The studies on the effect of aminoacid doping on the crystal properties of the established nonlinear inorganic material, potassium dihydrogen phosphate (KDP), grown by the slow evaporation method, form the essence of this chapter. The structural characterization of doped KDP was done by powder X ray diffraction, FTIR and EDAX techniques. The linear and nonlinear optical characterization of these samples was carried out. The SHG efficiency has been found to be considerably enhanced for the doped KDP samples, showing that they are good nonlinear optical crystals.

5.1 Introduction

Potassium Dihydrogen Phosphate (KDP) single crystal is being considered as one of the best representatives of nonlinear optical crystals. It is used as a standard to characterize other nonlinear materials. It finds several device applications because of its good structural quality. It possesses good mechanical and piezoelectric properties as well. The crystal also has moderate
laser damage threshold and non-linear optical coefficient and is suitable for phase and amplitude modulation applications [1, 2].

The successful growth of large sized KDP crystals [3] as well as KDP crystals with additives [4] has favored the use of these crystals for device application on a large scale. Recently the development of new semi-organic non-linear optical (NLO) materials which possess the advantages of both organic and inorganic materials in terms of high thermal and mechanical stability as well as broad optical frequency range, higher second harmonic generation (SHG) efficiency and high damage threshold has attracted much research attention[5-7]. The quality of KDP crystals grown by solution methods is affected by many factors such as additives, supersaturation, pH value etc which influence the physical properties of the crystals like growth kinetics [8-11] and surface morphology of crystal faces [12-14]. The doping of KDP with suitable dopants modifies the properties positively.

Amino acids exhibit specific features of interest [15] such as

i) molecular chirality, which attributes noncentro symmetric structure,

ii) absence of strongly conjugated bonds, which leads to wide transparency ranges in the visible and UV spectral regions, and

iii) zwitter ionic nature of the molecule, which favors crystal hardness for applications in devices.

Amino acids may be used as dopants in order to modify the nonlinear optical properties of inorganic materials such as KDP [16-18]. In the present work the aminoacids L-citrulline and L-lysine have been used as dopants for the growth of doped KDP single crystals by the slow evaporation technique. Studies on the growth and dielectric properties of L-lysine doped KDP crystals have been reported [19].
5.2 Crystal Growth

Potassium dihydrogen phosphate (1M) was dissolved in distilled water, to which L citrulline (.025M) was added and stirred for 2 hrs and kept for evaporation. Seed crystals were collected and grown in the supersaturated solution. Good quality crystals of L citrulline (CKDP) and L-lysine (LKDP) doped KDP crystals were harvested in 30 days and collected for characterization. No fungus was seen during the growth process even after 2 months. Crystals are found to have good chemical stability when stored at room temperature and do not have any degradation. The photographs of the grown, aminoacid doped KDP crystals are shown in Fig: 5.1(a) and (b).

Fig: 5.1(a) Photographs of L citrulline doped KDP crystals

Fig: 5.1(b) Photographs of L-lysine doped KDP crystals
5.3 Characterisation

5.3.1 Powder XRD studies

The crystals were crushed into a fine powder and the powder X-ray diffraction studies were carried out using the Bruker D8 advance diffractometer with Cu K\(_\alpha\) radiation (\(\lambda = 1.5418\) Å). The powder XRD patterns of the doped samples are compared with that of KDP and displayed in Fig: 5.2. From the powder X-ray diffraction data, the structure of the doped KDP crystals was determined by direct method and refined by Pawley method using Topaz version program and the single crystal X-ray data for pure KDP. The crystal data of KDP and L- citrulline and L- lysine doped KDP are presented in Table.5.1.

![XRD patterns of the pristine and doped KDP samples](image)

*Fig: 5.2 XRD patterns of the pristine and doped KDP samples*
Effect of Aminoacid Doping on the Properties of Potassium Dihydrogen Phosphate Nonlinear Optical Crystals

Table 5.1. Crystal parameters of KDP and doped KDP samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>KDP</th>
<th>CKDP</th>
<th>LKDP</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>7.448(Ao)</td>
<td>7.467(Ao)</td>
<td>7.487(Ao)</td>
</tr>
<tr>
<td>b</td>
<td>7.448(Ao)</td>
<td>7.467(Ao)</td>
<td>7.487(Ao)</td>
</tr>
<tr>
<td>c</td>
<td>6.977(Ao)</td>
<td>6.977(Ao)</td>
<td>7.029(Ao)</td>
</tr>
<tr>
<td>α</td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>β</td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
</tr>
<tr>
<td>γ</td>
<td>90°</td>
<td>90°</td>
<td>90°</td>
</tr>
</tbody>
</table>

Crystal system / Space group
- Tetragonal I42 d
- Tetragonal I42 d
- Tetragonal I42 d

It is seen that both the pure and doped crystals crystallize in tetragonal crystal system with I42 d space group. There are slight variations in the lattice parameters of the doped crystals, compared to the pure one, due to the incorporation of the dopants in the pristine crystal. The doped crystals have the same crystal structure as that of KDP.

5.3.2 EDX spectral studies

The chemical composition of the material can be determined by EDX. The EDX spectrum is a curve between binding energy and intensity of the emitted photoelectron. The peak heights is a measure of the quantity of the concerned elements in the specimen. To confirm the presence of the dopants in the samples, EDX spectra were recorded using integrated feature of a scanning electron microscope (SEM (JEOL Model JED – 2300)) and are shown in Fig:5.3. The main components of aminoacids like carbon and oxygen are present in the EDX spectrum, showing the effectiveness of doping.
Fig: 5.3 EDX spectrum of (a) L- citrulline doped KDP (b) L- lysine doped KDP
5.3.3 FTIR spectral studies

The FTIR spectra of pure and doped KDP samples were recorded to study the vibrational assignments of the different bonds associated with the samples. The FTIR spectra are portrayed in Fig: 5.4 and the corresponding vibrational assignments are displayed in Table 5.2.

The O-H stretching vibration of hydrogen bond for CKDP is at 3319 cm\(^{-1}\), and for LKDP at 3402 cm\(^{-1}\). P-O-H asymmetric stretching occurs at 2950 cm\(^{-1}\) for CKDP and at 2755 cm\(^{-1}\) for LKDP. N-H bending mode corresponds to 1623 cm\(^{-1}\) for CKDP and to 1621 cm\(^{-1}\) for LKDP. P=O stretching vibrations are found at 1313 cm\(^{-1}\) and at 1096 cm\(^{-1}\) for CKDP and at 1303 cm\(^{-1}\) and 1099 cm\(^{-1}\) for LKDP respectively. The rocking NH\(_2\) mode occurs at 895 cm\(^{-1}\) for CKDP and at 904 cm\(^{-1}\) for LKDP. On comparing the FTIR data of the doped KDP samples with that of pure KDP, it is observed that there are no significant changes in characteristic group frequency peak positions. Broad bands corresponding to the aminoacid group vibrations are observed around 3300/3400 cm\(^{-1}\) in both the doped KDP samples. This gives further confirmation that the aminoacid doping of the KDP crystals has been quite effective.

![Fig: 5.4(a) FTIR spectrum of KDP](image-url)
Fig: 5.4(b) FTIR spectrum of L- citrulline doped KDP

Fig: 5.4(c) FTIR spectrum of L- lysine doped KDP
Table 5.2 Vibrational assignments of the doped samples

<table>
<thead>
<tr>
<th>Wavenumber (cm(^{-1}))</th>
<th>Vibrational assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>3319/3402</td>
<td>O-H Stretching of Hydrogen bond</td>
</tr>
<tr>
<td>2950/2755</td>
<td>P-O-H asymmetric stretching</td>
</tr>
</tbody>
</table>
| 2496/2439                | O                              \[\|\]
|                          | P - OH stretching                     |
| 1623/1621                | N-H Bending of the aminoacid           |
| 1313/1303                | P=O stretch                           |
| 1096/1099                | P-OH stretching                        |
| 895/904                  | Rocking NH\(_2\)                       |

5.3.4 UV-Vis absorption spectral studies

For optical device applications, the crystal should possess a wide transparency region. The absorption spectra of the doped samples were recorded and the spectra are shown in Fig: 5.5. Both the doped crystals are found to be transparent in the entire visible region. The crystal has low absorption in the visible and NIR regions and high absorption in the UV region.

For optical transitions, \(\alpha h\nu = A (\alpha h\nu - E_g)^n\) where \(\nu\) is the frequency of the incident photons, \(h\), the Planck’s constant, \(A\) and \(B\) are constants and \(E_g\) is the optical energy gap and \(n=1/2\) for direct allowed transition. The band gap of the doped samples is determined by plotting the energy along the X axis and \((\alpha h\nu)^2\) along the y axis as shown in the Fig:5.6,where \(\alpha\) is the absorption coefficient and \(h\nu\) the photon energy. When the straight portion of the graph
of \((\alpha h\nu)^2\) against \(h\nu\) is extrapolated to \(\alpha=0\), the intercept gives the band gap. The band gap for CKDP is 4.85eV and for LKDP, 4.1eV.

![UV-Vis absorption spectra of doped KDP samples](image1)

**Fig: 5.5** UV-Vis absorption spectra of doped KDP samples

![Plots to determine the band gap (a)CKDP (b) LKDP](image2)

**Fig: 5.6** Plots to determine the band gap of (a)CKDP (b) LKDP
5.3.5 TGA studies

The thermal properties were studied using the thermal analyzer as explained earlier and from the thermo grams shown in Fig: 5.7, it is seen that the L-citrulline doped KDP is stable upto 225°C while L-lysine doped KDP is stable up to 221°C. The degradation temperature of pure KDP is 215°C. Doping has increased the thermal stability compared to that of pristine crystal. The good thermal stability establishes the prospects of the use of these crystals in laser applications.

![TGA graphs of the samples](image)

**Fig: 5.7 TGA graphs of the samples**

5.3.6 Studies on Second harmonic generation efficiency

The second harmonic generation efficiency of the doped samples was determined by Kurtz powder technique using Nd: YAG Q-switched laser source. For a laser input power of 4.2 mJ, the second harmonic signal was obtained at 532 nm for both the samples. The measured output voltages are
shown in Table 5.3. The SHG efficiency of CKDP is found to be 2.2 times that of KDP and that of LKDP is 1.3 times that of KDP. Doping of KDP with aminoacids has enhanced the second harmonic generation efficiency significantly.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SHG output (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CKDP</td>
<td>51</td>
</tr>
<tr>
<td>LKDP</td>
<td>32</td>
</tr>
<tr>
<td>KDP(ref)</td>
<td>23</td>
</tr>
</tbody>
</table>

5.3.7 Z scan studies

The nonlinear optical properties can be well studied by the open aperture z scan technique. In the present work, a Q switched Nd-YAG laser (532nm, 7ns, 10Hz) was used as the light source. The sample was moved in the direction of light. The transmitted beam energy, reference beam energy and their ratio were measured simultaneously by an energy meter. The plot of the transmittance verses z axis in open aperture z scan technique is shown in Fig: 5.8. The open aperture curve exhibits a normalized transmittance valley. The nonlinear absorption coefficient $\beta$ was obtained by theoretical fitting for two photon absorption. $\beta$ is found to be equal to $9.7 \times 10^{-10}$ m/W for CKDP and equal to $4 \times 10^{-10}$ m/W for LKDP. It is inferred that doping KDP with L-citrulline and L-lysine has enhanced the third order nonlinearity considerably.
Effect of Aminoacid Doping on the Properties of Potassium Dihydrogen Phosphate Nonlinear Optical Crystals

Fig: 5.8(a) Open aperture Z scan curve for CKDP

Fig: 5.8(b) Open aperture Z scan curve for LKDP
5.3.8 Etching studies

Etching is the selective dissolution of the crystal which reveals the crystal symmetry and lattice defects. Considerable information on the growth process and growth mechanism of the crystal can be had from the patterns observed on surfaces like spirals, hillocks and step patterns. When a crystal surface is etched, well defined etch patterns are produced at the dislocation sites. The etching studies were carried out on the (1 0 0) plane of the single crystals of L-citrulline doped KDP and L lysine doped KDP using demonized water as the etchant at room temperature for an etching time of 5s. The crystal sample was completely immersed in the etchant and then the etched sample was cleaned using a tissue paper and the etch patterns were observed using an optical microscope in the reflection mode. Well defined etch pits were observed. The etch patterns are depicted in Fig: 5.9. It is seen that the growth mechanism is 2dimensional nucleation.

![Fig: 5.9 Etch patterns of (a) CKDP (b) LKDP](image-url)
5.4 Conclusions

Good quality nonlinear optical crystals of KDP, doped with L-citrulline and L-lysine have been grown by slow evaporation technique. The crystals have been characterized by powder XRD, EDX, FTIR, UV-Vis absorption spectral analysis, SHG, open aperture z scan and etching studies. Doping of KDP by the aminoacids has positively enhanced the optical properties. The doping has increased the SHG efficiency of the KDP crystals to a large extent, highlighting the prospects of aminoacid doped KDP for applications in higher harmonic frequency generation.

5.5 References


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