5. THERMAL PROPERTIES

The thermal analyses carried out on the undoped samples prepared in the present study are dealt with in this Chapter.

5.1. Thermogravimetric Analysis (TGA)

Thermogravimetry (TG) or Thermogravimetric analysis (TGA) provides a quantitative measurement of any weight changes associated with thermally induced transitions. For example, TG can record directly the loss in weight as a function of temperature or time (when operating under isothermal conditions) for transitions that involve dehydration or decomposition. Thermogravimetric curves are characteristic of a given compound or material due to the unique sequence of physical transitions and chemical reactions that occur over definite temperature ranges. The rates of these thermally induced processes are often a function of the molecular structure. Changes in weight result from physical and chemical bonds forming and breaking at elevated temperatures. These processes may evolve volatile products or form reaction products that result in a change in weight of the sample. TG data are useful in characterizing materials as well as in investigating the thermodynamics and kinetics of the reactions and transitions that result from the application of heat to these materials. The usual temperature range for TG is from ambient to 1200°C in either inert or reactive atmospheres [212].

Thermogravimetric analysis was carried out for the undoped $(\text{CdS})_{1-x}(\text{MnS}_2)_x$ (where $x = 0.0, 0.25, 0.50, 0.75$ and 1.0) nanocomposites using a Perkin-Elmer apparatus.
5.2. Differential Thermal Analysis (DTA)

DTA is the simplest and most widely used thermal analysis technique. The difference in temperature, $\Delta T$, between the sample and a reference material is recorded while both are subjected to the same heating programme. If an endothermic thermal event ($\Delta H$ positive, such as melting) occurs in the sample, the temperature of the sample, $T_s$, will lag behind the temperature of the reference, $T_r$, which follows the heating programme. If the output from the thermocouples, $\Delta T = T_s - T_r$, is recorded against $T_r$ (or the furnace temperature, $T_f \sim T_r$). If an exothermic process ($\Delta H$ negative, such as oxidation) occurs in the sample, the response will be in the opposite direction. Such the definition of $\Delta T$ as $T_s - T_r$ is rather arbitrary, each DTA curve should be marked with either the endo or exo direction. The area under the endotherm (or exotherm) is related to the value of the enthalpy change, $\Delta H$, for the thermal event.

**The reference material should have the following characteristics**

(i) It should undergo no thermal events over the operating temperature range.

(ii) It should not react with the sample holder or thermocouple.

(iii) Both the thermal conductivity and the heat capacity of the reference should be similar to those of the sample [213].

Differential thermal analysis (DTA) was carried out for the undoped (CdS)$_{1-x}$(MnS)$_x$ (where $x=0.0$, 0.25, 0.50, 0.75 and 1.0) nanocomposites using a Perkin Elmer apparatus.
5.3. Results and Discussion

The thermogravimetric analysis (TGA) was carried out to understand the thermal stability of the as-prepared nanocomposite. Differential thermal analysis (DTA) was carried out to know the exothermal and endothermal process of the as prepared nanocomposite. The TG/DTA results of undoped (CdS)\(_{1-x}\) (MnS\(_2\)\(_x\)) (where x = 0.0, 0.25, 0.50, 0.75 and 1.0) nanocomposites are discussed here. The corresponding TG / DTA curves are shown in Figures 23-27.

The TG/DTA results for pure CdS nanocomposite are shown in Figure 23. In TGA the sample is found to be stable upto 250\(^\circ\)C. The 12% weight loss takes place between 251 and 300\(^\circ\)C due to the evaporation of the physically adsorbed water and hydroxyls contained in the sample. No weight loss takes place between 301 and 637\(^\circ\)C. There is a slight fall after 637\(^\circ\)C. In DTA curve the sample shows small endothermic peak at 290\(^\circ\)C. Above 291\(^\circ\)C an exothermic peak is seen. The pattern of DTA result is similar to that reported in the literature [214].

The TG/DTA results for (CdS)\(_{0.75}\) (MnS\(_2\)\(_{0.25}\)) nanocomposite are shown in Figure 24. In TGA, the sample is found to be stable up to 230\(^\circ\)C. The 20% weight loss takes place between 231 and 296\(^\circ\)C due to the evaporation of the physically adsorbed water and hydroxyls contained in the sample. No weight loss takes place between 297 and 641\(^\circ\)C. There is a slight fall after 641\(^\circ\)C. In DTA curve, the sample shows endothermic and exothermic peaks. The first endothermic peak at 150\(^\circ\)C is due to adsorption of water molecules. The small exothermic process takes place between 151 and 250\(^\circ\)C. The volatile substance, SO and H\(_2\)O are liberated. Two endothermal processes take place at 295.23 and 795.92\(^\circ\)C.
Figure 23: TG / DTA patterns for pure CdS nanocrystal

Figure 24: TG / DTA patterns for pure (CdS)_{0.75}(MnS)_{0.25} nanocrystal
Figure 25: TG / DTA patterns for pure (CdS)$_{0.50}$(MnS$_2$)$_{0.50}$ nanocrystal

Figure 26: TG / DTA patterns for pure (CdS)$_{0.25}$(MnS$_2$)$_{0.75}$ nanocrystal
A large exothermal process takes place between 300 and 650°C. The pattern of DTA is similar to that reported for in the literature [214]. The presence of CdS and MnS$_2$ compounds is confirmed by the TG/DTA results.

The TG/DTA results for (CdS)$_{0.50}$(MnS$_2$)$_{0.50}$ nanocomposite are shown in Figure 25. In TGA the sample is found to be stable up to 195°C. The 35% weight loss takes place between 196 and 310°C due to the evaporation of physically adsorbed water and hydroxyls contained in the sample. The second weight loss of 6% takes place between 311 and 500°C. In the third stage we find the presence of MnSO$_3$ compound in the sample [215]. Weight gain takes place between 500 and 850°C due to the reaction of the sample with the surrounding atmosphere. This also shows oxidation of the metal sample. Above 850°C the sample is decomposed. The DTA curve shows a very small endothermic peak at 180°C. A very large exothermal
process takes place above 180°C. The presence of MnSO₃ is confirmed [215]. An exothermal peak is seen at 333.79°C. The liberation of SO₂ and H₂O takes place above 180°C. The presence of CdS, MnS₂ and MnSO₃.H₂O is confirmed in the as-prepared nanocomposite by the TG / DTA results.

The TG/DTA results for (CdS)₀.₂₅ (MnS₂)₀.₇₅ nanocomposite are shown in Figure 26. In TGA, the sample is found to be stable up to 190°C. The 35% weight loss takes place between 191 and 310°C is due to the evaporation of physically adsorbed water and hydroxyls contained in the sample. The second weight loss of 10% takes place between 310 and 525°C. Presence of MnSO₃ is confirmed in the second weight loss [215]. The 8% of weight gain takes place between 526 and 800°C due to the oxidation of the metal present in the nanocomposite. The sample decomposes beyond 800°C. In DTA curve, a very small endothermic peak is found at 175°C. A very large exothermal process takes place above 176°C. In this exothermal process the liberation of SO₂ and H₂O is observed. In the DTA curve, an exothermic peak is seen at 343.25°C. The presence of CdS, MnS₂ and MnSO₃.H₂O compounds in the as-prepared sample is confirmed by the TG/DTA results.

The TG/DTA results for pure MnS₂ nanocomposite are shown in Figure 27. The sample is stable up to 70°C. 38% weight loss takes place between 71 and 320°C due to the evaporation of physically adsorbed water and hydroxyls contained in the sample. The second weight loss of 15% takes place between 321 and 690°C. In this temperature range MnSO₃ is present [215]. The 2% of weight gain takes place between 691 and 810°C. Above 810°C the sample decomposes. In the DTA curve the
sharp endothermic peak observed at 100°C is due to the adsorption of water molecules. Above 100°C the exothermal process takes place. The liberation of SO₂ and H₂O takes place above 100°C. The other two small endothermic peaks are observed at 321.60°C and 465.47°C. Above 466°C exothermal process takes place. The presence of MnSO₃.H₂O along with MnS₂ is confirmed in the TG/DTA results obtained for the as-prepared sample.

Table 16 : The observed DTA results for (CdS)₁₋ₓ(MnS₂)ₓ (where x=0.0, 0.25, 0.50, 0.75 and 1.0) nanocrystals

<table>
<thead>
<tr>
<th>Endotherm or Exotherm</th>
<th>Sample</th>
<th>CdS</th>
<th>(CdS)₀.₂₅(MnS₂)₀.₇₅</th>
<th>(CdS)₀.₅₀(MnS₂)₀.₅₀</th>
<th>(CdS)₀.₇₅(MnS₂)₀.₂₅</th>
<th>MnS₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iᵣ endotherm</td>
<td>peak at (°C)</td>
<td>-</td>
<td>295.23</td>
<td>-</td>
<td>-</td>
<td>321.60</td>
</tr>
<tr>
<td>Area (mJ)</td>
<td></td>
<td>-</td>
<td>434.85</td>
<td>-</td>
<td>-</td>
<td>318.175</td>
</tr>
<tr>
<td>Enthalpy ΔH(J/g)</td>
<td></td>
<td>-</td>
<td>74.8326</td>
<td>-</td>
<td>-</td>
<td>19.3482</td>
</tr>
<tr>
<td>IIᵣ Endotherm</td>
<td>peak at (°C)</td>
<td>-</td>
<td>795.92</td>
<td>-</td>
<td>-</td>
<td>465.47</td>
</tr>
<tr>
<td>Area (mJ)</td>
<td></td>
<td>-</td>
<td>659.729</td>
<td>-</td>
<td>-</td>
<td>848.202</td>
</tr>
<tr>
<td>Enthalpy ΔH (J/g)</td>
<td></td>
<td>-</td>
<td>113.5313</td>
<td>-</td>
<td>-</td>
<td>51.5792</td>
</tr>
<tr>
<td>Exotherm</td>
<td>peak at (°C)</td>
<td>-</td>
<td>-</td>
<td>333.79</td>
<td>343.25</td>
<td>-</td>
</tr>
<tr>
<td>Area (mJ)</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-8510.851</td>
<td>-20485.875</td>
<td>-</td>
</tr>
<tr>
<td>Enthalpy ΔH(J/g)</td>
<td></td>
<td>-</td>
<td>-</td>
<td>-1476.5504</td>
<td>-2857.0890</td>
<td>-</td>
</tr>
</tbody>
</table>

The particle size of the sample influences the DTA results. The smaller the particle size, the larger is the exothermic peak area of the DTA curve because the decomposition of a sample with a large particle size is slower than that of a sample with a large specific surface area [214, 216]. The observed peak areas of the DTA
curves of all the nanocomposites are very broad, which indicate that the size of the particles are very small. This also supports that the as-prepared nanocomposites are in nano-order ranges. Table 16 shows the peak area under the endotherm (or exotherm) which is related to the value of the enthalpy change $\Delta H$. 