Chapter 6

Synthesis and characterization of $\text{Sb}_2\text{S}_3$

microspheres
6.1. Introduction

V-VI group binary chalcogenides \( (A_2V_2B_3VI; A=\text{As}, \text{Sb}, \text{Bi}; B=\text{S}, \text{Se}, \text{Te}) \) have attracted much attention due to their good photovoltaic properties and high thermoelectric power, which allow potential applications in optical, electronic and thermoelectric cooling devices\(^1\). Binary chalcogenides compound have received attention recently because of their potential for optical storage\(^2\).

Antimony sulfide \( (\text{Sb}_2\text{S}_3) \) (stibnite) is a direct band gap and highly anisotropic V-VI group binary chalcogenide semiconductor with a layered structure parallel to growth direction and crystallizes in an orthorhombic phase well known for its high photosensitivity and high thermoelectric properties\(^3\). Antimony sulfide \( (\text{Sb}_2\text{S}_3) \) has been extensively studied due to its device applications in photoconducting targets of television cameras, electronic devices, optoelectronics devices and infrared spectroscopy\(^4,5\).

One important function of \( \text{Sb}_2\text{S}_3 \) is that it can be used as the starting material for synthesizing other related compounds\(^6,7\). It has also been used in thermoelectric cooling technologies and optoelectronics in the IR region \(^8,5\).

The literature survey shows that several morphologies of antimony trisulfide (stibnite) have been fabricated including nanoparticles\(^9\), nanorods\(^10,11,12\), nanowhiskers\(^13\), microtubular\(^14,15\) and microspheres\(^16\) by various methods. But a very few workers have prepared the microspheres via solvothermal method. Here in we prepared \( \text{Sb}_2\text{S}_3 \) microspheres using \( \text{SbCl}_3 \) (Antimony chloride) and sulfur powder as a starting material. The structural, optical and thermal properties of the prepared \( \text{Sb}_2\text{S}_3 \) microspheres were studied and the results obtained are discussed in detail in this chapter.
6.2. Synthesis of Sb$_2$S$_3$ microsphere using solvothermal method

- All of the chemical reagents used in this experiment were of analytical grade and were used without further purification.
- In a typical procedure, 0.23 g antimony chloride (SbCl$_3$) and 0.45 g tartaric acid were dissolved in 16 mL N$_2$N-dimethylformamide (DMF).
- In this solution about 0.244 g sulfur powder was added with stirring.
- This mixed solution was transferred into a teflon-lined stainless steel autoclave.
- The autoclave was sealed and maintained at 120°C for 4 h and then cooled to room temperature naturally.
- The precipitates were collected and washed with distilled water for several times. Then, the precipitates were dried in air.
- Finally, the resultant burgundy colored powder sample were obtained and characterized by various techniques. The layout diagram for synthesis of Sb$_2$S$_3$ microsphere is shown in Fig. 6.1.
Fig. 6.1. Block diagram of synthesis procedure of Sb$_2$S$_3$ microspheres.
6.3. Results and Discussion

6.3.1. Energy dispersive analysis of X-rays (EDAX)

Fig. 6.2. EDAX spectra of Sb$_2$S$_3$ microspheres.

Fig. 6.2. shows the EDAX spectra of prepared Sb$_2$S$_3$ microspheres suggesting that the sample contain only antimony and sulfur elements. Table 6.1. provides the elemental composition in terms of weight percentage of elements obtained from EDAX results revealing the desirable stoichiometry of Sb$_2$S$_3$.

Table 6.1. Elemental composition of Sb$_2$S$_3$ microspheres.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Wt% of elements in Sb$_2$S$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sb$_2$S$_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Sb</td>
</tr>
<tr>
<td></td>
<td>71.08</td>
</tr>
</tbody>
</table>

Table 6.1. Elemental composition of Sb$_2$S$_3$ microspheres.
6.3.2. X-ray diffraction (XRD)

![XRD pattern](image_url)

**Fig. 6.3.** The powder XRD pattern of the prepared Sb$_2$S$_3$ microspheres.

XRD pattern of Sb$_2$S$_3$ microspheres is shown in **Fig. 6.3.** in the 20 range of 0-90°. All the diffraction peaks were indexed with the help of powder-X software to a pure orthorhombic phase of Sb$_2$S$_3$ with calculated lattice parameters $a = 11.24$ Å, $b = 11.31$ Å, and $c = 3.84$ Å, which matches well with the values reported in JCPDS 42-1393.

6.3.3. X-ray photoelectron spectroscopy (XPS)

The chemical state, purity and composition of the as-obtained product was further checked by XPS analysis. **Fig. 6.4. (a)** shows the scanned XPS spectra of the product. The peaks arising from Sb$_2$S$_3$ (Sb
4d, 3d, 3p and S 2s, 2p) are clearly seen, and a small contaminant C1s peak is also evident. The high-resolution XPS spectra of Sb 3d, 4d and S 2p were obtained using C1s as the reference at 287.5eV. In order to analyze the composition of the as-obtained product in detail, curve fitting of S 2p and Sb 3d, 4d were performed.

Fig. 6.4. (a) XPS pattern of survey scan of the as obtained product Sb$_2$S$_3$ microspheres (b) high resolution S 2p region (c) high resolution Sb 3d region (d) high resolution Sb 4d region.

Pallavi N. Sakariya /Ph.D. Thesis/Department of Physics/Sardar Patel University/2014
**Fig. 6.4. (b)** shows the high-resolution spectra of the S 2p with the peak at 161.19 eV whereas the high resolution spectra of the Sb 3d is shown in **Fig. 6.4. (c)** which shows the presence of two peaks for Sb 3d_{5/2} and Sb 3d_{3/2} at 530.29 eV and 539.69 eV, respectively. **Fig. 6.4. (d)** represents the high-resolution spectra of the Sb 4d with the peak at 33.52 eV. The peak position for both Sb and S agree well with those reported in the literature\(^{17}\). The average weight percentage ratio obtained from quantification of Sb3d and S2p peaks is 73:27, which is close to anticipated value and are supporting the EDAX results also.

**6.3.4. Scanning electron microscopy (SEM)**

The surface morphology of the Sb\(_2\)S\(_3\) microspheres is studied by SEM. The three SEM images of the sample were obtained at different places with same magnification. **Fig. 6.5.** shows that the product contains sphere like structure and the diameter of these spheres varies from 1 to 5\(\mu\)m.
Fig. 6.5. SEM images of $\text{Sb}_2\text{S}_3$ microspheres.
6.3.5. Transmission electron microscopy (TEM)

Further, we studied the detailed structure and morphology of the sample by TEM analysis and is presented in Fig. 6.6. The TEM image in Fig. 6.6. (a) shows individual sphere of Sb$_2$S$_3$ with a diameter range from 100nm to 300nm and selected area electron diffraction pattern (SAED) of

![ TEM image of Sb$_2$S$_3$ microspheres ](image)

![ SAED pattern of Sb$_2$S$_3$ microspheres ](image)

**Fig. 6.6.** (a) TEM images of Sb$_2$S$_3$ microspheres (b) SAED pattern of the Sb$_2$S$_3$ microspheres.
these spheres is given in Fig. 6.6. (b) which shows diffraction spots indicating single crystalline nature of these Sb$_2$S$_3$ microspheres. Few diffraction spots are indexed based on orthorhombic structure of Sb$_2$S$_3$ which is shown in Fig. 6.6. (b) and the zone axis determined as [001] suggests the preferred orientation.

6.3.6. Raman spectroscopy

![Raman spectrum of the Sb$_2$S$_3$ microsphere.](image)

Fig. 6.7. Raman spectrum of the Sb$_2$S$_3$ microsphere.

Raman spectra was obtained at room temperature with Ar$^+$ laser source as excitation source which is displayed in Fig. 6.7. The appearance of the peaks at 151, 188, 252, 305, 372 and 450 cm$^{-1}$ is in good agreement with the reported Raman spectra$^{18}$. The presence of sharp peaks at 151 cm$^{-1}$, 188 cm$^{-1}$ and 252 cm$^{-1}$ suggests the formation of
well crystalline products\textsuperscript{19}. The low intensity peak at 305 cm\textsuperscript{-1} and 372 cm\textsuperscript{-1} can be assigned to the unit SbS\textsubscript{3} pyramid of the material having C\textsubscript{3v} symmetric mode\textsuperscript{20}. The presence of a relatively broad peak at 450 cm\textsuperscript{-1} may be due to the symmetric stretching of the Sb-S-S-Sb bond of Sb\textsubscript{2}S\textsubscript{3}, which can be accounted on the basis of existing literature\textsuperscript{21}.

\subsection*{6.3.7. Thermogravimetric analysis (TGA)}

A TGA spectrum in air of the prepared Sb\textsubscript{2}S\textsubscript{3} microspheres is shown in Fig. 6.8, which reflects weight loss between 178-292°C. The weight loss may be due to formation of oxide of antimony and sulfur evaporation in this temperature range. We have used the theoretical models viz. Broido (BR)\textsuperscript{22}, Coats Redfern (CR)\textsuperscript{23} and Piloyan-Novikova (PN)\textsuperscript{24} relations for calculating the activation energy in the weight loss region of TGA curve. The corresponding plot of BR, CR and PN models is shown in Fig. 6.9. The calculated values of activation energy from these relations are shown in Table 6.2.
Fig. 6.8. TGA plot of $\text{Sb}_2\text{S}_3$ microspheres.

Table 6.2. Calculated values of activation energy (eV) obtained from BR relation, PN relation and CR relation.

<table>
<thead>
<tr>
<th>Name of Model</th>
<th>Broido relation</th>
<th>Coats-Redfern relation</th>
<th>Piloyan-Novikova relation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy</td>
<td>0.79eV</td>
<td>0.64eV</td>
<td>0.16eV</td>
</tr>
</tbody>
</table>
Fig. 6.9. Plot of BR, CR and PN model of TGA in the weight loss region.
Since Sb$_2$S$_3$ is important from the optoelectronic application point of view and hence its band gap determination is done by obtaining UV-Vis absorption spectra. The direct band gap energy ($E_g$) for the sample is determined by fitting the absorption data to the direct transition equation $(ahv)^2=A(hv-E_g)$, where $a$ is the optical absorption coefficient, $hv$ is the corresponding photon energy, $E_g$ is the direct band gap energy of the semiconductor and $A$ is a constant. The plot $(ahv)^2$ vs $hv$ is shown in Fig. 6.10. The band gap is determined by extrapolating the linear part of the curve $(ahv)^2$ with respect to $hv$ on the x-axis and is found to be 1.62 eV which is comparable with the reported values. This value of the band gap energy for Sb$_2$S$_3$ microsphere is near the optimum value for photovoltaic conversion, suggesting that Sb$_2$S$_3$ microspheres are suitable for applications in solar energy and optoelectronics. It is also noted that these microspheres do not show quantum confinement effect,
a fact also established by these workers. This may be attributed to the lower Bohr’s radius of this material.

6.3.9. Photoluminescence spectroscopy (PL)

![Photoluminescence spectra of the Sb$_2$S$_3$ microspheres.](image)

Fig. 6.11. Photoluminescence spectra of the Sb$_2$S$_3$ microspheres.

A luminescence spectrum is important for evaluating the optical nature of the materials. The PL spectra of the Sb$_2$S$_3$ microspheres was recorded at different excitation wavelength 350, 400 and 430 nm, as shown in Fig. 6.11. The observed emission peak values for different excitation wavelength are given in Table 6.3.
Table 6.3. Emission peak values at three-excitation wavelength.

<table>
<thead>
<tr>
<th>Excitation wavelength</th>
<th>Peak1</th>
<th>Peak2</th>
<th>Peak3</th>
<th>Peak4</th>
</tr>
</thead>
<tbody>
<tr>
<td>350nm</td>
<td>384 V(3.23)</td>
<td>476 B(2.61)</td>
<td>574 Y(2.16)</td>
<td>667 R(1.86)</td>
</tr>
<tr>
<td>400nm</td>
<td>439 V(2.83)</td>
<td>545 G(2.27)</td>
<td>656 R(1.89)</td>
<td>762 R(1.63)</td>
</tr>
<tr>
<td>430nm</td>
<td>472 B(2.63)</td>
<td>586 Y(2.12)</td>
<td>646 R(1.92)</td>
<td>705 R(1.76)</td>
</tr>
</tbody>
</table>

From results shown in Table 6.3. and Fig. 6.11. It is clear that Sb$_2$S$_3$ microspheres are showing luminescent behavior in different regions of the spectrum and probably this property can be utilized for its further applications.

6.4. Conclusion

- Sb$_2$S$_3$ microspheres were successfully synthesized by solvothermal method using SbCl$_3$ and sulfur as raw materials.

- Sb$_2$S$_3$ microspheres of desired stoichiometry are obtained as shown in EDAX results.

- 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 indicating single crystalline nature of microspheres.
Chapter 6

➢ 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 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.
Chapter 6

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Chapter 6


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Chapter 6


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