5. OPTICAL AND MECHANICAL STUDIES ON AMINO ACID DOPED SODIUM ACID PHTHALATE (NaAP) SINGLE CRYSTALS

5.1 INTRODUCTION

Nonlinear optical materials have attracted many researchers due to its potential applications in the field of photonics, lasers, electro-optic switches and frequency conversion etc. [90-100]. During the past decade, number of organic and inorganic materials with high nonlinear susceptibilities has been synthesized. However, their device applications have been impeded by the inadequate optical transmittance, poor optical quality and low laser damage threshold [101]. The molecules in pure organic crystals are often bonded by weak Vander Waals forces of hydrogen bonds, which result in poor mechanical robustness. In the case of inorganic NLO materials, they have excellent mechanical and thermal properties but relatively modest optical susceptibilities due to the lack of π–electron delocalization [102-105, 42]. Phthalic acid family crystals are potential nonlinear optical materials and are widely used in variety of applications [106]. Sodium acid phthalate is an excellent material for SHG applications [107, 108]. In the present work, attempts were made to grow amino acids (L-alanine, L-arginine, Glycine) doped sodium acid phthalate by slow evaporation technique. Effect of dopants is significant, because of the influence of doping on intrinsic defects [109-114]. The results and characterization reveal that the presence of dopants enhances optical, mechanical properties etc.

5.2 RESULTS AND DISCUSSION

5.2.1 Single crystal X-ray diffraction analysis

The amino acid doped sodium acid phthalate crystals were subjected to single crystal X-ray diffraction analysis using by ENRAF NONIUS CAD4 single crystal X-ray diffractometer. The lattice parameters are measured and are shown in Table 5.1. All the grown crystals belong to orthorhombic crystal
system having space group of B2ab which is in good agreement with that of the literature [107, 108].

Table 5.1: Lattice parameters for Pure and doped crystals

<table>
<thead>
<tr>
<th>compound Name</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Unit cell parameters</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaAP (pure)</td>
<td>Orthorhombic</td>
<td>B2ab</td>
<td>a = 6.60 Å, b = 9.08 Å, c = 25.84 Å, α = β = γ = 90°</td>
<td>V = 1548 Å³</td>
</tr>
<tr>
<td>NaAP + 1mole% L-alanine</td>
<td>Orthorhombic</td>
<td>B2ab</td>
<td>a = 6.73 Å, b = 9.24 Å, c = 26.25 Å, α = β = γ = 90°</td>
<td>V = 1631 Å³</td>
</tr>
<tr>
<td>NaAP + 3mole% L-alanine</td>
<td>Orthorhombic</td>
<td>B2ab</td>
<td>a = 6.74 Å, b = 9.23 Å, c = 26.28 Å, α = β = γ = 90°</td>
<td>V = 1635 Å³</td>
</tr>
<tr>
<td>NaAP + 5mole% L-alanine</td>
<td>Orthorhombic</td>
<td>B2ab</td>
<td>a = 6.77 Å, b = 9.28 Å, c = 26.35 Å, α = β = γ = 90°</td>
<td>V = 1655 Å³</td>
</tr>
<tr>
<td>NaAP + 1mole% L-arginine</td>
<td>Orthorhombic</td>
<td>B2ab</td>
<td>a = 6.78 Å, b = 9.29 Å, c = 26.38 Å, α = β = γ = 90°</td>
<td>V = 1661 Å³</td>
</tr>
<tr>
<td>NaAP + 3mole% L-arginine</td>
<td>Orthorhombic</td>
<td>B2ab</td>
<td>a = 6.77 Å, b = 9.30 Å, c = 26.39 Å, α = β = γ = 90°</td>
<td>V = 1662 Å³</td>
</tr>
<tr>
<td>NaAP + 5mole% L-arginine</td>
<td>Orthorhombic</td>
<td>B2ab</td>
<td>a = 6.87 Å, b = 9.45 Å, c = 26.76 Å, α = β = γ = 90°</td>
<td>V = 1737 Å³</td>
</tr>
<tr>
<td>NaAP + 1mole% Glycine</td>
<td>Orthorhombic</td>
<td>B2ab</td>
<td>a = 6.68 Å, b = 9.19 Å, c = 26.06 Å, α = β = γ = 90°</td>
<td>V = 1600 Å³</td>
</tr>
<tr>
<td>NaAP + 3mole% Glycine</td>
<td>Orthorhombic</td>
<td>B2ab</td>
<td>a = 6.74 Å, b = 9.28 Å, c = 26.29 Å, α = β = γ = 90°</td>
<td>V = 1644 Å³</td>
</tr>
<tr>
<td>NaAP + 5mole% Glycine</td>
<td>Orthorhombic</td>
<td>B2ab</td>
<td>a = 6.81 Å, b = 9.38 Å, c = 26.62 Å, α = β = γ = 90°</td>
<td>V = 1701 Å³</td>
</tr>
</tbody>
</table>
5.2.2 FTIR studies

The presence of functional groups and vibrational frequencies of pure and doped NaAP single crystals identified by FTIR spectroscopy. The recorded spectrum of the grown crystals were carried out between the range 400-4000 cm\(^{-1}\) using Perkin - Elmer spectrum one and is shown in Figures. 5.1- 5.3. An absorption band in the range 538-858 cm\(^{-1}\) appears due to C-H out-of-plane deformations of the aromatic ring. The spectral band attributed at 1118 cm\(^{-1}\) is due to C-H in-plane deformation of the aromatic ring. The C-O stretching vibrations obtained as peak at 1354 cm\(^{-1}\). The peak at 1613 cm\(^{-1}\) assigned due to C-C skeletal aromatic ring vibrations. The carboxyl group C=O vibrations appear near 1696 cm\(^{-1}\). All these assignments are in very good agreement with NaAP crystals that of the reported values [108].

The L-alanine dopants assigned at 2867 cm\(^{-1}\) due to NH\(_3^+\) asymmetric stretching mode and 1468 cm\(^{-1}\) assigned for deprotonated carboxylic group (COO\(^-\)) characteristic absorption band. In the L-arginine dopants the peaks at 3501 cm\(^{-1}\) NH\(_2\) asymmetric stretching vibrational mode, C-H stretching of CH\(_2\) vibrations assigned at 2468 cm\(^{-1}\), the minute peak at 1466 cm\(^{-1}\) due to NH\(_2\) symmetric bending mode.

And the Glycine dopants identified at 3161 cm\(^{-1}\) due to NH\(_3^+\) Asymmetric stretching vibrational mode, C-O symmetric stretching mode assigned at 1467 cm\(^{-1}\), and the peak at 1125 cm\(^{-1}\) for NH\(_3^+\) rocking mode for out plane bending respectively. From the above assignments verified that amino acids were presence as dopants in NaAP single crystals.
Figure. 5.1: FTIR Spectra of L-alanine doped NaAP crystals

Figure. 5.2: FTIR Spectra of L-arginine doped NaAP crystals
5.2.3 UV-Vis-NIR spectral analysis

The UV-Vis-NIR spectrum of the grown crystals was recorded in the range 300-800 nm using Perkin Elmer Lambda 35 UV-Vis spectrophotometer and the resultant spectra is shown in Figures. 5.4, 5.5, and 5.6. The optical absorption studies reveal that amino acids doped NaAP crystals show good transparency in entire visible region and the UV cut off wavelength is found to be around 313 nm, 320 nm and 317 nm for L-alanine, L-arginine and Glycine doped NaAP crystals respectively. Moreover it is observed that the absorbance decreases with increase in the doping concentration for all the three dopants. This proves that the presence of dopants enhance the optical property of the material. The very low absorbance in the entire visible region suggests its suitability for the fabrication of optoelectronic devices [115].
Figure. 5.4: Absorption spectra of L-alanine doped NaAP crystals

Figure. 5.5: Absorption spectra of L-arginine doped NaAP crystals
The optical absorption coefficient ($\alpha$) was calculated from the transmittance using the following relation,

$$\alpha = \frac{1}{t} \log \left( \frac{1}{T} \right)$$

(5.1)

Where $T$ is transmittance and $t$ is thickness of the crystal.

Owing to the direct band gap, the crystal under study has an absorption coefficient ($\alpha$) obeying the following relation for high photon energies ($h\nu$);

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu}$$

(5.2)

Where $E_g$ is optical band gap of the crystal and $A$ is a constant.
Figure 5.7: Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ for pure and L-alanine doped NaAP crystals.

Figure 5.8: Plot of $(\alpha h\nu)^2$ vs. $(h\nu)$ for pure and L-arginine doped NaAP crystals.
The plot of variation of $(\alpha h\nu)^2$ vs. $h\nu$ is shown in Figures. 5.7, 5.8, 5.9. $E_g$ is evaluated by the extrapolation of the linear part and the band gap for pure NaAP crystal is found to be 4.050 eV. But for L-alanine doped NaAP the band gap values are 4.070, 4.075 and 4.077 eV respectively for 1mole%, 3mole%, 5mole% concentrations. Similarly, for L-arginine doped NaAP, $E_g$ is found to be 4.048, 4.051 and 4.052 eV respectively for 1mole%, 3mole%, 5mole% concentrations. Whereas for glycine doped NaAP the values are 4.054, 4.063 and 4.066 eV respectively for 1mole%, 3mole%, 5mole% concentrations.

### 5.2.3.1 Determination of optical constants

The optical behaviour of materials is important to determine its usage in optoelectronic devices. Knowledge of optical constants of a material such as optical band gap and extinction coefficient is quite essential to examine the material's potential opto-electronic applications. Further, the optical
properties may also be closely related to the material's atomic structure, electronic band structure and electrical properties. The extinction coefficient (K) for the grown crystals can be determined using formula

\[ K = \frac{\alpha \lambda}{4\pi} \]  

(5.3)

The plot of K vs. photon energy (hv) is shown in the Figures. 5.10-5.12. It is observed that the K decreases with increase in energy.

The reflectance (R) in terms of photon energy (Figures. 5.13-5.15) is derived from the relation,

\[ R = \frac{1+\exp(-\kappa d) + \exp(\kappa d)}{1+\exp(-\kappa d)} \]  

(5.4)

Figure. 5.10: Extinction Coefficient of L-alanine doped NaAP crystals
Figure. 5.11: Extinction Coefficient of L-arginine doped NaAP crystals

Figure. 5.12: Extinction Coefficient of Glycine doped NaAP crystals
Figure. 5.13: Reflectance of L-alanine doped NaAP crystals

Figure. 5.14: Reflectance of L-arginine doped NaAP crystals
Figure. 5.15: Reflectance of Glycine doped NaAP crystals

The optical conductivity ($\sigma_{op}$) is a measure of the frequency response of the material when irradiated with light (Figures 5.16-5.18)

$$\sigma_{op} = \frac{\alpha n c}{4\pi}$$  \hspace{1cm} (5.5)

Where $c$ is the velocity of light.

Figure. 5.16: Optical Conductivity of L-alanine doped NaAP crystals
Also, the electrical conductivity has been determined for the grown crystals by optical method using the relation

\[ \sigma_{\text{elec}} = \frac{2\lambda \sigma_{\text{op}}}{\alpha} \]  \hspace{1cm} (5.6)

and the electrical conductivity is shown in Figures. 5.19-5.21.
Figure 5.19: Electrical Conductivity of L-alanine doped NaAP crystals

Figure 5.20: Electrical Conductivity of L-arginine doped NaAP crystals
5.2.4 Microhardness measurements

The title crystals were carried out to Vickers microhardness tests using Leitz Wetzler Microhardness tester with a diamond pyramidal indenter. A diamond indenter was pressed the plane of pure and doped NaAP crystals under the known load 25 –100g and the resulting indentation was measured. The indentation time was 25s for all trials. The Vickers hardness number was calculated using the relation

\[ H_v = 1.8544 \left( \frac{P}{d^2} \right) \text{ kg/mm}^2 \]  

(5.7)

Where P is the applied load in kg and d is the diagonal length of the indentation impression mm. The variation of it \( H_v \) when the applied load P is shown in Figures. 5.22-5.24. The microhardness value is gradually increases after load 50g which is lightly increased in the range of load from 25 to 100g for different mole% of L-alanine doped NaAP crystals. The same results were observed for different mole% of L-arginine and Glycine doped NaAP crystals.
crystals. Thus we can conclude that the presence of dopants increases the hardness of the material.

Figure. 5.22: Hardness number of L-alanine doped NaAP crystals

Figure. 5.23: Hardness number of L-arginine doped NaAP crystals
5.2.5 Nonlinear Optical studies

The second harmonic generation efficiency of pure and amino acid doped sodium acid phthalate single crystals were studied using Q-switched Nd: YAG laser by Kurtz powder test. The fundamental radiation of 1064 nm, with pulse energy was 850 mj per second, pulse width of 9ns, and repetition rate was 10Hz of infrared light beam focused on the powder samples of amino acids doped NaAP crystals. The SHG efficiency of the doped crystal is found to be lesser than that of KDP crystal. The relative SHG efficiency for different doping concentration is shown in the Figure. 5.25.
5.3 CONCLUSION

Single crystals of amino acid doped sodium acid phthalate single crystals were grown by slow evaporation solution growth technique at room temperature. Single crystal X-ray diffraction analysis reveals that the title crystals belong to orthorhombic system having space group B2ab. The functional groups of the presence of dopants revealed with parent material. The optical absorption spectra reveal that the amino acid dopants enhanced the optical properties of the materials. The mechanical hardness study reveals that the hardness increases with increase in the doping concentration. The SHG efficiency is found to be lesser than that of KDP crystal. All these studies confirm that the amino acid doped NaAP crystal could be considered as a potential candidate for the fabrication of optoelectronic devices.