CRYSTAL GROWTH, STRUCTURE AND CHARACTERIZATIONS OF AN ORGANIC OPTICAL MATERIAL – L–ALANINE OXALATE (LAO)

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ABSTRACT
An organic crystal of L-Alanine oxalate [C₈H₁₆N₂O₈], abbreviated as LAO material has been successfully grown by slow evaporation methods. Crystal of dimensions up to 20×3×2mm³ is reported. The presence of functional groups and the coordination of metal ions to L-alanine were confirmed by FTIR analysis. The powder X-ray diffraction of the crystal has been recorded and the various planes of reflection. A transmission spectrum reveals that the crystal has low UV cutoff of 269nm and has a good transmittance in the entire visible region thereby confirming the enhancement of NLO property. The thermal stability of the crystal has been investigated by using thermogravimetric analysis (TG), differential thermal analysis (DTA) and differential scanning calorimetry (DSC). The dielectric property of crystal is measured as function of three different frequencies for varying temperatures suggests good candidate for electro optic modulators.

Keywords: Crystal growth, infrared spectrum, optical transmission, thermal analysis and dielectric measurement.

INTRODUCTION
A wide variety of organic materials are being investigated for frequency doubling. Organic single crystals possess unique opto-electronic properties and its molecules have delocalized electrons, namely, conjugated electron systems exhibit various photo responses such as photoconductive, photovoltaic, photo catalytic behaviour¹,². The organic materials with intermolecular charge transfer compounds having large second order nonlinear optical effects³. Here L-alanine is a non-polar hydrophobic amino acid, it contains an asymmetric carbon atom and non-centrosymmetric space groups, which make them optically active. In particular optically active amino acids possess wide optical transparency range in UV-Vis spectral region, favorable hardness due to their zwitterionic nature and large hyperpolarizability make them ideal candidates for nonlinear optical devices⁴. In this continuation of our work some, new nonlinear optical crystals like L-alanine acetate⁵, L-alanine cadmium chloride⁶, L-alanine tetrafluoroborate⁷ and L-alanine formate⁸ have been already reported. So crystals of amino acids are subjected to extensive investigation. We reported in this paper, oxalic acid is combined with L-alanine to form an organic optical material and systematic investigation has been carried out on the growth of LAO subjected to FT-IR, Powder XRD, optical transmission, thermal analyses and dielectric constant and microhardness measurement.

EXPERIMENTAL
The starting material was synthesized by taking L-alanine and oxalic acid in a 2:1 stoichiometric ratio. The required amount of starting materials for the synthesis of L-alanine oxalate (LAO) crystal was calculated according to the following reaction:

\[ \text{C}_8\text{H}_{16}\text{N}_2\text{O}_8 + 2\text{C}_2\text{H}_2\text{O}_4 \rightarrow \text{C}_8\text{H}_{16}\text{N}_2\text{O}_8 \text{C}_2\text{H}_2\text{O}_4 \]

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\[ 2[C_3H_7NO_2] + C_2H_2O_4 \rightarrow C_8H_{16}N_2O_8 \] (1)

The calculated amount of oxalic acid was first dissolved in deionized water. L-alanine was then added to the solution. The solution was agitated with a magnetic stirring device for 8h continuously and filtered after complete dissolution of the starting materials. The solution was filtered using a standard filter paper of porosity 0.1 mm. Good qualities of transparent seed crystals (Fig.1) were obtained within 29 days by slow evaporation technique.

![Fig.-1: As shown in LAO](image)

**Table-1: Elemental analysis of LAO crystals.**

<table>
<thead>
<tr>
<th>Element</th>
<th>Experimental (%)</th>
<th>Theoretical (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>45.06</td>
<td>48.04</td>
</tr>
<tr>
<td>H</td>
<td>7.77</td>
<td>8.063</td>
</tr>
<tr>
<td>N</td>
<td>12.01</td>
<td>14.00</td>
</tr>
</tbody>
</table>

![Fig.-2: FT-IR spectrum of LAO crystal.](image)
RESULTS AND DISCUSSION

Elemental analysis

The percentage compositions of the constituent elements present in L-alanine oxalate [LAO] crystals were determined by Elementar Vario EL III instrument. The percentages of carbon, hydrogen and nitrogen are presented in Table 1. The experimental values are close to the theoretically values.

FTIR analysis

Fourier transform infrared radiation of LAO crystal was carried out in the middle IR between 4000 and 400 cm$^{-1}$, using a Thermo Nicolet, Avatar 370 Spectrophotometer and the spectrum is shown in Fig.2. The absorption band at 3241 cm$^{-1}$ is due to the presence of NH$_3^+$ asymmetric stretching vibration.
and the CH\textsubscript{2} symmetric stretching vibration is observed at 2915 cm\textsuperscript{-1}. The small broad bands observed between 3400-3600 cm\textsuperscript{-1} respectively corresponds to OH and NH stretching vibrations. C=O stretching band at 1589 cm\textsuperscript{-1} is assigned by indicates the presence of carboxylic acid group. The peak at 1412 cm\textsuperscript{-1} was assigned to symmetric stretching of the COO\textsuperscript{-} group\textsuperscript{9}. The peaks between 912 and 1111 cm\textsuperscript{-1} are assigned to asymmetrical coupled vibration of oxalic and alanine group\textsuperscript{5}. The sharp peaks at 1451 and 1251 cm\textsuperscript{-1} are due to CH\textsubscript{3} bending mode and NH\textsubscript{3}\textsuperscript{+} rocking vibration respectively. The observed NH\textsubscript{3}\textsuperscript{+} stretching frequency is lowered due to the intermolecular hydrogen bonding. C-C stretching at (817 cm\textsuperscript{-1}) and COO deformation at (610 cm\textsuperscript{-1}) are assigned from the spectrum\textsuperscript{10}. These vibrations prove the presence of expected functional groups in the compound.

Fig.-5: TG/DTA/DSC Curve of LAO crystal.

Fig.-6: Dielectric Constant of LAO crystal.
Powder XRD analysis
The powder from the LAO specimen was subjected to PXRD analysis and the recorded spectrum using Rich-Seifert X-ray diffractometer Bruker AXS D8 Advance Cu, Wavelength (1.5406 Å) is depicted in Fig.3. The Bragg’s diffraction peaks were indexed and observed prominent peaks confirm the crystalline nature properties of grown LAO crystal.

Optical transmission study
An optical transmission spectrum was measured on crystal cut from LAO compound shown in Fig.4. The optical behavior of the crystal was assessed by using Varian, Cary 5000 instrument in the range of 200-800nm. The lower cutoff the LAO crystal occurs at 269nm and it is noted that there is no remarkable transmittance in the entire region of the spectra. So it can be used as a potential material for SHG and related optoelectronic applications.

Thermal analyses
The thermal stability of LAO crystals has been recorded using a simultaneous thermal analyzer Q600 SDT and Q20 and DSC instruments. The TG/DTA and DSC curves of LAO crystal are illustrated in Fig.5. From the DTA curve shows that the melting point of the material takes place in the vicinity of 175 ºC, which indicates no phase transition before this temperature. The sharpness of this endothermic peak shows the high degree of crystalline and purity of the sample. TG curve shows that the gradual weight loss between 175 ºC and 305 ºC due to the liberation of CO, CO2, NH3 etc., and the total decomposition of the compound is observed above 800 ºC. Further it indicates there is no weight loss below 175 ºC, which shows the material can be exploited for NLO application up to 175 ºC. In DSC curve, there is a broad exothermic peak at 175 ºC to 235 ºC, which corresponds to the decomposition as observed in TG analysis.

Dielectric Constant (εr)
The dielectric property of crystal was studied by using Agilent A 2484. The dielectric constant (εr) of crystal was found by measuring the capacitance and dielectric loss, which is used to calculate the dielectric constant at various temperatures ranging between room temperature to 150ºC for three different frequencies(100Hz, 10KHz and 1MHz). From the figure the dielectric constant increased with increased the temperature. The current investigations showed that dielectric constant was observed maximum at 150ºC, since all types of polarization such as electronic, ionic, orientation and space charge polarizations occur at higher temperature. The variation of dielectric constant is shown in Fig.6.

CONCLUSION
A potential organic crystal of L-alanine oxalate have been grown by slow evaporation technique in mixed solvent of deionised water at room temperature. Vibrational frequencies were assigned from FT-IR spectral analysis, which confirm the presence of functional groups of the LAO crystal. The sharp well defined Bragg’s peaks confirm the crystalline nature of the materials. The optical transmittance study reveals the lower cut off wavelength at 269nm, thus, to as certain the fact that the crystal can be used for laser applications. The thermal studies confirm that the crystal structure is stable up to 175ºC and indicate its suitability for application in lasers field. From the dielectric studies it is seen that the dielectric constant increased with increased temperature.

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