Chapter - 1

Crystal and Crystallography
Chapter 1 Crystal and Crystallography

1.1 Introduction

Crystals have been admired from time immemorial for their beauty. The gems and crystals delivered by mother earth have always attracted our attention since the birth of mankind from early Stone Age to modern space or electronic age. The scientific and technological advancement has relied mainly on availability of materials in crystalline form. Crystals have found their place in every walk of life. Crystals are the pillars of modern technology. Without crystals, there would be no electronic industry, no photonic industry, and no fiber-optic communication.

A crystalline material is called as anisotropic substance due to directional properties. A crystal has a sharp melting point. It possesses a regular shape and if it is broken, all broken pieces have the same regular shape. A crystalline material can either be a single (mono) crystal or poly crystalline. A polycrystalline material consists of many crystals separated by well defined boundaries whereas a single crystal consists of regular arrangement of atom, molecules or group of molecules throughout the substance(s).

Constituent particles in amorphous solids are not arranged in an orderly manner. They are randomly distributed. So they are called as ‘isotropic’ substances because they do not have directional properties. They have wide range of melting point and do not possess a regular shape.

Examples: Glass, Plastic, Rubber etc.,

Atomic Arrangement in Crystals
1.2 Crystals

Crystal is any solid material in which the component atoms are arranged in a definite pattern and whose surface regularity reflects its internal symmetry. A crystal is a solid material whose constituents (i.e. atoms, molecules or ions) are arranged in a highly microscopic structure and such structure extends in all directions. A single crystal or monocrystalline solid is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries. The absence of the defects associated with grain boundaries can give monocrystals unique properties, particularly mechanical, optical and electrical, which can also be anisotropic, depending on the type of crystallographic structure. These properties, in addition to making them precious in some gems, are industrially used in technological applications, especially in optics and electronics.

The technologists involved in the growth of single crystals have gained reputation and recognition from the researcher in the scientific community due mainly to their efficiency in the high technology, and advanced knowledge they provide in modern applications of few synthetically grown single crystals are listed in Table 1.1. Good single crystals are essential for variety of scientific and commercial purposes.
Table 1.1 Grown Single Crystals and their Applications

<table>
<thead>
<tr>
<th>Sr. no</th>
<th>Single Crystal</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Si, Ge, GaAs</td>
<td>Transistor</td>
</tr>
<tr>
<td>2</td>
<td>GaAs</td>
<td>Tunnel diodes, parametric diodes, single diodes</td>
</tr>
<tr>
<td>3</td>
<td>Si, Ge (As, P)</td>
<td>Strain gauges</td>
</tr>
<tr>
<td>4</td>
<td>YIG</td>
<td>Microwave limiters and tunable filters</td>
</tr>
<tr>
<td>5</td>
<td>CaWo₄, CaF₂,ruby, GaAs, ZnP, InSh, ZnAs, Ge(As, P)</td>
<td>Masers and lasers</td>
</tr>
<tr>
<td>6</td>
<td>Quartz, Rochelle sale, CdS, GaAs, ADP</td>
<td>Electromechanical transducers</td>
</tr>
<tr>
<td>7</td>
<td>Quartz</td>
<td>Filters and oscillators</td>
</tr>
<tr>
<td>8</td>
<td>CaF₂, LiF, Quartz, Calcite</td>
<td>Optical uses</td>
</tr>
<tr>
<td>9</td>
<td>Anthracene, KCl, Si,GaAs, NaI(Tl), Ge(Li), TGS</td>
<td>Radiation detectors</td>
</tr>
<tr>
<td>10</td>
<td>CdS</td>
<td>Ultrasonic amplifiers</td>
</tr>
<tr>
<td>11</td>
<td>Sapphire</td>
<td>Industrial bearings</td>
</tr>
<tr>
<td>12</td>
<td>Diamond, Sic, Sapphire</td>
<td>Cutters and abrasives</td>
</tr>
<tr>
<td>13</td>
<td>Si and Ge</td>
<td>Rectifiers</td>
</tr>
<tr>
<td>14</td>
<td>GaP, GaAs, Ge, (As, P)</td>
<td>Electro luminescent devices</td>
</tr>
<tr>
<td>15</td>
<td>KDP,LiNbO₃,barium sodium, niobate barium, strontium niobate</td>
<td>Laser modulators, harmonic generators and parametric devices</td>
</tr>
<tr>
<td>16</td>
<td>BaTiO₃</td>
<td>Ferroelectrics</td>
</tr>
<tr>
<td>17</td>
<td>BaFe₁₂O₉, GaCa₄O(B(O)₃)₃, FeGa (Galfenel), Bi₂ZnOB₂O₆, Lead Magnesium Niobate-Lead Titanate, SiC and GaN, LiW:Eu,LiF:W,Nal:EU, Thiourea and Metal Doped Thiourea</td>
<td>Microwave&lt;br&gt;Piezoelectric for High T&lt;br&gt;Novel Sensor&lt;br&gt;High Order NLO material&lt;br&gt;Energy Harvesting&lt;br&gt;Power Accelerometer&lt;br&gt;High T Power Electronics&lt;br&gt;Scintillators&lt;br&gt;NLO Materials</td>
</tr>
</tbody>
</table>
1.3 Significance of Single Crystals:

The word ‘Crystal’ is described from the Greek word “Krystallos " means clear ice. The emergence of the crystals is natural and in loads in the shape of gems and Ratnas. They have always enticed humankind because of their shapes, colours, transparency and healing power. There is a limited supply of crystals of desired type, size and quality from nature. On the other hand, there is growing need for large single crystals for applications in industries, science and technology. This need cannot be met with by crystals in nature. It is therefore very necessary to carry out research in crystal growth.

Single crystals are important for high efficiency photovoltaic cells and detector for alternative energy and medicine, and for fabrication of bright long lifetime Light Emitting Diode (LED) s, illumination for traffic lights, Integrated Circuits and optoelectronic devices. Single crystals of SiC and GaN are useful for high temperature high power electronics. Crystals of high power lasers and radiation resistant frequency multiplying crystals of oxide compounds are useful for laser fusion energy generators. Oxide superconductors have great and wide potential applications in Morden science. The ever increasing applications of semiconductor based electronics create an enormous demand for high quality semiconductors, Ferro electronic and piezoelectric crystals. The increasing demand for single crystals arising from electronic industries, optoelectronic industries and other modern technologies like information technology, nanotechnology etc. and it depicts the task of science and technology of crystal growth. Relatively larger crystals of high quality are essential to understand the structures of biological macromolecules such as proteins, enzymes etc which is of fundamental importance in the field of Molecular Biology. A decrease of crystal defects and in homogeneities is demanded simultaneously with the development of greater crystal dimensions.

The photonic device evolution we see today is due to the advent of compound semiconductor crystals like III-V compounds (GaAs, InP,InSb, GaSbetc). GaAs used for microwave devices and semi insulating GaAs are useful in recent advance of mobile communication and digital telephony. InP is well established as base material for optoelectronic components. The growth of large oxide crystals progress significantly and used as the active components in large systems ( Nd :YAG, Ti :Al₂O₃, Cr : Al₃O₃, LiNbO₃, LiTaO₃ and Gd₅Ga₅O₁₂). Alkali halide scintillators like NaI : Tl, CsI :Na, CsI :Tl, CsI, LiF
:W, LiW : Eu and fluoroperovskites such LiBaF₃, KMgF₃, KCaF₃, CsCaBr₃, CsCrBr₃ and RbMgF₃ are grown. Various kinds of organic and inorganic non linear optical (NLO) crystals have been developed. Some of the examples are YCa₄(BO₃)₃, GaₓY₁₋ₓCa₄O(BO₃)₃ KDP, ADP, Thiourea and metal doped thiourea.

Single crystals are essential in research especially condensed-matter physics, materials science, surface science etc. Only in single crystals it is possible to study directional dependence of various properties. Furthermore, techniques such as scanning tunneling microscopy are only possible on surfaces of single crystals. In superconductivity there have been cases of materials where superconductivity is only seen in single crystalline specimen. They may be grown for this purpose, even when the material is otherwise only needed in polycrystalline form. Recently grown technologically important single crystals are summarized in Table.1.1 and shown in Fig.1.2 (a), (b) and (c).
Figure 1.2(a) recently grown technologically important single crystals
Figure 1.2 (b) recently grown technologically important single crystals
Figure 1.2 (c) recently grown technologically important single crystals
Figure 1.3 shows the overall percentage of worldwide crystal production with their utility.

1.3.1 Application of Single crystals

1. Semiconductor Industry

Single crystal silicon is used in the fabrication of semiconductors. On the quantum scale that microprocessors operate on, the presence of grain boundaries would have a significant impact on the functionality of field effect transistors by altering local electrical properties. Therefore, microprocessor fabricators have invested heavily in facilities to produce large single crystals of silicon.

2. Optics

Monocrystals of Sapphire and other materials are used for lasers and nonlinear optics.

3. Materials Engineering

Another application of single crystal solids is in materials science in the production of high strength materials with low thermal creep, such as turbine blades. Here, the absence of grain boundaries actually gives a decrease in yield strength, but more importantly decreases the amount of creep which is critical for high temperature, close tolerance part applications. Single crystals provide a means to understand, and perhaps realize, the ultimate performance of metallic conductors.
Of all the metallic elements, silver and copper have the best conductivity at room temperature. The conductivity of commercial conductors is often expressed relative to the International Annealed Copper Standard, according to which the purest copper wire available in 1914 measured around 100%. The purest modern copper wire is a better conductor, measuring over 103% on this scale. The gains are from two sources. First, modern copper is more pure. However, this avenue for improvement seems at an end. Making the copper purer still makes no significant improvement. Second, annealing and other processes have been improved. Annealing reduces the dislocations and other crystal defects which are sources of resistance. But the resulting wires are still polycrystalline. The grain boundaries and remaining crystal defects are responsible for some residual resistance. This can be quantified and better understood by examining single crystals.

From cell phones to satellite, crystals are critical elements of practically all technological items in the modern world. Crystal growth is a major stage of a crystallization process. Crystal growth is not new subject but it is newly develop industry. Over the period of time a better understanding of the process has lead to the growth of single crystals. Good crystals are essential for a variety of scientific and commercial purposes. Next chapter is deliberated on crystal growth methods used for growth of single crystals.

### Bismuth

Bismuth in bulk form is a semimetal and therefore is not a good thermal electrical material. The nanowires of bismuth (~10mm) have a thermal electric figures while gives a semiconductor behaviour.

- It is a lustrous reddish white semi metal
- Atomic number – 83
- Atomic radius - 160 (143) pm
- Electron configuration - [Xe] 4f\(^{14}\) 5d\(^{10}\) 6s\(^2\) 6p\(^3\)
- Oxidation states (Oxide)- 3,5
- Crystal structure – Monoclinic
Applications of Bismuth:

- Easy availability in sufficiently pure form.
- Single crystal can be easily grown by the conventional method.
- Cleavage plane provides a very good surface for optical studies and mechanical characterization.
- It is most diamagnetic and has lower thermal conductivity except the mercury.
- Bismuth has few commercial applications, used into metallurgical additives for casting and galvanizing, research and other uses.
- Bismuth forms low melting alloys which are extensively used, for safety devices in fire detection and extinguishing systems.
- It is recognized as one of the safest element in growing number of industrial applications.
- It also has application as a carrier of $^{233}$U or $^{235}$U fuel in atomic reactor.

1.4 Introduction of Bismuth sulphide (Bi$_2$S$_3$)

In recent years, because of their physical and chemical properties, growth and synthesis of semiconducting chalcogenides group $A_2$ (V) $B_3$(VI) ($A =$ As, Sb, Bi and $B = $ S, Se, Te) are fascinating. Compounds containing a chalcogen element as an anion (particularly S, Se and Te) are commonly termed as chalcogenides. The most well known chalcogenides systems of Bismuth possess unique properties and have drawn significant interest owing to their optical and electrical properties and find applications in a number of commercial devices.
The semiconducting chalcogenide family of materials is considered to be most important from scientific and technological point of view. One of the most promising areas is their use in thermoelectric refrigeration. Basic physical properties of Bismuth (Bi) and Sulphur elements are summarized in Table 1.2.

Table 1.2 Basic physical properties of Bismuth (Bi) and Sulphur (S) elements.

<table>
<thead>
<tr>
<th>Property</th>
<th>Bismuth (Bi)</th>
<th>Sulphur (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic Number</td>
<td>83</td>
<td>16</td>
</tr>
<tr>
<td>Atomic weight (g-moH)</td>
<td>208.98040</td>
<td>32.065</td>
</tr>
<tr>
<td>Electron configuration</td>
<td>[Xe] 4f^{14}5d^{10} 6s^{2}6p^{3}</td>
<td>[Ne] 3s^{2} 3p^{4}</td>
</tr>
<tr>
<td>Electrons per shell</td>
<td>2, 8, 18, 32, 18, 5</td>
<td>2, 8, 6</td>
</tr>
<tr>
<td>Density</td>
<td>9.78 g/cm³</td>
<td>2.07</td>
</tr>
<tr>
<td>Melting point (K)</td>
<td>544.7</td>
<td>388.36</td>
</tr>
<tr>
<td>Boiling point (K)</td>
<td>1837</td>
<td>717.8</td>
</tr>
<tr>
<td>Heat of fusion (kJ/mol)</td>
<td>11.30</td>
<td>(mono) 1.727</td>
</tr>
<tr>
<td>Heat of vaporization (kJ/mol)</td>
<td>151</td>
<td>(mono) 45</td>
</tr>
<tr>
<td>Heat capacity (25 °C) (J/mol.K)</td>
<td>25.52</td>
<td>22.75</td>
</tr>
<tr>
<td>Electro negativity (Pauling scale)</td>
<td>2.02</td>
<td>2.58</td>
</tr>
<tr>
<td>Ionization energies (kJ/mol)</td>
<td>1st : 703</td>
<td>1st : 999.6</td>
</tr>
<tr>
<td></td>
<td>2nd : 1610</td>
<td>2nd : 2252</td>
</tr>
<tr>
<td></td>
<td>3rd : 2466</td>
<td>3rd : 3357</td>
</tr>
<tr>
<td>Atomic radius (pm)</td>
<td>156</td>
<td>100</td>
</tr>
<tr>
<td>Covalent radius (pm)</td>
<td>148±4</td>
<td>102</td>
</tr>
<tr>
<td>VanderWaals radius (pm)</td>
<td>207</td>
<td>180</td>
</tr>
<tr>
<td>Electrical 'resistivity</td>
<td>1.29 μΩ.m</td>
<td>2 ×10^{15}μΩ.m (at 20 °C)</td>
</tr>
<tr>
<td>(at 20 °C)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal conductivity (300K)</td>
<td>7.97 W/(m.K)</td>
<td>0.205W/(m.K)</td>
</tr>
</tbody>
</table>
Table 1.3 Basic Properties of Bi$_2$S$_3$

<table>
<thead>
<tr>
<th>PROPERTIES</th>
<th>Bismuth Sulphide (Bi$_2$S$_3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Cell parameters</td>
<td>a = 11.15 Å, b = 11.30 Å, c = 3.98 Å</td>
</tr>
<tr>
<td>Unit cell volume</td>
<td>501.01 Å$^3$</td>
</tr>
<tr>
<td>Z (No. of atoms/unit cell)</td>
<td>4</td>
</tr>
<tr>
<td>Luster</td>
<td>Metallic</td>
</tr>
<tr>
<td>Diaphaneity (transparency)</td>
<td>Opaque</td>
</tr>
<tr>
<td>Colour</td>
<td>Lead gray to Tin white</td>
</tr>
</tbody>
</table>

Bi$_2$S$_3$ is belongs to the family of solid-state materials which is very useful for photodiode arrays and in cooling technologies. Bismuth sulphide (Bi$_2$S$_3$) is an important ore of bismuth. The optical (electronic) properties of semiconducting compounds result from band structures of semiconducting materials and are very important in a large number of applications. The reported band gap of bulk Bi$_2$S$_3$ is 1.3 eV. The more recent value of band gap is reported to be in the range 1.3-1.7 eV, which lies in the visible solar energy spectrum.

It has potential applications in photovoltaic and thermoelectric. The use of polymer coated bismuth sulphide nanoparticles as a potentially safe contrast agent for X-ray computed tomography application with superior stability at high concentrations, higher absorption of X-rays and longer circulation times compared to standard iodinated molecules. It has large absorption coefficient. Thus it is an ideal candidate for solar cells and photo detectors in the visible wavelength region.
1.4.1 Crystal Structure of Bi$_2$S$_3$

Bismuth trisulphide (Bi$_2$S$_3$) has an orthorhombic crystal structure with 4 molecules per unit cell. There are three or four additional neighbours at distances that are slightly larger as shown in Fig. 1.5. There are two bismuth atoms and 3 sulphide atoms in each molecule which add up to 20 atoms per unit cell. Bi$_2$S$_3$ occurs naturally in the form of bismuthinitewhich has a lead-gray streaked colour with a metallic luster.

![Crystal Structure of Bi$_2$S$_3$](image)

**Figure 1.5 Crystal structure of Bi$_2$S$_3$**

This structure can be considered as being made up of puckered sheets or planes of stoichiometric composition perpendicular to the (001) direction. The bonding between these sheets is considerably weaker than that within the sheets. This suggests that cleavage would take place on (010) planes, and crystal growth in the (001) direction, this property is found to belong to these compounds. Bi$_2$S$_3$ compounds are nearly isomorphous. Infrared data suggest that Bi$_2$S$_3$ is slightly polar. The values of atomic positions in Bi$_2$S$_3$ samples are shown in Table 1.4.

**Table 1.4 Atomic positions of Bi$_2$S$_3$.**

<table>
<thead>
<tr>
<th></th>
<th>Mi</th>
<th>m2</th>
<th>Xi</th>
<th>X2</th>
<th>X3</th>
</tr>
</thead>
<tbody>
<tr>
<td>U</td>
<td>0.326</td>
<td>0.536</td>
<td>0.880</td>
<td>0.559</td>
<td>0.189 38</td>
</tr>
<tr>
<td>V</td>
<td>0.030</td>
<td>0.355</td>
<td>0.055</td>
<td>0.869</td>
<td>0.214</td>
</tr>
</tbody>
</table>
1.4.2 Applications

- There are several actual and potential technological applications of chalcogenide materials due to the possibility of modifying their physical properties such as optical band gap and index of refraction.
- Bismuth sulphide (Bi$_2$S$_3$) is a kind of layer structure direct band gap semiconductors.
- Also used as a starting material to produce many other bismuth compounds.
- Powder metal sulphides have been used in the following applications: batteries, lubricants and lubricant additives, photovoltaic materials, infrared filters, and sputtering targets.
1.5 Existing Literature Survey on Growth of Bulk Bi$_2$S$_3$

1. Bi$_2$S$_3$ single crystal: Bi$_2$S$_3$ single crystals are grown by slow cooling Bridgman-Stockbarger technique. In this design, a slow speed motor was used to obtain a slow motion of the charged ampoule inside the three-zone tube furnace, which is fixed in a vertical position. The design has been performed to obtain a suitable rate (1.66 mm/h). According to this technique the samples have been prepared by the direct melting of the starting materials and then placed in quartz ampoule sealed under vacuum of about $10^{-6}$torr. The silica ampoule and its charge were mounted in the first zone of the furnace where the temperature was higher than the melting point and was kept for 24h for mixing the starting materials. The temperature of the middle zone of the furnace was 1048 K corresponding to the crystallization temperature of Bi$_2$S$_3$. When the ampoule and its contents entered the third zone, gradual Solidification is occurred since the temperature was less than the melting point. Eleven days were required to obtain Bi$_2$S$_3$ as silvery dark metallic crystals.

2. Liquid encapsulated crystal growth of Bi$_2$S$_3$ was grown by the liquid encapsulated solidification method. Dependence of their electrical resistivities of stoichiometry was studied. Instead, impurities or macroscopic defects could be responsible for a high hole concentration. Doping of both compounds was attempted. A self-compensation-like effect prevents Bi$_2$S$_3$ from undergoing n- to p-type conversion. However, this compound exhibit quite weak sensitivity to impurities.

3. Skeleton crystals of Bi$_2$S$_3$ have been prepared via a solvothermal route using BiCl$_3$ and anhydrous sodium sulphite as starting reagents. The rod-based skeleton crystals have three-dimensional network morphologies. The influence of reaction time, the temperatures and possible growth mechanism was studied.
1.6 Existing Literature Survey on Synthesis of Bi$_2$S$_3$ Nanomaterials

1. Bi$_2$S$_3$ nanostructures with a sheaflike morphology are obtained via reaction of bismuth acetate-oleic acid complex with elemental sulphur in 1 octadecene. These structures may form by the splitting crystal growth mechanism, which is known to account for the morphology some mineral crystals assume in nature. By control of the synthetic parameters, different shapes are obtained, analogous to those which have been observed to occur by crystal splitting in minerals.

2. **Crystalline Bi$_2$S$_3$ nanorods and nanowires**

Crystalline Bi$_2$S$_3$ nanorods and nanowires were produced using a solventless synthesis. The aspect ratio depends on the sulfur source: the thermolytic decomposition of bismuth thiolate molecular precursor gives nanowires, whereas the addition of elemental sulfur gives nanorods. At higher reaction temperatures, crossed nanowires formed with epitaxial interfacing—termed “nanofabric”.
3. Ultralong Bi$_2$S$_3$ nanoribbons have been synthesized by a solvothermal process, using a mixture of aqueous NaOH solution and glycerol as the solvent. These nanoribbons are 50–300 nm wide, 20–80 nm thick, and up to several millimeters long, and the initial formation of the precursor polycrystalline NaBiS$_2$ phase is crucial to their formation. The nucleation and growth process was interpreted as a solid–solution–solid transformation.

4. Orthorhombic Bi$_2$S$_3$ nanorods were synthesized via hydrothermal treatment from a novel kind of single source precursors, the adducts of bi(S$_2$COR)$_3$ [R = sec-beuty1] with neutral ligands (pyridine [C$_5$H$_5$N] or 1, 10-phenanthroline [C$_{12}$H$_8$N$_2$]. The decomposition of the complex [Bi(S$_2$COC$_4$H$_9$)$_3$(C$_5$H$_5$N)$_2$] produces Bi$_2$S$_3$ nanorods with diameters in the range of 20-35 nm and lengths of hundreds of nanometers. The nanodispersed Bi$_2$S$_3$ in dichloromethane maintains a long–term stability and shows a blue shift on the optical band edge with a band gap $E_g$ 1.67 eV. High resolution transmission electron microscopy studies reveal that the Bi$_2$S$_3$ nanorods are oriented in 1 [001] growth direction.

5. Synthesis of Bi$_2$S$_3$ nanotubes from rolling the quasi-two-dimensional (2-D) layered precursor represents new progress in the synthetic approach and adds new members to the present inorganic fullerene family. These nanotubes display multiwalled structures that resemble that of a multiwalled carbon nanotube. The successful synthesis of Bi$_2$S$_3$ nanotubes highlights the feasibility of inorganic fullerene-like structure from other chemicals that possess layered crystalline structure, not only the well-known 2-D family, but possible also those quasi-2-D members.
6. Synthesis of Bi$_2$S$_3$ Nanostructures
Uniform 5 µm Bi$_2$S$_3$ microspheres and 8 µm micro flowers were solvothermally complex without any templates or surfactants. Bi$_2$S$_3$ microspheres composed of synthesized in acetyl acetone solution through thermolysis of the Bi$^{3+}$dithizonenanorods with a diameter of 20-40 nm were synthesized at 180 ºC for 12 h. In similar conditions at 240 ºC for 3 days, micro flowers composed of nanowires with lengths up to several micrometers and diameter of 20-40 nm were obtained. Field- emission scanning electron microscopy (FESEM) showed in the initial stage in the formation process that smooth spherical cores were observed, then on the surface of the cores nanoparticles appeared, and finally nanorods or nanowires grew out and microspheres and microflowers formed.

7. Synthesis of Bi$_2$S$_3$ Nanoribbons
Facile solvothermal method by using mixed solvents for the large-scale synthesis of Bi$_2$S$_3$ nanoribbons with lengths of up to several millimeters. These nanoribbons were formed by a solvothermal reaction between Bi$^{III}$glycerol complexes and various sulfur sources in a mixed solution of aqueous NaOH and
glycerol. The Bi$_2$S$_3$ nanoribbons prepared by the use of different sulfur sources have a common formation process: the initial formation of NaBiS$_2$ polycrystals, which serve as the precursors to Bi$_2$S$_3$, the decomposition of NaBiS$_2$, and the formation of Bi$_2$S$_3$ seeds in the solution through a homogeneous nucleation process; the growth of Bi$_2$S$_3$ nanoribbons occurs at the expense of NaBiS$_2$ materials. Some crucial factors affect nanoribbon growth, such as, solvothermal temperature, volume ratio of glycerol to water, and the concentration of NaOH.

8. Bi$_2$S$_3$ nanotubes: Facile synthesis

A facile solution-based method has been designed to fabricate uniform Bi$_2$S$_3$ nanotubes with average size of 20 nm × 160 nm using only bismuth nitrate (Bi(NO$_3$)$_3$), 5H$_2$O) and sulfur powder (S) as the reactants and octadecylamine (ODA) as the solvent and the classic rolling mechanism was applied to explain their formation.

9. Bi$_2$S$_3$ Nanowires Fabricated Via HVPC Growth Technique

Bi$_2$S$_3$ Nanowires was successfully fabricated using Horizontal Vapor phase crystal growth technique. A 35 mg of bismuth sulfide powder with purity rate of 99.9 % was utilized. The growth temperature was varied at 600 °C to 1200 °C with growth time of 4 to 8 hours where the ramp time was set at 60 minutes. The optimum growth was at 1200 °C deposited on zone 2 on a fused silica tube. The energy band gap was 2.58 eV which has blue spectra. The nanowires demonstrated its functionality as photo sensor in a metal–semiconductor–metal planar structure based on the voltage time spectra obtained.

10. Development of bismuth sulphide quantum dot’s in silicate glass matrix. The successful growth of Bi$_2$S$_3$ nanocrystals in glass matrix using SiO$_2$ (silicon Dioxide), K$_2$O (potassium Oxide), Na$_2$O (Sodium Dioxide), B$_2$O$_3$ (Boron Trioxide), ZnO (Zinc Oxide) and TiO$_2$ (Titanium Dioxide) as key components is done using the fusion method. Different sizes of nanocrystals in glass matrix were grown by annealing the glass (dispersed with Bi$_2$S$_3$ nucleons) under two different conditions. The glass was annealed between 6 and 48 hrs at constant temperature of 550 °C. The glass was also annealed at the temperature between 550°C, 575°C and 600 °C at constant annealing time 6 hrs. The photocatalytic H$_2$ generation under solar light has been performed and utmost H$_2$ generation i.e 5545 µ mole h$^{-1}$g$^{-1}$ has been achieved, which is higher than Bi$_2$S$_3$ powder.
11. 3D Hierarchical Bi$_2$S$_3$ Nanostructures

A solvothermal method has been employed to synthesize bismuth sulfide (Bi$_2$S$_3$) with three-dimensional (3D) hierarchical architectures. The influences of different types of surfactants and Cl$^-$ species on the size and morphology were investigated. A possible formation mechanism was also proposed on the basis of time-dependent experiments. The photo response properties show that the conductivity of Bi$_2$S$_3$ micro-flowers is significantly enhanced and the photocurrent is approximately two orders of magnitude larger than the dark current. It is expected that hierarchical architectures Bi$_2$S$_3$ may provide a new pathway to develop advanced nonmaterial for high-speed and high-sensitivity photoelectrical switches and photo detecting devices.

12. Oriented Growth of Single-Crystalline Bi$_2$S$_3$ Nanowire Arrays

Highly oriented single crystal Bi$_2$S$_3$ nanowire arrays are formed inside anodised alumina membranes (AAMs) using a new solventless approach. A high yield of pour filling is achieved by injecting the melted single source precursor liquid into the channels followed by thermolysis. The absorption profile (bandgap) of these nanowires shifts to higher energies as the mean diameter of the nanowires decreases.
Chapter 1

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Crystalline Bi$_2$S$_3$ nanorods, nanotapes and nanocrystals were obtained from the solvent thermalysis of bismuth trisxanthate precursors and related bismuth dithiocarbamate species in ethylene glycol at 197 °C. Precursors with different structural motifs were designed to produce compounds with different thermal decomposition temperatures, i.e. the dimeric motif of Bi(S$_2$COR)$_3$ when R= methyl and ethyl was found to have a lower decomposition temperature compared to precursors adopting the polymeric structure, so that solvothermalysis of the former gave rise to short nanocrystals, while in the case of the latter, long nanofibers were produced instead. Chemical vapor deposition on silicon substrates yielded well-defined nanorods of various lengths and diameters for almost all precursors. Internal microstructure of the nanorods was studied by high-resolution transmission electron microscopy.

14. 3D hierarchical Bi$_2$S$_3$ Nanostructures

A solvothermal method has been employed to synthesize bismuth sulfide(Bi$_2$S$_3$) with three-dimensional (3D) hierarchical architectures. The influences of different types of surfactants and Cl$^-$ species on the size and morphology were investigated. A possible formation mechanism was also proposed on the basis of time-dependent experiments. The photo response properties show that the conductivity of Bi$_2$S$_3$ micro-flowers is significantly enhanced and the photocurrent is approximately two orders of magnitude larger than the dark current. The response and decay times are estimated to be 142 and 151 ms, respectively. It is expected that hierarchical architectures Bi$_2$S$_3$ may provide a
new pathway to develop advanced nanomaterial for high-speed and high-sensitivity photoelectrical switches and photodetecting devices.

Figure 1.6 (a), (b) Typical SEM images of V-Bi$_2$S$_3$.

(c), (d) TEM image and HRTEM image of V-Bi$_2$S$_3$, respectively.

Figure 1.7: The typical SEM images of Bi$_2$S$_3$ structure synthesized a blank, without surfactants, b CTAB, c SDS, and d PVP
Figure 1.8 FE-SEM images of the products obtained at different time periods (a) - 2h, (b) - 6h, and (c) - 24h
1.7 The Goal of Present Work:

Looking to the numerous potential applications of Bismuth sulphide mentioned in this chapter from literature survey, these seems to be a good reason to study different properties of Bismuth sulphide amongst all V2-VI3 semiconductor compounds. Further there are very few reports available in the literature on single crystal (bulk form) growth of Bi$_2$S$_3$. Synthesis of nonmaterial has become a prolific area of investigation due to their wide range of applications and huge work is carried out in this nanoregime.

Synthesis of crystal is an important aspect of materials science. The art and the science of crystal growth has developed very much like any other branch of science. Over the past few decades, semiconducting chalcogenides compounds (A$_2$B$_3$) have been receiving much attention because of their wide range of applications in various fields of science and technology. Bismuth Sulphide (Bi$_2$S$_3$) is a ferroelectric semiconductor having Para electric phase and exhibiting interesting photo conducting behaviour. Bi$_2$S$_3$ are narrow band gap semiconductor with layered structure and are interesting and important because of major contribution in solar cells, photo detectors, opto-electronic light amplifiers, Lasers, photo electronic etc. Nano crystals of Bi$_2$S$_3$ in different shape and sizes have applications in hydrogen storage, high energy battery and catalytic field. By looking to wide applications of and importance of the Bi$_2$S$_3$ single crystals, these crystals were grown from melt using modified Bridgeman Stock burger, Chemical Vapor Transport method, and Skeleton layered structured crystals were grown by hydrothermal method. Flower like nanobelts, Straw-tied nano wires are synthesized by Facile decomposition and precursor solution method , but no attempt have been made to grow single crystals of the Bi$_2$S$_3$ using simple and inexpensive Zone Refining method and Gel technique. The present work is an attempt to grow such important crystals using these two methods.

The science and art of this research lies in carrying out more meaningful research with very modest research facilities and it should be at inexpensive methods of growing such technological and important single crystals. There are few places in India can afford very sophisticated instruments and very expensive research facilities for characterization of grown crystals. We have utilized these facilities for grow Bi$_2$S$_3$ crystals and summarized in this thesis.
Chapter I
Crystal and Crystallography

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