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Research Paper

# Growth and characterization studies of pure and glutamic acid doped potassium dihydrogen phosphate crystals

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***Abstract*—** The present investigation deals with study of effect of glutamic acid on various properties of pure KDP crystals. The crystals were grown at room temperature by evaporation method. Transparent and rectangular shaped crystals were grown after 25 days. The various characterizations such as elemental, structural, FTIR spectroscopic and optical were carried out on the grown crystals. The elemental analysis showed the presence of dopant atoms. The structural analysis showed the single-phase nature of the doped crystals. The FTIR analysis showed the presence of characteristic vibrations of glutamic acid along with KDP. The SHG analysis showed reduction in SHG efficiency of doped crystals. The UV-Vis analysis showed reduction in transmittance and optical energy band gap energy of doped crystals.

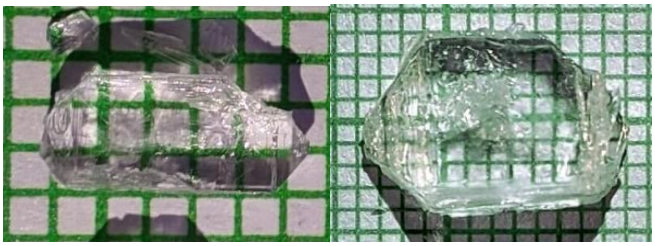
***Keywords*—** KDP, Powder X, FTIR, SHG, UV-Vis

## 1. Introduction

Potassium dihydrogen phosphate, having formula $KH_2PO_4$ and popularly known as KDP is a very important inorganic material belongs to the family of dihydrogen phosphate. The single crystal of KDP has a very good efficiency of frequency conversion. The doping of big size amino acid molecules can affect its efficiency. Many researchers have reported in the literature the effect of amino acid doping on the efficiency of KDP that already been mentioned in our previous publications [1]. The effect of doping of amino acid and change in its concentration in terms of wt% and/or mol% may observed either in terms of increase or decrease in efficiency as well as other optical and structural properties of pure KDP. In the literature, growth of amino acid doped KDP crystal is reported by varying the mol% of amino acid [2], stoichiometrically amino acid doped KDP crystal is reported [3], amino acid doped by wt% is reported [4]. In the present investigation glutamic acid (GA) is selected as a dopant and 0.2wt% is chosen as its concentration. Glutamic acid has a long side chain ($CH_2 – CH_2 – COOH$). It is linked with other carboxyl group attached with α-carbon atom. In the solution, there are various possibilities of losing proton by carboxylic acid and amino group, which is reflected in terms of increase or decrease in efficiency of doped KDP crystal.

## 2. Experimental Technique

Pure KDP crystal was grown by preparing the saturate solution of AR grade KDP in 100 ml distilled water. The solution was stirred for two hours and then transferred into petri dish after filtration. The petri dish covered with filter paper and left it for evaporation in an isolated place. For the growth of GA doped KDP crystal, 0.2gram GA was added into saturate solution of KDP. This solution was stirred for two hours, then filtered and transferred into petri dish. Petri dish was covered with filter paper and left it by covering with filter paper for evaporation in an isolated place. After 25 days, good quality, transparent and rectangular shaped pure and 0.2wt% GA doped KDP crystals were observed to grow in petri dish. The crystals were taken out carefully for various characterizations. Figure 1a-b shows pure and doped KDP crystals.



(1a) (1b)

Figure 1. Grown crystal of (a) Pure KDP and (b) 0.2wt% GA doped KDP

## 3. Results and Discussion

***EDAX study***

The presence of dopant atoms in the doped KDP crystal is confirmed by elemental analysis, i.e., EDAX. The presence of wt% of the atoms in pure and doped KDP crystals is tabulated in the table 1.

Table 1. EDAX Result

| Sample Number and Name | Carbon (C) | Potassium (K) | Oxygen (O) | Phosphorous (P) | Nitrogen (N) |
|---|---|---|---|---|---|
| | Wt % | | | | |
| 1. Pure KDP | - | 34.35 | 48.29 | 22.03 | - |
| 2. 0.2wt% GA doped KDP | 3.44 | 30.36 | 43.43 | 21.88 | 0.80 |

The chemical formula of dopant GA is $C_5H_9NO_4$. Therefore, in the GA doped KDP, the presence of carbon (C) and nitrogen (N) indicates the successful doping of dopant GA in the crystal lattice of pure KDP.

***Powder XRD analysis***

Figure 2 shows the Powder XRD patterns of pure KDP crystal and 0.2wt% GA doped KDP crystal, while the unit cell parameters, cell volume and X-ray density are represented in table 2.

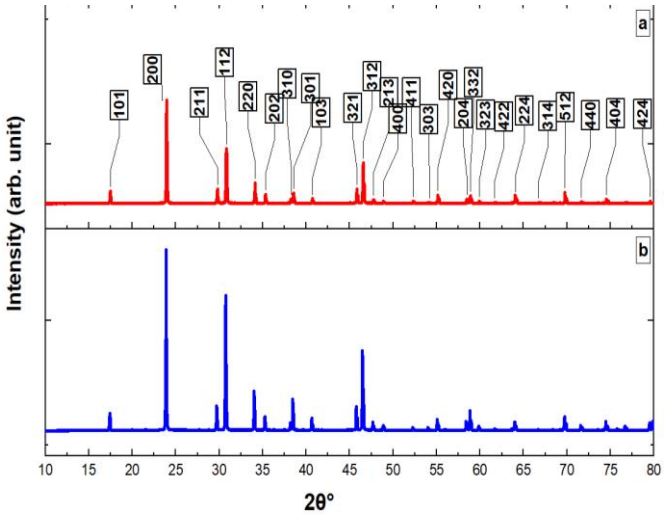



Figure 2. Powder XRD patterns patterns of (a) Pure KDP and (b) 0.2wt% GA doped KDP

Table 2. Unit cell parameters, cell volume and X-ray density of pure and GA doped KDP crystals

| Sample Number | Wt% of GA | a = b (Å) | c (Å) | Volume cell (Å3) | X-ray density (g/cm3) |
|---|---|---|---|---|---|
| Sample 1 | 0 | 7.4410 | 6.9646 | 385.62 | 2.3436 |
| Sample 2 | 0.2 | 7.45 | 6.9742 | 387.08 | 2.3348 |

From the XRD pattern, it is observed that pure and GA doped KDP possess single phase nature because there is no presence of any additional peak is observed. Pure and doped crystals possess the characteristic peaks as reported in the previous publication [1] and tetragonal crystal system. The diffraction peaks are sharp, which is an indication of good quality of crystallinity of the crystals. The effect of doping of 0.2wt% GA is clearly observed in the most intense peak (200) of pure KDP in terms of increase in intensity, reduction in FWHM and reposition of this peak towards lower diffraction angle. This is shown in the enlarged image of peak (200) in the figure 3.

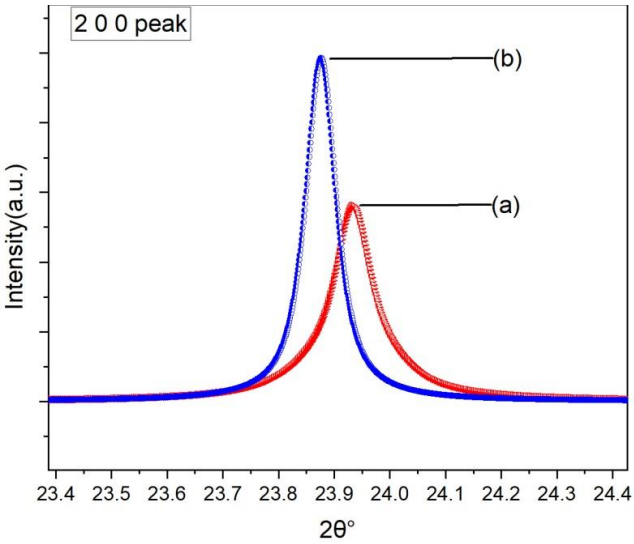



Figure 3. Variation of (200) peak of (a) Pure KDP and (b) 0.2wt% GA doped KDP

***FTIR spectroscopic study***

Figure 4 shows the FTIR spectra of pure and 0.2wt% GA doped KDP crystals, while observed absorption frequencies and their assignments are listed in table 3.

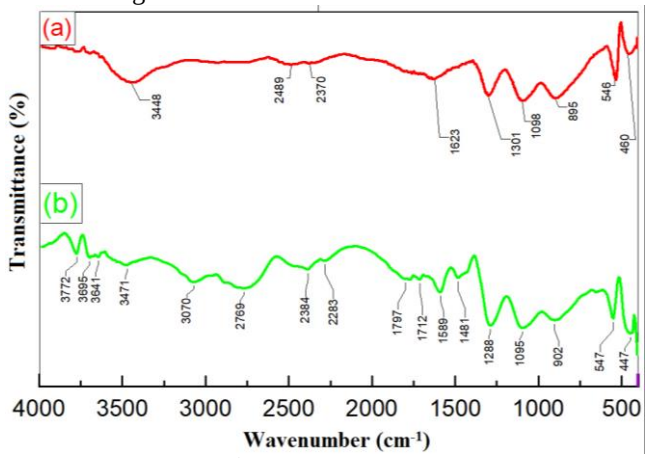



Figure 4. FTIR spectra of (a) Pure KDP and (b) 0.2wt% GA doped KDP

The absorption at wavenumber 3448 $cm^{-1}$ in pure KDP can be assigned to the O – H stretching vibration [5]. But 0.2wt% GA doped KDP shows absorption within wavenumber range 3500 to 3700 $cm^{-1}$, which can be attributed to the free O – H stretching vibration and indicates the effect of a carboxyl group present in the glutamic acid. The presence of CH stretching and bending vibrations of $CH_2$ group present in the GA is observed at 2769 and 3070 $cm^{-1}$ [5] and at 1481 $cm^{-1}$ [6], which clearly shows the successful effect of doping.

Table 3. Functional group assignments

| **Assignments** | **Wavenumber ($cm^{-1}$)** | |
|---|---|---|
| | **Pure KDP** | **0.2wt% GA doped KDP** |
| O – H Stretching and NH stretching | 3448 | 3471, 3641, 3695, 3772 |
| CH stretching vibration of $CH_2$ | ----- | 2769, 3070 |

| | | |
|---|---|---|
| C – H bending vibration of $CH_2$ | ----- | 1481 |
| Stretching vibration of P-OH | 2489, 2370 | 2384 |
| C = O stretching vibration | ----- | 1712, 1797 |
| O=P-OH stretching vibration | 1623 | ----- |
| carboxylate and/or N – H bending vibrations | ----- | 1589 |
| P=O stretching vibration | 1301 | 1288 |
| Anti-symmetric stretching mode ($\nu_3$) of phosphate | 1098 | 1095 |
| A symmetric stretching mode ($\nu_1$) of phosphate | 895 | 902 |
| A symmetric bending mode ($\nu_4$) of phosphate | 546 | 547 |
| A symmetric bending mode ($\nu_2$) of phosphate | 460 | 447 |

Further, the presence of GA is also confirmed by the presence of characteristic C = O stretching vibrations of COOH group at wavenumber 1712 and 1797 $cm^{-1}$ [5] and carboxylate and/or N – H bending vibrations observed at wavenumber 1589 $cm^{-1}$ [5,6]. While both the crystals possess the characteristic vibrations of phosphate group [7] as mentioned in the table 3, with slight shifting due to the effect of doping.

***SHG analysis***

The NLO property of both the crystals is proved by performing the Kurtz powder test on both the samples, the details of which along with formula is given in previous publication [1]. The SHG efficiency of pure and 0.2wt% GA doped KDP is 1 and 0.70, respectively. In the study of doped KDP crystal, reduction in the value of SHG efficiency is not surprise because the reports are available in the literature [8,9]. Decreased efficiency indicates that the carboxylic and/or amino group of GA might not be acted as a proton donor, which may be due to the very low concentration (0.2wt%) of GA doping. Further, the 0.2wt% doping of GA into the crystal structure of KDP, may lead to decrease in non-centrosymmetry of KDP and hence, results into decrease of non-linearity of 0.2wt% GA doped KDP crystals.

***UV-Vis analysis***

Figure 5 shows optical transmittance spectra of pure and 0.2wt% GA doped KDP crystals.

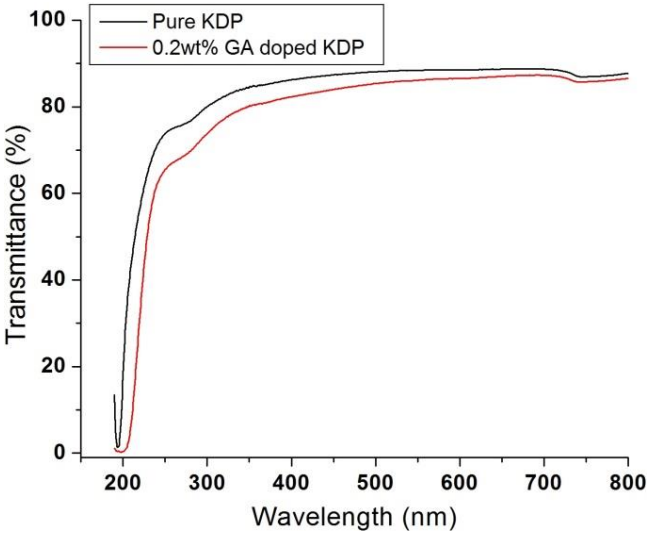



Figure 5. Transmission spectra

It is observed from the transmittance plot that the doping of 0.2wt% GA in KDP reduces the transmittance of pure KDP. The cut off wavelength of pure KDP is 195 nm; while it is 201.23 nm for GA doped KDP. So, the reduction in transparency and shifting of cut off wavelength towards higher wavelength side in the case of 0.2wt% GA doped KDP indicates the optimum effect of dopant on the transmittance property of pure KDP.

The optical energy band gap (Eg) is calculated for both the crystals by using Tauc's equation [10]

$$\alpha h\nu = A(h\nu - Eg)n,$$

Where, the meaning of the symbols is discussed in previous publication [1]. A plot drawn between $(\alpha h\nu)^2$ on y axis and energy in eV on x axis, known as Tauc's plot, which is shown in the figure 6 for both the crystals.

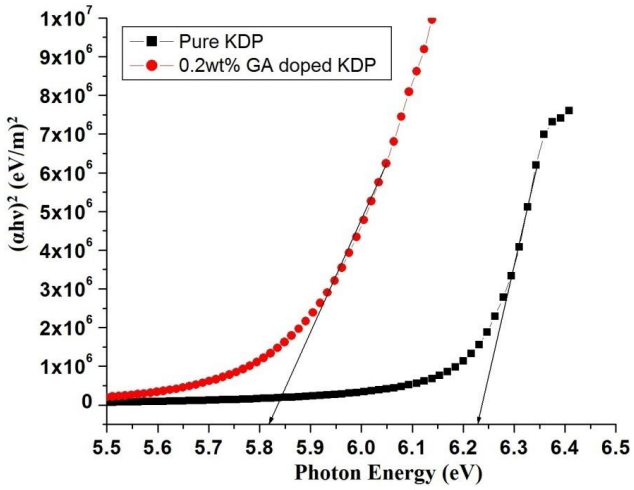



Figure 6. Tauc's plot

The extrapolation of the straight line on the x axis gives the value of optical energy band gap. In the present case, pure and 0.2wt% GA doped KDP gives the value of optical energy band gap as 6.21 eV and 5.82 eV, respectively. The energy band gap can also be estimated by using a KM function and energy

band gap relation, given in the literature [11]. A plot between photon energy on x axis and KM function on y axis is known as KM function plot, which is shown in the figure 7.

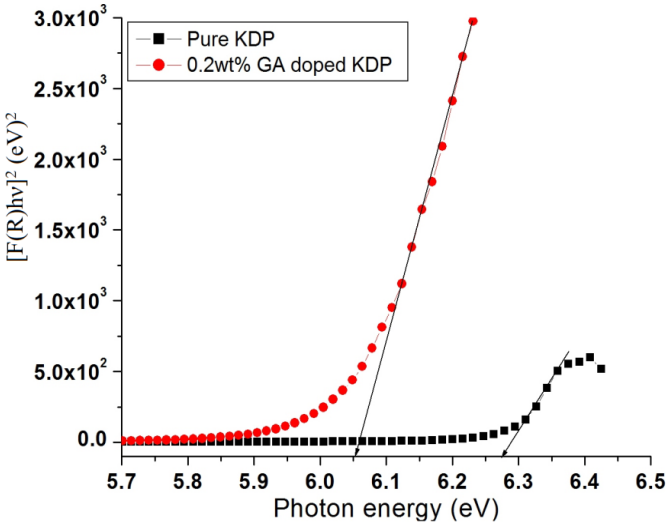



Figure 7. KM function plot

The extrapolation of straight line on the x axis gives the value of optical energy band gap. By KM function, pure and 0.2wt% GA doped KDP gives the value of optical energy band as 6.25 eV and 6.05 eV, respectively.

The energy band gap evaluated by both the methods shows slight reduction in the value after doping. The reason may be the formation of recombination centre in the forbidden gap of the pure sample. The reduced value of energy band gap also indicates the reduced ability of the doped KDP to be polarized.

**Refractive index dependence on wavelength:**

In the present investigation, the refractive index (n) of pure and 0.2wt% GA doped KDP is evaluated by using the formula given in the literature [11]. Figure 8 shows the plot of n versus wavelength (λ) in (nm) for both the crystals.

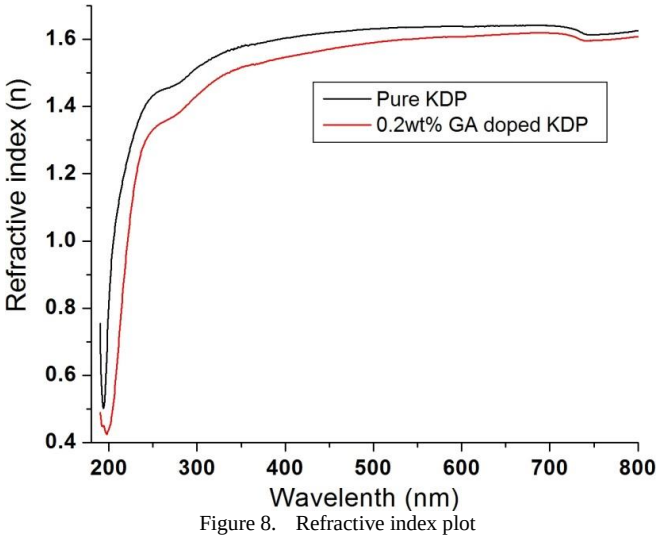



Figure 8. Refractive index plot

From the figure 8, it is observed that n rises with wavelength and becomes almost constant. Compared to pure KDP, 0.2wt% GA doped KDP shows slight reduced value of n in the visible region. This is in agreement with the reduction of transmittance of 0.2wt% GA doped KDP.

## 4. Conclusion

Pure and 0.2wt% GA doped KDP crystals are grown by slow solvent evaporation method employed at room temperature. The elemental analysis confirms the successful doping of GA. The powder XRD analysis confirms the single-phase nature of GA doped KDP crystals. The lattice strain is observed to reduce and crystallite size is observed to increase in the case of GA doped KDP crystals. The SHG analysis confirms the NLO behavior of both pure and doped KDP with reduction in efficiency of doped KDP crystals. UV-Vis analysis exhibit good transparency in the entire visible region with reduction in transparency and optical energy band gap of GA doped KDP crystals.

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**DATA AVILIBILITY**

The raw data required to ongoing study, hence it cannot be shared.

**CONFLICTS OF INTEREST**

The authors declare that there are no competing interests.

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**AUTHOR CONTRIBUTION**

Experimental, conceptional study, data collection: H.Bhuva; Analysis & interpretation of results : Dr.H.O.Jethva, H.Bhuva; Draft manuscript design : D.B.Mankad, H.K.Ladani & V.J.Pandya; Supervising & editing manuscript : Dr.H.O.Jethva;

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