CHAPTER - V

GROWTH AND CHARACTERIZATION OF ETHYLENE DIAMINE TETRA ACETATE DOPED LITHIUM SULPHATE MONOHYDRATE (ELSMH) CRYSTALS

5.1. INTRODUCTION

As organic materials possess good optical transmission characteristics, ultrafast nonlinear response time and high optical damage threshold, they attracted chemists and material scientists. But organic materials are soft in nature due to weak Vander Walls and hydrogen bonds with conjugated π-electrons by which these materials are constituted. So, it is difficult to polish these materials for device applications. Moreover these materials have more absorption in UV region. Due to these difficulties, the search for new frequency conversion materials has led to the growth of new class of materials such as metal organics or semi organics [1]. Semi organic NLO crystals have both the properties of organic and inorganic materials. Ideally, the large nonlinearities of π-conjugated organics and the favourable crystal growth characteristics and mechanical properties of ionic salts have led into a semi organic NLO crystal. Hence, in recent years there has been considerable interest on the synthesis of semi organic nonlinear optical materials with excellent second-order optical nonlinearities because of their potential applications in telecommunication, optical computing, optical data storage and optical information processing [2].

Doping on pure crystals by foreign impurities is increasingly interesting because of the fact that dopants may significantly change the properties. Unknown impurities present in growth medium or known impurities intentionally added to it, generate new chemical interactions. Apart from purely electrostatic forces, these
chemical interactions include covalent, Vander Waals and hydrogen bonds. Description of the action of impurities at the atomic level relies on our understanding of how these interactions work in the bulk mother phase and at the crystal fluid interface. Due to the specificity of chemical bonds, the differences in the observed effect of a given set of related impurities are usually caused by differences in the chemical affinity of the impurity towards some components of the system. In some cases, the effect of an impurity is modified by changes in temperature and pressure or by the presence of other impurities in the system. This type of modification in the activity of the impurity is associated with the modified interactions due to changes in growth conditions. In general, interfacial properties are more sensitive to the presence of impurities due to their tendency to adsorb on all the surfaces present.

Bulk properties are also modified by the presence of impurities, but to a lesser extent than the surface properties unless a high concentration (several per cent) of the impurity is added to the system. Rajasekaran et al. [3] investigated the impurity effects with different dopant such as lithium, sodium, rubidium and cesium on KDP crystal and compared with pure KDP. It is reported that the hardness is high for heavier metal ions (Rb and Cs) doped KDP crystals and the hardness is low for lighter ion (Li and Na) doped KDP crystals. By analyzing the influence of urea on the optical, nonlinear and strength characteristics of KDP crystals, Podder [4] showed urea-doped KDP crystals to have a higher mechanical strength in comparison with the pure crystals. Pritula et al. [5] reported the structural, optical and strength characteristics of KDP crystals grown from the solutions doped with urea. It is reported that second harmonic generation efficiency increased in comparison with that of pure KDP crystal by approximately 20 per cent.
Many authors have reported the investigations on KDP crystals doped with various amino acids [6-14]. It has been reported that doping of L-arginine in KDP increases NLO properties of KDP in terms of increase in second harmonic generation efficiency [15]. It is known that organic impurity may influence the growth habit, surface phenomena and structural defects as well as optical quality of the crystals [16]. Most of the amino acids itself exhibit nonlinear optical properties due to donor amino group NH$_3^+$, acceptor carboxyl group COO$^-$ and intermolecular charge transfer is also possible [17]. Therefore amino acids can be used as dopants and it is observed that there is enhancement in the material properties such as nonlinear optical and ferroelectric properties [18]. Several dopants can affect the structure and physical properties of the host compounds [19-23]. Many researchers have reported the semiorganic crystals doped with various amino acids [24-26]. Among these, at present, inorganic crystals such as lithium iodate (LiIO$_3$), lithium niobate (LiNbO$_3$) and lithium tantalate (LiTaO$_3$) have attracted much attention due to their potential applications. Balakrishnan et al., Suresh Kumar et al., Dhanraj et al. and Pasupathi et al. have grown crystals based on lithium complexes which possess NLO property [27-29]. Motivated by the above considerations, in the present chapter, Ethylene Diamine Tetra Acetate (EDTA) doped Lithium Sulphate Mono Hydrate crystals (ELSMH) have been grown and reported in detail.

Nearly hundred years ago Groth (1908) had described the lithium sulphate monohydrate Li$_2$SO$_4$.H$_2$O, with its monoclinic point group [30]. It has remarkable piezo electric and electro-optic properties. The crystal is also having high pyroelectric coefficient among the group of non-ferroelectric polar crystals [31,32]. The dopant
EDTA is an artificial amino acid and it usually binds to a metal cation through its two amines and four carboxylates, that is, (4 oxygen atoms from carboxylate groups and 2 nitrogen atoms from amino groups) [33,34].

In this work, we report on the growth and characterization of EDTA doped lithium sulphate monohydrate crystals by slow evaporation technique, as no reports are available on the growth and characterization of our title crystal with EDTA as dopant. Hereafter, the grown semi organic crystals are named as ELSMH (EDTA doped Lithium Sulphate Mono Hydrate).

5.2. EXPERIMENTAL TECHNIQUE

EDTA doped lithium sulphate monohydrate (ELSMH) single crystals are grown from anlar grade lithium sulphate monohydrate and ethylene diamine tetra acetate. Using doubly distilled water, the super saturated lithium sulphate monohydrate is prepared. The parent and dopant (lithium sulphate monohydrate, EDTA) are added in the ratio 1: P, where P=0.01, 0.02, 0.03, and 0.04 with pH=5.0, 5.3, 5.6 and 5.9 and respectively. The pH variations are carried out using dilute sulphuric acid. The solution is filtered using (Whatman no. 450) filter paper and tightly closed for controlled evaporation of the solvent. Slow evaporation of the solvent produced ELSMH crystals in a time span of 20-24 days. Good transparent harvested single crystals are as shown in Fig. 5.1.

Fig. 5.1: As grown ELSMH Crystals
When the solution is at pH 5.0 and parent dopant molar ratio is 1:0.01, it is observed that the crystal growth rate and the quality of the crystal are much better. It is found that pH value of the solution has a strong effect on the formation of ELSMH crystals [35]. The minute amounts of EDTA can effectively suppress the impurities and promote the crystal quality. Higher dopant concentration may lead to the formation of structural grain boundaries, which in turn may lead to deterioration of crystal perfection. The observed results are in good agreement with the reported observations [36-39].

RESULTS AND DISCUSSION
5.3. X-RAY DIFFRACTION STUDIES

The BRUKER NONIUS CAD4 single crystal X-ray diffractometer is used to record the single crystal X-ray diffraction (XRD) pattern and also powder XRD pattern (Fig. 5.2) is recorded using RICH-SEIFERT powder diffractometer with Cu Kα radiation (λ=1.5405Å). The single crystal XRD result confirms the grown ELSMH crystal belongs to the monoclinic system with the lattice parameter values, a=5.443(3) Å, b=4.863(1) Å, c=8.150(3) Å, V=206.0(2) Å³, β=107.32°

The lattice parameters from the powder XRD pattern are calculated with the help of the computer program, TJB Holland and SATRED FERN 1995. The lattice parameters of both powder XRD and single crystal XRD of the grown ELSMH are shown in Table 5.1. The observed 2θ, d and calculated hkl indices of the corresponding reflecting planes are shown in Table 5.2. Powder XRD has the highest intensity (14640) corresponding to 101̅ plane with 100 as it I/I₀ value.
G.E. Ziegler in Chicago, has investigated the structure of Li$_2$SO$_4$H$_2$O as monoclinic system with space group $C_2^2$ ($P2_1$) (x, y+1/2, z). The structure is characterized by tetrahedra of oxygen surrounding the sulphur and lithium atoms [30].

![Fig. 5.2: Powder XRD Pattern of ELSMH Crystal](image)

**Table 5.1: Comparison of Lattice Parameters of ELSMH**

<table>
<thead>
<tr>
<th></th>
<th>$a$</th>
<th>$b$</th>
<th>$c$</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Single crystal</td>
<td>5.457</td>
<td>4.874</td>
<td>8.149</td>
<td>90</td>
<td>107</td>
<td>90</td>
<td>216.78</td>
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<tr>
<td>Powder XRD</td>
<td>5.443</td>
<td>4.863</td>
<td>8.150</td>
<td>90</td>
<td>107.32</td>
<td>90</td>
<td>215.72</td>
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Table 5.2: X-ray powder diffraction data of ELSMH

<table>
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<tr>
<th>2θ(°)</th>
<th>d(Å)</th>
<th>hkl</th>
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<tr>
<td>11.280</td>
<td>7.8378</td>
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</tr>
<tr>
<td>16.940</td>
<td>5.2296</td>
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<td>17.520</td>
<td>5.0578</td>
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<td>21.580</td>
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<td>22.840</td>
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<td>002</td>
</tr>
<tr>
<td>23.220</td>
<td>3.8275</td>
<td>101</td>
</tr>
<tr>
<td>24.940</td>
<td>3.5673</td>
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<td>25.080</td>
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<td>110</td>
</tr>
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<td>29.320</td>
<td>3.0436</td>
<td>012</td>
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<tr>
<td>30.420</td>
<td>2.9360</td>
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<td>32.980</td>
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<td>38.540</td>
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<td>70.760</td>
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5.4. FT-IR SPECTRAL ANALYSIS

The FT-IR spectrum of ELSMH is recorded in the range 400-4000 cm\(^{-1}\) using Perkin-Elmer spectrometer (KBr pellet technique) and its frequencies are compared with that of pure lithium sulphate monohydrate [LSMH]. It is seen that the recorded ELSMH spectrum is having the same absorption peaks with slightly different frequencies. It is also observed that there are some more extra peaks in the ELSMH spectrum, which are absent in LSMH (parent). The functional groups present in the title compound have been identified from the transmission spectra of ELSMH, LSMH and EDTA are as shown in Figs. 5.3a, 5.3b and 4.4c, respectively. The characteristic peak due to COO\(^-\) of carboxylate ion group is exhibited in EDTA and ELSMH is at 1624 and 1616 cm\(^{-1}\) respectively. The OH bending frequencies are obtained at 650, 643 and 645 cm\(^{-1}\) of dopant, parent and the grown sample respectively [39-45]. The SO\(_4\) stretching frequencies of LSMH and ELSMH are assigned at 486 and 485 cm\(^{-1}\). Similarly, the bending frequencies of both are at 421 and 425 cm\(^{-1}\). The comparative FT-IR vibrational frequencies are given in Table 5.3.
Table 5.3: Functional group Assignment of ELSMH in cm\(^{-1}\)

<table>
<thead>
<tr>
<th></th>
<th>EDTA</th>
<th>LSMH</th>
<th>ELSMH</th>
<th>Tentative group assignment</th>
</tr>
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<tr>
<td>3516</td>
<td>---</td>
<td>3524</td>
<td></td>
<td>NH bending</td>
</tr>
<tr>
<td>1624</td>
<td>---</td>
<td>1616</td>
<td></td>
<td>COO(^{-})carboxylate ion stretching</td>
</tr>
<tr>
<td>1383</td>
<td>1383</td>
<td>1365</td>
<td></td>
<td>OH stretching</td>
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<tr>
<td>648</td>
<td>643</td>
<td>645</td>
<td></td>
<td>OH bending</td>
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<tr>
<td>---</td>
<td>486</td>
<td>485</td>
<td></td>
<td>SO(_4) stretching</td>
</tr>
<tr>
<td>---</td>
<td>421</td>
<td>425</td>
<td></td>
<td>SO(_4) bending</td>
</tr>
</tbody>
</table>

Fig. 5.3a: The Recorded FT-IR Spectrum of ELSMH
5.5. UV-VIS-NIR SPECTRAL ANALYSIS

The transmission spectrum plays a vital role in identifying the potentiality of a NLO material because a given NLO material can be of utility only if it has a wide transparency window without any absorption at the fundamental and second harmonic wavelengths. The UV-Vis-NIR spectrum of the grown crystal is recorded in the wave length range of 190 and 1100 nm using LAMDA 35 UV-Vis-NIR spectrophotometer in order to determine the transmission range and hence the suitability of the crystals for optical applications [45,46]. The UV-Vis-NIR transmission spectrum is shown in the Fig. 5.4. From the figure, it is noted that the UV transparency cut off is around 200 nm. The absorption is negligible in the entire visible region of the electromagnetic spectrum. The transmission extends nearly from 200 nm to 1100 nm, makes it suitable for the applications requiring blue/green light. It is also an important requirement for NLO materials having nonlinear optical applications [28].
5.6. THERMAL ANALYSIS

Thermo gravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimetry (DSC) are carried out, using UNIVERSAL V4-5A-TA instrument at a heating rate of 20°C/min, recorded in the same chart are shown in Fig. 5.5. In the present case, the TGA and DTA are carried out between 0 and 400°C in the nitrogen atmosphere which provide an inert environment. In practice, a small sample weight is desirable for thermo gravimetric results [33] and hence the weight of the sample taken for investigation is 6.2870 mg.

The loss of water molecule is observed at 125°C. This is inferred from the exothermic peaks observed near 125°C in DTA and DSC. There is no decomposition up to the melting point [45]. This ensures the suitability of the material for possible device application in lasers. In DTA, the endothermic peak at around 174°C represents the melting point of the sample. As soon as the sample attains its melting point, there is decomposition, illustrated by the loss of mass in the temperature range 150°C-350°C, where gaseous fragments and other may be liberated.
DSC is a technique by which phase transitions or chemical reactions can be followed by observation of the heat absorbed or liberated: Fusion, change in the crystalline state and other physical changes of the sample while heating give sharp endothermic peak. Dehydration is indicated by a broad endothermic peak. Certain chemical changes such as oxidative degradations are aided by exothermic peaks [14].

The exothermic broad peak at ~125.9°C indicates the loss of water molecule from the grown crystal. The endothermic peak at ~174°C is indicative of the melting point of the sample.

![Fig. 5.5: The recorded TGA, DTA and DSC of ELSMH](image)

5.7. ESTIMATION OF EDTA

The inclusion of dopant is confirmed by colorimetric estimation method. Ninhydrin is having the capacity to bind with EDTA and imparts stable colour (pale yellowish green) to EDTA, therefore it is added with our sample as already discussed in detail in chapter IV. The colour intensity (optical density) is measured by DEEP.
VISION COLORIMETER (digital) at 540 nm. Initially, the colorimeter is adjusted for null value with zero concentration (Blank). Then, the sample added with ninhydrin is introduced. The measured optical density is 0.082. With the help of standard graph, the amount of EDTA present in our crystal is found to be ~196µg /ml, which is less than the amount of EDTA (~2.75 mg/ml) present in the solution.

5.8. SECOND HARMONIC GENERATION STUDY

The SHG property of ELSMH is determined by the modified version of powder technique by Kurtz and Perry [48]. The microscopic origin of non-linearity in the NLO materials is due to the presence of delocalized π-electron systems, connecting donor and accepter groups, which enhance their asymmetric polarizability. Each type of constituent chemical bond is regarded as one part of the whole crystal that has contributions to the total nonlinearity. The distribution of valence electrons of the metallic elements is an important factor that strongly affects the linear and nonlinear properties of each type of constituent chemical bond [49]. The fundamental beam of 1064 nm from Q-switched Nd:YAG laser is used to test the SHG property of the grown crystal. The input pulse with energy 3.5 mJ/pulse and pulse width of 10ns with a repetition rate of 10 Hz is used. The fundamental beam is filtered by using IR filter. A photo multiplier tube (Philips photonics) is used as detector of the optical output signal emitted by the sample. Potassium dihydrogen ortho phosphate (KDP) [36 mV] is used as the reference material. The second harmonic generation is confirmed by the emission of green light having the wavelength around 532 nm and the output is 19 mV (0.53 times that of KDP).
5.9. CONCLUSION

EDTA doped lithium sulphate monohydrate single crystals has been grown by slow evaporation technique at room temperature. The lattice parameter values of ELSMH have been determined by single crystal XRD. The sharp well defined Bragg’s peak confirms the crystalline nature of grown crystal. The presence of carboxyl functional groups is identified by FT-IR analysis. The optical transparency and the lower cut-off wavelength are identified from the UV-Visible spectrum. Thermal analysis reveals that the grown crystals are thermally stable up to 125°C. The peak observed at 174°C in the DSC corresponds to the melting point of the material. The inclusion of the dopant is confirmed by colorimetric estimation method. The concentration of EDTA in the grown crystal is ~196µg/ml. The Kurtz powder second harmonic generation test shows that the crystal is a promising candidate for optical second harmonic generation applications. The solvents other than water may be used. Our future plan is to solve the crystal structure and to increase the SHG efficiency.
REFERENCES


