Growth and Characterization of Sulphamic Acid Lithium Chloride Single Crystal

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ABSTRACT
The third order nonlinear optical single crystal of Sulphamic Acid Lithium Chloride (SALC) was grown by slow evaporation method at room temperature. The grown single crystal was characterized by single crystal X-ray Diffraction (XRD) analysis; it confirms the crystal belongs to the orthorhombic system. The vibrational mode of SALC was identified by Fourier Transform Infrared (FTIR) spectral analysis. UV-Vis-NIR absorption studies were performed to know the optical behaviour of the SALC single crystal. The response of the dielectrics studies with respect to the frequency range of 50 Hz to 5 MHz has been investigated and results are discussed. Further the Third order nonlinearities of the SALC crystal was studied by Z-scan techniques. The values of non-linear refractive index ($n_2$), absorption coefficient ($\beta$), and third order non-linear susceptibility ($\chi^3$) were found.

Keywords: Solution growth, Single crystal XRD, FTIR, Optical studies, Dielectric, Z-Scan

INTRODUCTION
The upcoming modern world requires the larger amount of Non-linear Optical (NLO) materials with high quality and good NLO responses for their numerous applications in the field of telecommunication, optical disk data age, remote sensing, scintillation detectors and colour displays [1-3]. Due to this reason, many researchers are focused on developing new high quality NLO crystal in organic and inorganic compounds [4,5]. The inorganic materials show strong absorption in the visible region and hence are not suitable for various applications but they are widely used in the applications of high melting point, high mechanical strength, and high degree of chemical inertness [6]. Researchers in discrete aspects of grow inorganic NLO single crystal is on the way to increase the NLO efficiency and lesser its absorbance in the UV-Visible regions. Sulphamic Acid ($H_2NSO_3H$) is the monoamide of sulphuric acid, which is strongly inorganic acid while mixing it with water it exhibits zwitterionic forms and its derivatives have wide industrial applications such as anticorrosive agent (or) cross linking agent for polymers [7,8]. The growth and various characterisation studies on sulphamic acid single crystal were reported [9-13]. The attempts are made to grow the Sulphamic Acid Lithium Chloride (SALC) and here we report a systematic study of the growth and characterization of a sulphamic acid lithium chloride a third order NLO single crystal for the first time.

EXPERIMENTAL PROCEDURE
The SALC single crystal was grown but taking the equimolar ration of highly pure $H_2NSO_3H$ and lithium chloride. Both the salts are dissolved in double distilled water, the saturated homogeneous solution was prepared by using the magnetic stirrer. The prepared saturated homogeneous solution was filtered and transferred the solution into the beaker. Good quality crystals of SALC were obtained by slow evaporation method at room temperature in a period of 30 days.

RESULTS AND DISCUSSION

Single crystal XRD
The grown single crystal of SALC was subjected to XRD analysis by using Enraf Nonius CAD4 diffractometer with incident radiation of CuKα ($\lambda=1.541$ Å) radiation at room temperature. The results reveal that SALC crystal belongs to the orthorhombic system with lattice-parameter values $a=8.064(3)$ Å, $b=8.103(2)$ Å, $c=9.235(3)$ Å, volume $V=602.2(3)$ Å$^3$ and with the Centro symmetric space group of Pbcna. The calculated lattice parameters and volume of the cell for grown crystal is slightly deviated from the pure sulphamic acid single crystal [14,15]. The Figure 1 shows the photograph of SALC single crystal.
Fourier Transform Infrared (FTIR) spectroscopy

The FTIR spectroscopy studies are used to identify the functional group present in the grown SALC single crystal and to determine the molecular vibrations. Figure 2 shows FTIR spectra of SALC crystal, the wave number is recorded between the range of 500 and 4000 cm$^{-1}$ by using the KBr pellet Elmer RXI FTIR spectrometer. The presence of broad band at 3000-3500 cm$^{-1}$ and the weak band around 2800 cm$^{-1}$ due to the mode of NH$_3^+$ bonding and N-H stretching is observed in SALC single crystal. The bands between 2538 and 1706 cm$^{-1}$ are due to triobands combinations on hydrogen bonded OH bending modes. The bands at 1539 cm$^{-1}$ and 1430 cm$^{-1}$ are due to the symmetric vibration of NH$_3^+$ and asymmetric stretching vibration of NH$_2$ mode, whereas as the incorporation of LiCl in the sulphamic acid, hence it is clearly observed that these bands are slightly shifted (1549 and 1440 cm$^{-1}$) with decreased in its intensity. The rocking mode of vibration of NH$_3^+$ is occurs at 1002 cm$^{-1}$, which confirmed the zwitterionic nature of H$_2$NSO$_3$H crystal [16]. The band occurs at 545 cm$^{-1}$ is due to degenerated SO$_3$ deformation. All the observed IR bands are good agreement with the earlier report [17]. The alteration in peak intensities and changes in peak positions in the SALC crystal confirms the incorporation of LiCl into the SA single crystal. Other characteristic vibration was established to identity the functional groups present in the compounds are represented in the Table 1.

Table 1: Observed vibrational wavenumber and their assignments of SALC

<table>
<thead>
<tr>
<th>Wavenumber (cm$^{-1}$)</th>
<th>Assignments</th>
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<tbody>
<tr>
<td>3264</td>
<td>Degen. NH$_3^+$ stretching vibration</td>
</tr>
<tr>
<td>2860</td>
<td>N-H stretching vibration</td>
</tr>
<tr>
<td>1539</td>
<td>Symmetric NH$_3^+$ vibration</td>
</tr>
<tr>
<td>1264</td>
<td>Degen. SO$_3^-$ stretching vibration</td>
</tr>
<tr>
<td>1002</td>
<td>Rocking mode of NH$_2^+$</td>
</tr>
<tr>
<td>686</td>
<td>NH$_3$ and Wagging</td>
</tr>
<tr>
<td>545</td>
<td>Degen. SO$_3$ deformation</td>
</tr>
</tbody>
</table>

UV-Vis-NIR spectroscopy studies

The optical absorption spectrum of SALC single crystal was recorded by using Philips PV8700 Spectrometer in the wavelength range of 200-1100 nm. Figure 3 shows that the recorded absorption spectrum. The reported UV cut off wavelength for pure H$_2$NSO$_3$H is 270 nm [2]. Whereas, the obtained UV cut off wavelength for SALC single crystal was 238 nm. Hence it is confirms that the presence of LiCl in SALC single crystals, which improves the optical transmission and there is no considerable absorption is found in the wavelength range of 240-1100 nm. It clearly indicates the incorporation of LiCl was increase the optical window of pure H$_2$NSO$_3$H single crystal.
Dielectric measurements

Dielectric studies were carried out for grown SALC using HIOKI 352-50 LCR HITESTER instrument in the frequency range 50 Hz to 5 MHz. Dielectric constant and dielectric loss were studied. From Figure 4 indicates that the observed dielectric constant decreases with increases in frequencies. The dielectric constant is high at low temperature is because of the space charge polarization [18]. The Figure 5 shows that the variations of dielectric loss with frequency at room temperature. At low frequencies the large value of tan δ and εr are owing to the presences of all the four polarizations namely ionic, orientation, space charge and electronic polarizations. Polarization decreases due to the space charge cannot sustain and comply with the external field as frequency increases [19]. According to the Miller rule at higher frequency, the dielectric loss is low which reveals that the large optical efficiency of the crystal with negligible electrically active defects which is essential for the nonlinear optical applications [20].

Third order nonlinear optical studies - Z-scan technique

The third order non-linear refractive index (n2) and nonlinear absorption coefficient (β) were evaluated by using Z-scan technique. Figures 6 and 7 Shows the open and closed aperture Z-scan cure for SALC crystal and the experimental results indicate that the SALC crystal exhibit reverse saturable absorption with a positive absorption coefficient (β) and the shape of open aperture suggest that the SALC crystal exhibits two-photon absorption [21]. The curve obtained from the closed aperture suggests that the large valley to peak value represent the change in refractive index of the crystal was positive exhibiting strong self-focusing effect. The value of the nonlinear refractive index (n2) was calculated by using the formula:

\[ n_2 = \frac{\Delta \phi}{k I_0 L_{eff}} \text{ (cm}^2\text{/w)} \]

Where, $I_0$ is the intensity of laser beam at the focus ($z=0$) and $k=2\pi/\lambda$ ($\lambda$ is the wavelength of laser beam). The effective thickness of the sample ($L_{\text{eff}}$) can be calculated using the relation:

$$L_{\text{eff}} = \frac{1}{\alpha} \left[ 1 - \exp(-\alpha L) \right]$$

Where, $\alpha$ is the linear absorption coefficient and $L$ is the thickness of the sample. The non-linear absorption coefficient ($\beta$) can be calculated using the following relation:

$$\beta = 2\sqrt{2} \Delta T / I_0 L_{\text{eff}} \text{ (cm/w)}$$

Where, $\Delta T$ is one peak value at open aperture of Z-scan curve. The value of $\beta$ will be positive for saturable absorption and negative for two photon absorption process. The real and imaginary parts of the third order nonlinear optical susceptibility ($\chi^{(3)}$) are defined as:

$$\text{Re} \left( \chi^{(3)} \right) \text{ (esu)} = 10^{-4} \left( \epsilon_0 C^2 n_0^2 \bar{n}^2 \right) / \pi \text{ (esu)}$$

$$\text{Im} \left( \chi^{(3)} \right) \text{ (esu)} = 10^{-2} \left( \epsilon_0 C^2 n_0^2 \lambda \beta \right) / 4\pi^2 \text{ (esu)}$$

Where, $\epsilon_0$ is the vacuum permittivity, $n_0$ is the linear refractive index of the sample and $c$ is the velocity of light in vacuum. Table 2 summarizes the experimental details and the results of the Z-scan technique for SALC.

The calculated values of third order nonlinear refractive index ($n_2$) is $3.656 \times 10^{-11}$ cm$^2$/w, nonlinear absorption coefficient ($\beta$) = $1.352 \times 10^{-6}$ cm/w. The positive value of nonlinear refraction reveals the self-focusing nature and nonlinear absorption co-efficient ($\beta$) exhibits the two-photon absorption process. Real and imaginary value of third order susceptibility of SALC is $1.966 \times 10^{-8}$ esu and $3.6627 \times 10^{-6}$ esu respectively. The third order susceptibility ($\chi^{(3)}$) is $4.157 \times 10^{-6}$ esu and it is due to the $\pi$-electron cloud movement from the donor to acceptor which makes the molecule highly polarized [22].

Figure 6: Z-scan open aperture for SALC crystal

Figure 7: Z-scan open and closed aperture for SALC crystal

Table 2: Obtained data from Z-scan technique for SALC crystal

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
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<tbody>
<tr>
<td>Laser beam wavelength ($\lambda$)</td>
<td>632.8 nm</td>
</tr>
<tr>
<td>Lens focal length (f)</td>
<td>18.5 cm</td>
</tr>
<tr>
<td>Optical path distance ($Z$)</td>
<td>115 cm</td>
</tr>
<tr>
<td>Spot-size diameter in front of aperture ($\omega_a$)</td>
<td>1 cm</td>
</tr>
<tr>
<td>Aperture radius ($r_a$)</td>
<td>4 mm</td>
</tr>
<tr>
<td>Effective thickness ($L_{\text{eff}}$)</td>
<td>1.418 mm</td>
</tr>
<tr>
<td>Nonlinear refractive index ($n_2$)</td>
<td>$3.656 \times 10^{-11}$ cm$^2$/w</td>
</tr>
<tr>
<td>Nonlinear absorption coefficient ($\beta$)</td>
<td>$1.352 \times 10^{-6}$ cm/w</td>
</tr>
<tr>
<td>Real part of third order susceptibility ($\text{Re} \chi^{(3)}$)</td>
<td>$1.966 \times 10^{-8}$ esu</td>
</tr>
<tr>
<td>Imaginary part of third order susceptibility ($\text{Im} \chi^{(3)}$)</td>
<td>$3.6627 \times 10^{-6}$ esu</td>
</tr>
<tr>
<td>Third-order nonlinear optical susceptibility ($\chi^{(3)}$)</td>
<td>$4.157 \times 10^{-6}$ esu</td>
</tr>
</tbody>
</table>
CONCLUSION

The SALC single crystal was successfully grown by slow evaporation method. The crystal structure was confirmed by XRD studies and the lattice parameter was calculated. The absence of significant absorption in the entire visible region and lower cut-off wavelength at 238 nm indicates the suitability of SALC for optical applications. The FTIR vibration analysis confirms the various functional groups present in SALC. Both the dielectric constant and dielectric loss of the grown crystal decreases with increase in frequency and these low values at high frequencies reveal the desirable property of the crystal for NLO device applications. The third order nonlinear refractive index, absorption coefficient and optical susceptibility was calculated by the Z-scan techniques and it reveals that the SALC crystal possess self-focusing and two-photon absorption process.

REFERENCES