Chapter 8
Summary and future prospects
8.1. Summary

Increasing global interest in energy and environmental concerns has drawn attention to research in renewable and sustainable energy systems. Thermoelectric (TE) devices are promising because of their potential application as replacements or supplements to conventional energy conversion systems, such as waste heat recovery and environmentally-friendly refrigeration. Significant enhancement in the energy conversion efficiency of TE materials has been possible with morphologically nanostructured materials with low thermal conductivities. Main-group metal chalcogenides, V₂-Vl₃ (where A= As, Sb, Bi and B =S, Se, Te), have received ever increasing attention as valuable thermoelectric semiconductors. As a representative of good thermoelectric semiconductors, Bi₂S₃ and Sb₂S₃ have been attracting a considerable interest owing to its potential application in thermoelectric, electronic and optoelectronic devices and IR spectroscopy etc. In addition, they have an energy band gap of 1.3 to 1.7 eV, which is suitable for making photodiode arrays and photovoltaics. A band gap can be tuned depending on the size of the subcomponents. Hence, we have studied the properties like structural, electrical, optical and thermal of different morphologies (Single crystal, nanostructure) of Bi and Sb sulfide.

Single crystals of Bi₂S₃ have been successfully grown in our laboratory by chemical vapour transport technique in the shape of needle. EDAX analysis confirmed stoichiometry of grown Bi₂S₃ single crystals and powder XRD pattern indicated that Bi₂S₃ crystallizes in a pure orthorhombic structure with calculated lattice parameters \(a=11.14\,\text{Å}, \quad b=11.30\,\text{Å}, \quad c=3.96\,\text{Å}\) matching with the reported data. SEM images have shown that single crystals are grown by layer by layer mechanism. The activation energy determined from resistivity measurement comes out to be 0.38eV whereas scattering parameter...
determined from Seebeck coefficient measurements in the temperature range (31-27)×10⁻⁴K⁻¹ and (27-24)×10⁻⁴K⁻¹ comes out to be -0.16 and -0.18 which corresponds to scattering by acoustic phonons. Apart from this Seebeck and Hall measurements shows that grown Bi₂S₃ single crystals are n-type in nature. TGA has shown that Bi₂S₃ single crystals remains stable upto 500°C and then after 10% of weight loss is observed upto 700°C. The calculated value of figure of merit (ZT) in our case comes out to be very low which indicates that Bi₂S₃ pellets prepared from grown single crystals by chemical vapour transport technique are not suitable for thermoelectric application.

Bi₂S₃ nanorods were prepared at room temperature by simple chemical reaction method. The lattice parameters a = 11.15 Å, b = 11.30 Å and c = 3.98 Å determined from XRD and TEM are having close resemblance with each other whereas compositional verification of Bi₂S₃ sample by EDAX and XPS are closely matching. The optical absorption spectra shows an absorption edge at 262nm thereby showing blue shift in comparison to bulk form of the material (954nm). Raman spectra peaks obtained at 238cm⁻¹ and 972cm⁻¹ are matching with reported values corresponding to A₆ and surface phonon modes. TGA plot shows the continuous weight loss from room temperature to 750°C. The value of activation energy calculated from TGA plot by using BR, PN and CN model are 0.38eV, 0.055eV and 0.014eV respectively.

Single crystals of Sb₂S₃ were grown by chemical vapour transport technique using NH₄Cl as a transporting agent. EDAX result showed the desired stoichiometry of Sb₂S₃ single crystals. XRD measurements of Sb₂S₃ powder confirmed that Sb₂S₃ belongs to the orthorhombic structure with calculated lattice parameters a=11.239Å, b=11.313 Å and c=3.841 Å, which matched with the reported data and standard data (JCPDS No. 42-1393). Raman spectrum peaks observed at 115, 147, 190, 252, 282, 300 and 373 cm⁻¹ are matching with the reported values.
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TGA curve shows the average weight loss about 7% from room temperature to 575°C and thermal conductivity of Sb$_2$S$_3$ at 100°C is 0.422 Wcm$^{-1}$deg$^{-1}$. The single crystal of Sb$_2$S$_3$ grown by chemical vapour transport technique are showing very high values of resistance in MΩ in comparison to grown by Bridgman technique.

Sb$_2$S$_3$ microspheres are successfully synthesized by solvothermal method. EDAX results confirms the desired stoichiometry of synthesized Sb$_2$S$_3$ microspheres. XRD shows that Sb$_2$S$_3$ microspheres belong to pure orthorhombic phase (JCPDS 42-1393). The phase purity of the microspheres was also confirmed by XPS. SEM and TEM images show that Sb$_2$S$_3$ particles are spherical in shape having diameter in micrometer range and spot diffraction pattern of Sb$_2$S$_3$ microsphere indicated their single crystalline nature. TGA of Sb$_2$S$_3$ microspheres shows weight loss between 178-292°C. The band gap of the microspheres is found to be 1.62 eV, which is near to the optimum value for photovoltaic conversion, suggests that Sb$_2$S$_3$ microspheres can be used for application in solar energy and optoelectronic applications. Room temperature PL studies with different excitation wavelength suggests that Sb$_2$S$_3$ microspheres are showing luminescence behavior in different parts of the spectrum.

Bi$_2$S$_3$ nanorods shows antibacterial action against all bacterial cultures (Staphylococcus aureus, Bacillus subtilis, Escherichia coli and Salmonella paratyphi) whereas Sb$_2$S$_3$ microspheres is active only again gram positive bacteria (Staphylococcus aureus, Bacillus subtilis).

8.2. Future prospects

➢ In near future one can prepare thin films of Bi$_2$S$_3$, Sb$_2$S$_3$ with different thickness and find their application in thermoelectric devices.
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➤ One can also prepare Bi$_2$S$_3$ and Sb$_2$S$_3$ in other forms like nanotubes, nanobelts, nanoflowers etc. and can try to prove their utility as thermoelectric material and further extend their studies for antibacterial behaviour.

➤ The extension of this research can be focused to study different properties of other remaining compounds of V$_2$-VI$_3$ group in single crystal, nanostructure and thin film forms.

➤ Bi$_2$S$_3$ and Sb$_2$S$_3$ can be doped with other elements and then their properties can be studied and explored for application.

➤ Single crystals of V$_2$-VI$_3$ can be grown by Bridgman method and then their comparative study with vapour grown single crystals can be done.

➤ Photovoltaic applications of V$_2$-VI$_3$ can be also studied in near future.
List of Publications

National and International Publications

1. "Characterization of Bi$_2$S$_3$ nanorods prepared at room temperature".

2. "Study on Transport Properties of Bi$_2$Se$_3$ single crystals grown by vapour phase technique".

3. "Study on transport properties of Bi$_2$Se$_3$ single crystal grown by vapour phase techniques".
   M. P. Deshpande, Pallavi N. Sakariya and Nilesh N. Pandya.

4. "Characterization of CdSe thin films deposited by chemical bath solution containing triethanolamine".

5. "Electrical transport properties study of Mo$_{0.6}$W$_{0.4}$Se$_2$ single crystals".

6. "Synthesis and characterization of CdS nanocrystalline thin film and nanoparticles".
Co-authored by Pallavi N. Sakariya.

7. "Spectroscopy and structural study on CdSe thin films deposited by chemical bath deposition".

8. "Single crystal growth, surface microstructure and thermal studies of MoS2".
Sunil Chaki, M. P. Deshpande, Pallavi N. Sakariya, Nilesh Pandya.
1. "Sb$_2$S$_3$ microspheres prepared by solvothermal method".
Advance Science Letters (2013) (Reviewed and will be accepted after minor correction).

2. "Preparation and characterization of Bi$_2$S$_3$ compound semiconductor".
Bulletin of Materials Science (2014) (Reviewed and will be accepted after minor correction).
List showing papers presented and attended seminars/conferences/symposiums/workshops

1. Participated in the Golden Jubilee Seminar in Physics, held at Department of Physics, Sardar Patel University, Vallabh Vidyanagar on 20th January, 2009.


4. Presented paper entitled “Study on transport properties of Bi$_2$Se$_3$ single crystal grown by vapour phase techniques” in the 54th DAE Solid State Physics Symposium held at M. S. University of Baroda, Baroda during December 14th -18th , 2009.


6. Participated in “Frontiers Of Physics – An Introductory Seminar” held on 24th January, 2010 at Department of Physics, Sardar Patel University, Vallabh Vidyanagar.
7. Participated in one day Workshop on Physics of Hadrons and Nuclei organized by Department of Physics, Sardar Patel University, Vallabhbh Vidyanagar on 12th February, 2010.

8. Participated in the National Workshop on X-ray Diffraction Techniques and applications organized by Department of Physics, Saurashtra University, Rajkot (Gujarat) during March 17th -19th, 2010.


10. Attended and presented a paper on "Characterization of Bi$_2$S$_3$ nanorods prepared at room temperature" in
   1) National conference on Physics for tomorrow, St. Xavier's college, Ahmedabad, 3-4, March-2011.
   2) Two day symposium on innovations in science SPU Research Scholars Meet (ISSPURAM-2012) on 8th -9th JAN-2012 at Sardar Patel University, Vallabhbh Vidyanagar (won 3rd prize).

12. Attended and presented (poster) research paper entitled "Growth and characterization of Bi$_2$S$_3$ single crystal" in XXVII Gujarat Science Congress 2013 at Charotar University of Science & Technology, 24th February 2013, Changa.

13. Attended and presented research paper entitled "Sb$_2$S$_3$ microspheres prepared by solvothermal method" in
1) ICNN-2013 at Department of Applied Physics, Babasaheb Bhimrao Ambedkar University, 18th -20th November 2013, Lucknow.
2) UGC sponsored one day Seminar on Condensed Matter Physics (CMP-2014) at Department of Physis, Sardar Patel University, 3rd March 2014, Vallabh Vidyanagar.