CHAPTER 2

STRUCTURAL, SPECTRAL, THERMAL, MICRO HARDNESS, DIELECTRIC AND ETCHING STUDIES OF THIRD ORDER NONLINEAR OPTICAL MATERIAL CESIUM SULFAMATE

2.1 INTRODUCTION

The upcoming modern world requires large amounts of nonlinear optical (NLO) materials with high quality and good NLO responses for numerous optical device applications like optical switching, second and third harmonic generation, optical rectification and optical limiting, image processing, data storage, optical modulators and optical switches. Due to this reason many researchers have worked on developing new high quality NLO crystal in organic and inorganic crystals. When compared to organic counterparts the inorganic materials show high transmittance, good thermal and mechanical stability and easy to grow large size crystals and still inorganic NLO materials are used in the optical industry due to their high mechanical strength. Alkali halide materials consist of a monovalent cation (A+=Li+, Na+, K+, Rb+, Cs+,Ag+, NH4+, C(NH2)3+ or (CH3)3NCH2COOH+) and a sulfamate [NH2SO3]− anion are of great importance owing to their tremendous applications in the areas such as vacuum and gas based photon detectors, medical imaging, positron emission photography, UV detectors and photocathodes.
Cesium sulfamate is one such system which structure was previously reported by Schreuer. A through the literature shows that there is no other studies are available on this material. So, in the present investigation, we took an initiation to study its spectral, electrical, and thermal and Z-scan studies.

2.2 EXPERIMENTAL PROCEDURE

2.2.1 Material Synthesis

The good quality optical single crystals of Cesium Sulfamate were grown by slow evaporation solution growth technique. The chemicals used for the growth were Cesium Carbonate and Sulfamic acid of AR grade were taken in the molar ratio of 1:2 and dissolved in the deionised water solvent. Then the solution was stirred continuously for 3 hours using a magnetic stirrer to ensure the homogenous solution and finally it is filtered using Whatmann filter paper (No.42 grade) to remove the suspended impurities. The obtained filtrate was kept undisturbed dust free atmosphere for the growth of Cesium Sulfamate (CeS) crystals. Well-defined, colorless single crystals of title compound CeS were harvested after 30 days.

Figure 2.1 (a) The grown crystals of cesium Sulfamate crystal (b) BDFH Morphology diagram of Cesium Sulfamate Crystal
The Figure 2.1 (a) shows the obtained crystals of CeS with good transparency. The BDFH morphology was shown in Figure 2.1(b). The reaction scheme of CeS crystal is given below

\[ 2 \text{H}[\text{NH}_2\text{SO}_3] + \text{Cs}_2\text{CO}_3 \rightarrow 2 \text{Cs}[\text{NH}_2\text{SO}_3] + \text{H}_2\text{CO}_3 \]

2.2.2 Characterization Techniques

The harvested single crystal has been analyzed by different instrumentation methods in order to check its suitability for various applications. The as grown CeS single crystals were subjected to single crystal XRD using an Oxford-Diffraction X-Calibur with a sapphire CCD detector and enhance diffractometer (MoK\(\alpha\) radiation, graphite monochromator; \(\lambda=0.71073\)A). In order to confirm the presence of various functional groups the FTIR spectrum of CeS crystals was recorded in the wave number range 4000 - 400 cm\(^{-1}\) using SHIMADZU FTIR spectrometer. The TG/DSC analysis of Cesium Sulfamate crystals has been recorded using a simultaneous thermal analyzer Q600 SDT and Q20 instruments. The analysis was carried out from room temperature to 500 °C at a heating rate of 10°C in the atmosphere of nitrogen gas. Dielectric studies were carried out on the grown CT crystal using anHioki 3532-50 LCR meter at the frequencies in the range 50Hz to 5MHz at normal room temperature. The microhardness of the CeS crystal was measured using an HMV SHIMADZU microhardness tester. The etching patterns were observed using Magnus MLX computerized optical microscope attached with a high intense camera. The etching technique is used to visualize the dislocations in the single crystals. Nonlinear absorption coefficient (\(\beta\)), nonlinear refractive index (\(n_2\)) and third order nonlinear susceptibility (\(\chi^3\)) were estimated from the Z-scan studies.
2.3 RESULTS AND DISCUSSION

2.3.1 Single Crystal X-ray Diffraction Analysis

The single crystal XRD results indicate that the title compound belongs to the monoclinic system with a space group of P2₁/C. The lattice parameter values are found to be a= 8.204 Å; b = 7.625 Å; c = 8.410 Å. The volume of the CeS crystal was found to be 473 Å³. The obtained results are in good agreement with the earlier reported values (Haussühl 1995). The acquired and the reported values of CeS are given in Table 2.1.

Table 2.1 Comparison of single crystal XRD parameters of CeS with earlier results

<table>
<thead>
<tr>
<th>Serial No</th>
<th>Obtained Value (Å)</th>
<th>Reported Value (Å) (Haussühl, S. 1995)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unit Cell Parameters</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a= 8.204(2)</td>
<td>a= 8.205 (2)</td>
<td></td>
</tr>
<tr>
<td>b = 7.625(1)</td>
<td>b = 7.6246 (1)</td>
<td></td>
</tr>
<tr>
<td>c = 8.410 (2)</td>
<td>c = 8.400 (2)</td>
<td></td>
</tr>
<tr>
<td>Cell Volume</td>
<td>473 Å³</td>
<td>474 Å³</td>
</tr>
<tr>
<td>System</td>
<td>Monoclinic</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>P 2₁/C</td>
<td>P 2₁/C</td>
</tr>
</tbody>
</table>

2.3.2 FTIR Analysis for CeS

The FTIR analysis provides the information about the chemical bonding or molecular structure of CeS crystals. The recorded spectrum is depicted in Figure 2.2. from the figure the wave numbers 1122.63 cm⁻¹ and 1066.06 cm⁻¹ region is assigned to NH₂ stretching. It confirms the presence of amine group. The presence of sulfonyl group is confirmed from the peak values 1678.40 Cm⁻¹, 1637.46 cm⁻¹, 1607.23 cm⁻¹ and 1555.92 cm⁻¹ regions.
Thus, the disappearance of –OH peak indicates the formation of Cesium Sulfamate.

Figure 2.2 FTIR spectrum for Cesium Sulfamate Crystal

2.3.3 Thermal Analysis

The TG/ DSC and curves of CeS crystal are illustrated in Figure 2.3. In DSC there is a sharp endothermic at 228 °C is assigned to melting point of the compound which are fit well with the TG spectrum. TG curves indicate that there are no endothermic or exothermic transitions below the melting point. This shows that the material is moisture free and stable up to 228 °C. The sharpness of this endothermic peak shows the high degree of crystalline and purity of the sample. Also it confirms the absence of water molecules in the crystalline lattice.

TG measures the amount and the rate of weight (%) change of a material with respect to temperature. From the TG curve, the first stage of
decomposition is takes place from near 228°C up to 362°C, the weight loss is associated with the melting point of the compound and the second weight loss occurs between 410°C up to near 500°C due to the liberation of volatile substance like NH₂, N₂, NO and H₂.

The total decomposition of the compound is observed above 800°C. Further, it indicates spectacles that the material can be exploited for NLO applications up to 228 °C.

![Figure 2.3 TG/DSC thermogram of CeS](image)

**2.3.4 Vicker’s Microhardness Studies**

Vicker’s microhardness is one of the important mechanical properties of the crystal. Also, it gives a great role in the manufacturing of device fabrication. Vicker’s microhardness test is a microprobe technique for evaluating the bond strength, apart from being a measure of bulk strength. Highly transparent and well-polished crystals with crack free surface were selected for the microhardness measurements and the same crystal was
mounted on the base of the microscope. All the indentations were made at room temperature. The applied load P is varies between 10 to 25 g, and all the indentation time was kept as 9s for all the loads. The intended impression of Vicker’s was approximately square in shape. The shape of the impression is dependent on the structure, face and materials used. The Vicker’s microhardness number was calculated using the given expression

\[ H_v = 1.8554 \left( \frac{P}{d^2} \right) (kg/mm)^2 \]  

(2.1)

Where P is the applied load, d is the diagonal length of the indented impression (μm) and 1.8554 is a constant of a geometrical factor for the diamond pyramid. Figure 2.4 shows the Vicker’s microhardness number with applied load for CeS crystal. The elastic stiffness constant \( (C_{11}) \) were calculated using Wooster’s empirical relation. The calculated stiffness constant for different loads were shown in Table 2.2. The values of \( C_{11} \) give the idea of toughness of bonding between neighboring atoms. Here, the high values of \( C_{11} \) indicate the strong binding forces between the ions, while smaller values of \( C_{11} \) indicates the binding force between the ions are not quite as strong. Thus, the decrease of microhardness with load is attributed to the normal indentation size effect (ISE).

Table 2.2 Elastic stiffness constant for CeS crystals

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Load ( (10^3 \text{kg}) )</th>
<th>Hardness Values (Hv) ( \text{kg/mm}^2 )</th>
<th>( C_{11} \times 10^{14} \text{Pa} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>85.4</td>
<td>23.99</td>
</tr>
<tr>
<td>2</td>
<td>10</td>
<td>67.9</td>
<td>16.06</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>48.8</td>
<td>9.01</td>
</tr>
<tr>
<td>4</td>
<td>20</td>
<td>33.5</td>
<td>4.66</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>25.5</td>
<td>2.89</td>
</tr>
</tbody>
</table>
2.3.5 Dielectric Characterization

A study of the dielectric properties of solids gives information about the electric field distribution within the solid. The frequency dependence of these properties gives a great insight into the material’s applications. Also dielectric properties are correlated to the electro-optic property of the crystal. The different polarization mechanisms can be understood from the study of dielectric constant as a function of frequency and temperature.

The dielectric constant of the crystal was estimated from the measured capacitance by the following equation

$$\varepsilon_r = \frac{Cd}{\varepsilon_o A} \quad (2.2)$$
Where $C$ is the capacitance, $d$ is the thickness, $A$ is the cross sectional area and $\varepsilon_0$ is the free space permittivity of the sample. The plot of dielectric constant vs. frequency of CeS crystal at room temperature is shown in Figure 2.5. The dielectric constant has high values in the lower frequency region and decreases with an increase in frequency. The larger value of dielectric constant at low frequency region is ascribed to the existence of all the four types of polarizations namely electronic, ionic, orientation and space charge and its low value of high frequency is owing to the gradual significance loss of these polarizations. Space charge polarization is usually active in the low frequency region so it is very dominant in the present system.

![Graph showing dielectric constant vs log f](image)

**Figure 2.5 Dielectric constant vs log f**

The dielectric loss of the crystal with respect to frequency is shown in Figure 2.6. Dielectric loss is low in the high frequency region, which suggests that the crystal contains minimum defects. In the present investigation dielectric constant and loss values of the grown crystals were
found to be low, which is the suitable parameter for the electro-optical and microelectronics applications.

![Figure 2.6 Dielectric loss vs log f](image)

**Figure 2.6 Dielectric loss vs log f**

### 2.3.6 Chemical Etching Technique

The etching technique is the simplest characterization technique that can be used to visualize the dislocations in the single crystals. The etching patterns were observed using Magnus MLX computerized optical microscope attached with a high intense camera. Here, the etching pits were observed in CeS single crystal with water etchant for the time interval of 30 seconds, then immediately taken it out, the surface etchant was removed gently by using tissue paper and the recorded photograph was given in the Figure 2.7. From this figure, it is shown that the linear layered etch pits captured on the surface of the crystal due to reduced dislocation density. It gives the high crystalline nature of the material.
The third harmonic generation of the CeS crystals was measured by the Z-scan technique. Generally, this technique is used to determine both the nonlinear absorption coefficient ($\beta$) and nonlinear refraction ($n_2$). The nonlinear absorption can be measured by third order (z-scan) measurements. There are two processes adopted in the line of measurement. One is the open aperture technique in which the whole of the beam transmitted is detected and thus the light transmitted is absorbed by removing the aperture which sets up the transmittance to $S = 1$. Thus to observe two photon absorption, the nonlinear absorption coefficient $\beta$ is measured.

Whereas in the closed aperture technique, an aperture placed between the detector and the sample prevents the light to reach the detector. Hence the detector would be able to sense only...
the cone of the light from the central region. Hence the normalized transmittance would lie in the region to \(0.1 < S < 0.5\).

A CW He-Ne laser (\(\lambda = 632.8\) nm) with a repetition rate of 1 KHz was used as an excitation source. In this study, the sample has been translated to the Z-direction along the axis of a focused Gaussian beam and the far field intensity has been measured as a function of the sample position.

![Graph](image.png)

**Figure 2.8** (a) Normalized transmittance spectrum of CeS with open aperture
Figure 2.8 (b) Normalized transmittance spectrum of CeS with closed aperture

Figures 2.8 (a-b) shows the normalized transmittance $T$ with the open and closed aperture as a function of distance $Z$ along the lens axis in the far field. The peak and valley transmittance ($\Delta T_{p-v}$) difference is written in terms of phase shift $|\Delta \varphi|$.

$$\Delta T_{p-v} = 0.406 (1-S)^{0.25} |\Delta \varphi|$$  \hspace{1cm} (2.3)

Where, $\Delta \varphi$ is the on-axis phase shift and $S$ are the linear aperture transmittance and it is given by

$$S = 1 - \exp\left[-\frac{2r_a^2}{\omega_a^2}\right]$$  \hspace{1cm} (2.4)

Where, $r_a$ is the radius of aperture and $\omega_a$ is the beam radius at the aperture.

The third order nonlinear refractive index ($n_2$) was evaluated by the following relation

$$n_2 = \frac{\Delta \varphi}{k_l \lambda L_{eff}}$$  \hspace{1cm} (2.5)
Where, $k=2\pi/\lambda$, $\lambda$ is the wavelength of the laser, $I_o$ is the on-axis irradiation at the focus ($Z=0$) and $L_{\text{eff}}$ is the effective thickness of the sample.

\[
L_{\text{eff}} = \frac{1-e^{(-\alpha L)}}{\alpha}
\]  

(2.6)

Where, $\alpha$ is the linear absorption coefficient and $L$ is the thickness of the sample. From the open aperture curve nonlinear optical absorption coefficient ($\beta$) was evaluated

\[
\beta = \frac{2\sqrt{\Delta T}}{I_o L_{\text{eff}}}
\]  

(2.7)

The real and imaginary parts of the third order nonlinear optical susceptibility were determined by the following relations

\[
Re\chi^{(3)}(\text{esu}) = 10^{-4} \left(\frac{\varepsilon_0 c^2 n_0^2}{\pi} \frac{n^2}{W}\right)
\]  

(2.8)

\[
Im\chi^{(3)}(\text{esu}) = 10^{-2} \left(\frac{\varepsilon_0 c^2}{4\pi} \frac{\lambda^2 \beta}{n^2} \right) \left(\frac{cm}{W}\right)
\]  

(2.9)

Where, $\varepsilon_0$, the vacuum permittivity, $C$ is the velocity of light in vacuum. The absolute value of $\chi^{(3)}$ was obtained from the following relation

\[
\left|\chi^{(3)}\right| = \left[(Re\chi^{(3)})^2 + (Im\chi^{(3)})^2\right]^{1/2}
\]  

(2.10)

The values of nonlinear refractive index ($n_2$), nonlinear absorption coefficient and third order susceptibility of CeS are $3.4 \times 10^{-8}$ cm/W and $0.0001297 \text{cm}^2/\text{W}$ and $9.26 \times 10^{-8}$ esu indicates that the material reveals a positive refractive index, it results in the self-focusing nature and exhibits the two-photo absorption process of the crystal. This is one of the essential parameters for optical limiting applications. The evaluated third order nonlinear properties were listed in Table 2.3.
Table 2.3 Evaluated third order nonlinear properties of CeS crystal

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Laser Beam Wavelength (λ)</td>
<td>632.8 nm</td>
</tr>
<tr>
<td>Laser Power (P)</td>
<td>35 mW</td>
</tr>
<tr>
<td>Lens Focal length (f)</td>
<td>24 cm</td>
</tr>
<tr>
<td>Optical Path Distance (Z)</td>
<td>175 cm</td>
</tr>
<tr>
<td>Incident intensity at the focus at (Z = 0)</td>
<td>2 m W/cm²</td>
</tr>
<tr>
<td>Aperture radius of detector for closed (r_a)</td>
<td>4 mm</td>
</tr>
<tr>
<td>Aperture radius of detector for open (r_a)</td>
<td>30 mm</td>
</tr>
<tr>
<td>Effective thickness L_{eff} of the sample</td>
<td>1.95 mm</td>
</tr>
<tr>
<td>Nonlinear refractive index (n_2)</td>
<td>3.42 \times 10^{-8} Cm²/W</td>
</tr>
<tr>
<td>Nonlinear Absorption Coefficient (β)</td>
<td>0.0001297 Cm/W</td>
</tr>
<tr>
<td>Third-order nonlinear optical susceptibility (χ_3)</td>
<td>9.26 \times 10^{-8} esu</td>
</tr>
</tbody>
</table>

2.4 CONCLUSIONS

Optically transparent single crystals of Cesium sulfamate were grown by slow evaporation solution growth method at room temperature using deionised water as a solvent. The crystal parameters, Cell volume, system and space group were found is good agreement with that reported values. Single crystal XRD reveals that grown CeS crystallizes in monoclinic with the space group of P2_1/c at the room temperature. The vibrational frequencies are from FT-IR spectral analysis, which confirms the presence of sulfonyl functional groups of the cesium sulfamate material. The thermal studies confirm that the crystal structure is stable up to 228°C and designates its suitability for various applications. The micro hardness study exhibits the decrease of microhardness with load with the normal indentation size effect (ISE). The low value of dielectric constant and dielectric loss at high frequencies suggests that the crystal can be highly suitable for electro-optic and microelectronic applications. From the etching studies, the linear etch pits which were captured on the surface of the crystal is due to reduced dislocation density. Z-scan studies show the self-focusing nature of the material, which is a vital property for all optical switching and optical limiting applications.