CHAPTER VII

SEMIORGANIC NONLINEAR OPTICAL L-LYSINE SULPHATE

GROWTH AND CHARACTERIZATION

ABSTRACT

L-lysine sulphate (LLS), a semiorganic nonlinear optical (NLO) material useful for frequency doubling in the IR region, has been synthesized. The solubility studies have been carried out in the temperature range 30 - 50°C. Single crystals have been grown by slow evaporation method from an aqueous acetone solution of L-lysine and sulphuric acid. The grown crystals were bulk, bright and transparent. These crystals were characterized by X-ray and FTIR studies. Powder X-ray pattern indicates that LLS crystallizes in orthorhombic space group P2₁2₁2₁ with four unit cells. FTIR spectral studies were performed for conformation of the L-lysine molecule and hydrogen bonds. The optical transmission spectra of the grown crystal are tested by UV – vis spectrophotometer and found that the crystal was transparent over entire visible region. The second harmonic generation test of the LLS revealed the nonlinear nature of the crystal.
CHAPTER VII

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7.1 INTRODUCTION

In recent years the need of nonlinear optical materials is much more than other materials because of their applications in optoelectronics and photonics [79]. Second order nonlinear optical materials have recently attracted much attention because of their potential applications in emerging optoelectronic technologies [145,146]. Materials with large second order optical nonlinearities, short transparency cutoff wavelength and stable physicothermal performance are needed in order to realize many of these applications. Especially the organic NLO crystals are attracted attention because of the low cost and flexibility of molecular design, which we need for applications with using suitable donor and acceptor. Organic crystals are having some special properties of large optical nonlinearity and low cut-off wavelengths in UV region, therefore the organic NLO crystals are required for use in optical devices. Organic materials are often formed by weak vander Waals and hydrogen bonds and hence possess a high degree of delocalization. However, these organic crystals have certain limitations such as poor mechanical and thermal stability. To overcome these problems, the research of combination of organic and inorganic hybrid compounds leads to find a new class of materials for electronic industries, called semi-organic materials. In semi-organic materials the organic ligand is ionically bonded
with inorganic host, because of this, the new semi-organic crystals are having higher mechanical strength and chemical stability. The semi-organic crystals possess several attractive properties such as high damage threshold, wide transparency region and high nonlinear coefficient [147]. The contribution from the delocalized \(\pi\) - electrons belonging to the organic ligand results in wide optical transmittance and high nonlinear electro – optic coefficients. Many device applications of NLO require single crystals in the bulk form. This is achieved only with the semiorganic crystals, which exhibit wide transparency, large and bulky crystal morphologies. L - lysine sulphate is a semiorganic NLO material possessing large value of hyperpolarizability. Though the structure of LLS was reported earlier by S.Capasso et al [148], we are first reporting its growth technique, vibrational analysis, nonlinear properties.

7.2 EXPERIMENTAL DETAILS

Material synthesis and crystal growth

LLS crystals were grown by slow evaporation solution growth technique. Crystals obtained from an aqueous acetone solution of L-lysine and sulphuric acid, according to the equation

\[
C_{6}H_{14}N_{2}O_{2} + H_{2}SO_{4} \rightarrow C_{6}H_{16}N_{2}O_{2}^{2+} \cdot SO_{4}^{2-}
\]

Equimolar quantities of high purity L - lysine salts and analar grade sulphuric acid were dissolved in a mixture of acetone and water (1:1). After a week, salts of LLS were synthesized. The solubility of the synthesized material was investigated at different temperature in a mixture of acetone -
water and plotted in Fig. 7.1. The solution of LLS was slightly heated and kept in undisturbed condition. The synthesized salt was further purified by successive recrystallization and utilized for bulk growth of LLS. The supersaturation containing the recrystallized salt of LLS saturated at 40°C with optimized pH value. In order to obtain the optimum supersaturation at this temperature, the solution was tested by checking the dissolution of grown crystal over a period of a week. The crystals with perfect shape and free from macro defects were formed by spontaneous nucleation in the saturated solution at room temperature. After a week, transparent, colorless, bulk crystals of pyramidal shape with a well developed pinnacoids with a dimension of 12mm x 11mm x 5mm were harvested. The photograph of the grown crystal is shown in Fig. 7.2.

7.3 SPECTRAL MEASUREMENTS

Single crystal X-ray diffraction measurements

Well developed single crystal of LLS was mounted in random orientation on a goniometer head. Diffraction data were collected on a Enraf Nonius CAD4 diffractometer equipped in the graphite monochromated Mo Kα radiation (λ=0.71 – 0.73 Å) by using an ω scan technique. From the diffraction analysis, it has been found that the title compound crystallizes in orthorhombic system. The lattice parameters of the title crystals are in good agreement with the values reported by [148]. Table. 7.1 summarizes the crystallographic data of LLS. XRD diffraction analysis shows that it belongs to the space group P2₁2₁2₁ with four unit cells. The side chain of the L-lysine molecule adopts an unusual folded conformation, which allows
specific ion-pair interactions between the sulphate anion and the α- and ε-NH₃⁺ groups of the same molecule. This conformation might be found in proteins with an N-terminal lysine crystallized from ammonium sulphate solutions.

**FTIR measurements**

The Fourier transform infrared spectrum of the title crystal was recorded in the region 400 – 4000 cm⁻¹ using Perkin Elmer Spectrum RX1 spectrophotometer equipped with He–Ne laser source, KBr beam splitter and LiTaO₃ detector. The sample was prepared by pressing LLS with KBr into pellet form. The observed spectrum is shown in Fig. 7.3.

**7.4 RESULTS AND DISCUSSION**

**Crystal structure**

X-ray analysis has shown that LLS is held together by a complex network of hydrogen bonds. In the present structure the L-lysine molecule carries two positive charges at the α- and ε-amino groups, balanced by the two negative charges of the sulphate anion. The X-ray analysis clearly indicates the presence of the H atom attached to O of the carboxylic group and hydrogen bonded to O of the sulphate anion. This structural property makes this material as interesting system to observe the vibrational motion of hydrogen bonds. Vibrational modes are classified are assigned to vibrational frequencies of amino and carboxyl groups. The compound LLS crystallizes in the P2₁2₁2₁ space group with orthorhombic geometry. The crystal has four formula units. The specific interaction involves the
electrostatic attraction between the two positively charged – \( \text{NH}_3^+ \) groups and the negatively charged \((\text{SO}_4)^{2-}\) and also two N –H ...O hydrogen bonds. This interaction might be found in proteins with an N – terminal lysine crystallized from ammonium sulphate solutions. The crystal structure is stabilized by ionic interactions and hydrogen bonds. There are seven hydrogen bonds in the asymmetric unit of the crystal structure, one involving each hydrogen atom covalently bonded to N or O. The three H atom of the \( \varepsilon \)-amino groups are donated to O of three different sulphate ions. A similar situation occurs for the \( \varepsilon \)-\( \text{NH}_3^+ \) group. The strongest hydrogen bond connects the carboxylic – OH group to O of the sulphate anion.

**Vibrational analysis**

**\( \text{NH}_3^+ \) group vibrations**

The \( \text{NH}_3^+ \) group, which forms a part of the crystal has \( C_{3v} \) symmetry in the free state with a pyramidal structure [42]. Its normal modes of vibrations are \( v_1 \) (\( A_1 \)), \( v_2 \) (\( A_1 \)), \( v_3 \) (\( E \)) and \( v_4 \) (\( E \)). Among these vibrations the symmetric stretching and bending modes (\( v_1 \) and \( v_2 \)) are non degenerate where as asymmetric stretching and bending modes (\( v_3 \) and \( v_4 \)) are doubly degenerate. All these modes are IR active. The weak band at 3379 cm\(^{-1} \) in the FTIR is assigned to the asymmetric vibrations of the \( \text{NH}_3^+ \) group. The symmetric stretching vibrations are found at 3086 cm\(^{-1} \) as a medium band in FTIR. As all the three N-H bands of the amino group take part in intermolecular hydrogen bonding, the wavenumber of the stretching vibration is lowered. The appearance of medium band at 2824 cm\(^{-1} \) and the
splitting of degenerate mode suggest that the symmetry of NH$_3^+$ group is lowered from C$_{3v}$ to C$_1$ in the crystal. Further N-H...O hydrogen bond will cause the elongation in the cationic part of the complex due to transfer of the charge from the lone pairs of the electron. This principal effect of elongation is immediately followed by the structure shake-up of the cation leading to its concomitant blue shift in the N-H stretching wave number. The in phase displacement of three hydrogen atom of NH$_3^+$ changes the electronic environment of the lysine residues.

**Internal vibrations of SO$_4$ group**

The normal modes of vibration in an isolated SO$_4$ tetrahedron can be identified by the presence of two strong bands in the 1415 -1300 cm$^{-1}$ and 1200 - 1120 cm$^{-1}$ regions, due to the asymmetric and symmetric stretching vibrations respectively. The SO$_4$ observed in the LLS structure has the lower local symmetry Cs. This symmetry lowering gives rise to the splitting of the degenerate IR modes and activates the inactive ones. The bands are observed at 1428, 1353, 1216 and 1178 cm$^{-1}$. This corroborates the symmetry lowering of SO$_4$ in the solid state. This clearly indicates the deviation of the ideal symmetry of the (SO$_4$)$^{2-}$ ion in this crystal. All the other observed modes are assigned and presented in Table 7.2.

### 7.5 OPTICAL TRANSMISSION SPECTRUM

The transmission spectrum is shown in Fig. 7.4. The title crystal possesses good stability and do not show any hygroscopic effect for a long time. The transmission near the Nd: YAG laser fundamental (1064 nm) and
second harmonic wavelength (532 nm) is reduced which contributes the resistance of the material to laser damage threshold. The useful transmission range makes it valuable for applications that require blue green light [149]. This made us to come to a tangible conclusion that the material is better entrant for nonlinear optical applications. A major objective of this study was to determine the magnitude and the nature of the optical energy band gap. Hence the optical band gap study was performed for the title NLO crystal by considering the UV absorption edge around 240 nm. From the wavelength corresponding to the band gap of the material a sudden rise in absorption is noted. The threshold at which the absorption data showing an abrupt rise is determined graphically and it can be the band gap of the material [108]. The variation of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) in the fundamental absorption region are plotted in the Fig. 7.5. The extrapolation of the curve to zero $(\alpha h\nu)^2$ is direct band gap character around 5.2 eV. The energy gaps of semiconductors are much smaller than those of the semiorganic crystals. Since the material is wide band gap material the crystal under study has large transmittance in the visible region, which enables the material for higher harmonic generation.

**Hardness studies**

One of the important properties of any device material is its mechanical strength, represented by its hardness. Physically hardness is the resistance offered by a material to localized plastic deformation (moment of dislocations) caused by scratching or by indentation. This resistance is the intrinsic property of the crystal. The hardness is generally measured as
the ratio of applied load to the surface area of the indentation. Indentation hardness measurement can, in principle, be carried out at fairly high loads (~ 100 Kg). But for materials which have low hardness and which are available as small-sized sample, it is convenient to make measurements at low loads of < 200g. The low load hardness is called microhardness. The grown crystal with smooth and dominant face (001) was selected for microhardness studies. Indentations were carried out using Vickers indentor for varying loads (25-300 g), for each load, several indentations were made and the average value of diagonal length was used to calculate the microhardness. In ideal circumstances, measured hardness values should be independent of the applied load. But in practice, load dependence is observed. Vickers microhardness number was determined using $H_v = 1.8544 \frac{P}{d^2} \text{Kg/mm}^2$. The hardness number was found to increase with the load upto 200g and after a load of 200g $H_v$ suddenly decreases as cracks developed in the material. This may be due to the release of internal stresses generated locally by indentation. The plot drawn between the corresponding loads and hardness values of the LLS is shown in Fig. 7.6.

7.6 SECOND HARMONIC GENERATION EFFICIENCY

The quadratic NLO property was confirmed and the SHG relative efficiency in the powdered form was measured obeying the Kurtz Perry method [58]. The schematic diagram of the experimental set up is reported earlier [150]. KDP crystal was powdered to the identical size and was used as reference materials in the SHG measurement. The nonzero measured powder SHG signal is consistent with the SHG activity predicted from the
noncentrosymmetric crystal structure. The SHG relative efficiency of LLS with that of KDP has been measured. It is found that the efficiency of the title crystal (15 mV), which is 60 percent to that of KDP (9 mV). The result of SHG is also encouraging. This proposes the title crystal for capable applications in optoelectronics technology.

7.7 CONCLUSIONS

The nonlinear optical properties of LLS crystal has been investigated for the purpose of assessing the possibility for SHG applications. X-ray analysis confirms the noncentrosymmetric arrangement of crystal structure belonging to \( \text{P2}_1\text{2}_1\text{2}_1 \) space group. The IR spectral study enabled us to determine \( \text{SO}_4^{2-} \) vibrations. High frequency shift and good NLO property and other physicochemical properties make this material a good laser converter. It has been found that there is a network of hydrogen bonds in crystal that stabilizes its structure. From the optical assessment, LLS is a promising new nonlinear-optical crystal for frequency upconversion in the UV region of high-power laser sources.
**Table. 7.1**

Crystallographic data of C$_6$H$_{16}$N$_2$O$_2$$^{2+}$ . SO$_4$$^{2-}$

<table>
<thead>
<tr>
<th>Identification code</th>
<th>LLS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C$<em>6$H$</em>{16}$N$_2$O$_2$$^{2+}$ . SO$_4$$^{2-}$</td>
</tr>
<tr>
<td>Formula weight</td>
<td>244</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Space group</td>
<td>P2$_1$2$_1$2$_1$</td>
</tr>
<tr>
<td>Cell parameters</td>
<td></td>
</tr>
<tr>
<td>a(Å)</td>
<td>5.573</td>
</tr>
<tr>
<td>b(Å)</td>
<td>11.536</td>
</tr>
<tr>
<td>c(Å)</td>
<td>16.594</td>
</tr>
<tr>
<td>α(°)</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
</tr>
<tr>
<td>Volume (Å$^3$)</td>
<td>1066.8304</td>
</tr>
<tr>
<td>Z</td>
<td>4</td>
</tr>
<tr>
<td>Crystal size</td>
<td>12 x 11 x 5 mm$^3$</td>
</tr>
<tr>
<td>UV cut off length</td>
<td>240 nm</td>
</tr>
<tr>
<td>Band gap</td>
<td>5.2 eV</td>
</tr>
<tr>
<td>Hygroscopicity</td>
<td>Non hygroscopic</td>
</tr>
</tbody>
</table>
Table. 7.2  
Observed IR bands of LLS and its assignments

<table>
<thead>
<tr>
<th>FTIR</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>wavenumber(cm⁻¹)</td>
<td></td>
</tr>
<tr>
<td>3379 w</td>
<td>$v_{as}$(NH₃⁺)</td>
</tr>
<tr>
<td>3086 m</td>
<td>$v_s$ (NH₃⁺), $\nu$C-(OH)</td>
</tr>
<tr>
<td>2824 m</td>
<td>$v_s$ (NH₃⁺)</td>
</tr>
<tr>
<td>2736 s</td>
<td>$v_s$ (C – H)</td>
</tr>
<tr>
<td>2414 w</td>
<td>Overtones and combinations</td>
</tr>
<tr>
<td>1616 m</td>
<td>$\rho$ (NH₃⁺)</td>
</tr>
<tr>
<td>1428 s</td>
<td>$\tau$(NH₃⁺)</td>
</tr>
<tr>
<td>1353 s</td>
<td>$v_s$ (C – O)</td>
</tr>
<tr>
<td>1216 vs</td>
<td>$v_s$ (C-(OH))</td>
</tr>
<tr>
<td>1178 s</td>
<td>$\delta_{in\ plane}$(C-H)</td>
</tr>
<tr>
<td>1100 m</td>
<td>$\delta_{in\ plane}$(C-H)</td>
</tr>
<tr>
<td>1026 m</td>
<td>$v_s$ (C – C), $\nu$(C – N)</td>
</tr>
<tr>
<td>919 m</td>
<td>$\nu_{ring}$(C – C)</td>
</tr>
<tr>
<td>860 m</td>
<td>$\nu_{ring}$ (C – C)</td>
</tr>
<tr>
<td>761 m</td>
<td>$\delta$(C – N)</td>
</tr>
<tr>
<td>685 m</td>
<td>(COO⁻) scissoring $\delta_{in\ plane}$ (C-C-C)</td>
</tr>
<tr>
<td>590 w</td>
<td>$\delta_{in\ plane}$ (C-C=O), $\tau$ (NH₃⁺)</td>
</tr>
<tr>
<td>510 m</td>
<td>$\rho$(COO-)</td>
</tr>
<tr>
<td>452 w</td>
<td>$\delta_{in\ plane}$ (C-C=O)</td>
</tr>
</tbody>
</table>

vs, very strong; s, strong; m, medium; w, weak.
$v_s$, symmetric stretching; $v_{as}$, asymmetric stretching; $\rho$, rocking;
$\delta$, deformation; $\tau$, torsion.
Fig. 7.1 Solubility curve of LLS

Fig. 7.2 Photograph of LLS grown in aqueous acetone solution
Fig. 7.5. Plot of $(\alpha \nu)^2$ versus photon energy ($\nu$)

Fig. 7.6. Mechanical behaviour of LLS
REFERENCES


