8%), two molecules of N_2H_4 (8.7%), three molecules of S (13%) and one As_2S_2 molecule (29%).

Figure 5.22 : TGA curve of Compound 3.

The TGA plot of **Compound 4** (Fig. 5.23) shows weight losses at two stages – 18% and 15.5%. In the first stage, the loss corresponds to loss in formula weight of one ethylenediamine molecule (10.7%) and one molecule of S (5.7%). In the second stage, the loss corresponds to three S molecules (17.1%).

Figure 5.23 : TGA curve of Compound 3.

4.6 Magnetic Susceptibility Study

Compound 1 was subjected to Magnetic Susceptibility study. The plot of $1/\chi_m$ vs. T obeys the Curie – Weiss Law (Fig. 5.24)

$$\chi_m = C/(T-\theta)$$

where χ_m is the Magnetic Susceptibility, C is the Curie Constant, θ is the Weiss Constant and T is the temperature. Using the equation the value of Curie Constant (C) and Weiss constant (θ) were calculated as 4.12 emu K/mol and -5.9K respectively. The negative value of the Weiss constant indicates a weak anti-ferromagnetic behaviour between the Mn^{2+} ions.

Anti-ferromagnetism is a behaviour observed when the spins of neighbouring nuclei are ordered in an anti parallel arrangement. In the absence of an external magnetic field, the neighbouring magnetic moments cancel each other out and the crystal as a whole does not exhibit any net magnetic moment. On the application of an external magnetic field, a net magnetic moment about the crystal is observed. This magnetic moment increases with temperature until the maximum is reached, at a temperature known as Neel Temperature (T_N). Beyond the Neel Temperature, the magnetic moment starts to decrease, indicating a paramagnetic behaviour.

Figure 5.24 : Plot of $1/\chi_m$ vs. T for **Compound 1**.

The effective magnetic moment (μ_{eff}) of Mn^{2+} ion was estimated from the plot of μ_{eff} vs. T (Fig. 5.25) as $5.68\mu_{\text{B}}$. This value matches the value of the effective magnetic moment obtained by the formula

$$\mu_{\text{eff}} = (8C)^{1/2}.$$

This value is close to $5.92\mu_{\text{B}}$, which is the value of μ_{eff} for a free Mn^{2+} ion.

Figure 5.25 : Plot of μ_{eff} vs. T for **Compound 1**.

CHAPTER 6 Conclusions and Future Scope

6.1 Conclusion

Crystalline chalcogenides play an important role both in applied and fundamental sciences. Since the advent of the low temperature synthetic route, greater control has been applied in synthesising products to suit specific requirements. In this method of synthesis, the property of the reaction media and of the templating agent allows us to apply the control. The growing need for better control and specific multifunctional properties requires diverse synthetic methodologies and the subsequent processing of the product.

Literature reviews showed that currently the synthesis involved the use of ionic liquids as reaction media. Ionic liquids have several advantages; they have good solubility for chalcogens and due to their low melting point the energy expended in the process is vastly reduced. However, their prohibitive prices and limited availability pose a serious challenge to scaling up of the synthetic process.

This report investigates the use of alternatives to ionic liquids – surfactants. Surfactants have long been used to direct the structure of compounds. Their low prices and good solubility in the presence of excess chalcogen make them a lucrative substitute. Their inertness in the reaction is also a big advantage. Also the vast number of types of surfactants opens a vista of probable different structures with open frameworks.

6.2 Future Scope

It was observed that a change in surfactant resulted in a change in the crystal structure of the material. A further study may be conducted to ascertain the influence of different kinds of surfactants on specific aspects of the crystal structure, like the pore size and the dimensionality of the crystal.

A change in crystal structure has also been effected by a change in the synthetic environment, particularly, in this case the temperature. With the reactants being the same, by changing the temperature of the reaction, different crystal structures were obtained. A further investigation may be conducted to study the effect of change of other synthetic conditions like concentration of the reactants, temperature of the reaction and also the duration of the reaction in an attempt to further understand the kinetics of the reactions.

A study may also be made of the nature of the nucleation process that promotes crystal growth. Knowing when nucleation occurs is important as it may help further tune the process of synthesising single crystals.

The changes in crystal structure also affected properties like the band gap of the material. Band gap is an important property to the semi-conductor industry and is an important criterion in various fields like memory, sensing and photovoltaic applications. Since the surfactants play a key role in affecting the changes in crystal structure, this opens up a topic of investigation for the tailoring of band gaps of the material.

This report has outlined a novel method of synthesising chalcogenoarsenates; it holds great promise for further research into the use of different types of surfactants to control the structure of open frameworks.

The vast number of possible reactions also allow for a better study into the relationship between structure and reaction process.

Homologous series of thioarsenate like structures will also enable an investigation of the relation between morphology and properties of the crystals.

PUBLICATION

1. Wei-Wei Xiong, **Eashwer Umesh Athresh**, Yu Ting Ng, Junfeng Ding, Tom Wu and Qichun Zhang “*Growing Crystalline Chalcogenidoarsenates in Surfactants : from Zero dimensional Cluster to Three Dimensional Framework*”, *J. Am. Chem. Soc.*, 2013, **135**, 1256.

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