

Optical studies on pure and aminoacids doped KDP crystal

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Amino acids (L-Glutamic acid, L-Histidine, L-Valine) doped potassium dihydrogen phosphate crystals are grown by solution growth technique. Slow cooling as well as slow evaporation methods were employed to grow these crystals. The concentration of dopants in the mother solution was varied from 0.1 mole% to 10 mole %. The solubility data for all dopants concentration were determined. There is variation in pH value and hence, there is habit modification of the grown crystals were characterized with UV - VIS, FT-IR studies, SHG trace elements and dielectric studies reveal slight distortion of lattice parameter for the heavily doped KDP crystals. UV – Visible spectra confirm the improvement in the transparency of these crystals on doping metal ions. FT – IR spectra reveal strong absorption band between 1400 – 1600 cm^{-1} for metal ion doped crystals. TGA-DTA studies reveal good thermal stability. The dopants increase the hardness value of the material. Aminoacids doping improves the NLO properties. The detailed results on the spectral parameters, habit modifications and other properties are presented.

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1. Introduction

Optical crystals with a high degree of perfection find applications in critical technology areas such as high-power lasers, higher harmonic generation [1-3] and in the field of nuclear fusion. A class of such crystals can be grown from their supersaturated solution in water, during a slow cooling process. The fast developments in the field of optoelectronics necessitates the search for new and efficient non linear optical (NLO) materials, which can be used for optoelectronic applications such as optical computing, optical data storage, optical communications and electro-optic shutters [6-8]. During the past decade, a number of organic and inorganic materials with high nonlinear susceptibilities have been synthesized. However their device applications have been impeded by the inadequate optical transmittance, poor optical quality, and lack of robustness, low laser damage threshold and inability to be grown into large size crystals. The molecules in pure organic crystals are often bonded by weak van der Waals forces of hydrogen bonds, which result in poor mechanical robustness. To overcome these difficulties, the large nonlinearities of π -conjugated organics and the favorable crystal growth properties of ionic salts can be combined into a single NLO material called semi-organic. In this paper the crystal growth of aminoacids (L-Glutamic acid, L-Histidine, L-Valine) doped KDP has been described.

2. Crystal growth

A supersaturated solutions of KDP powder is prepared in distilled, deionized water. The amount of KDP salt to be dissolved is determined from its solubility at the average temperature of 35 °C. The solution is stirred long enough

to ensure complete dissolution of the solute, and filtered using Whatmann 100 filter paper to remove residual microscope particles. The solution is maintained at relatively high temperature for about 4 – 5 h using water circulation from the temperature control unit.

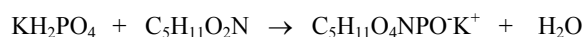
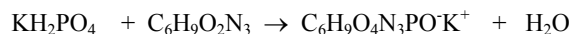
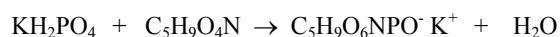
Pure KDP crystals were grown from aqueous solution by slow evaporation and also by slow cooling method (0.5 deg/day). The same method was followed for doped KDP crystals (0.1 mole% L-Glutamic acid or L-Histidine or L-Valine). The solubility of doped KDP in the solvent was determined for each dopant for four different temperatures, 30, 35, 40 and 45 °C, by dissolving the KDP salt in deionised water in an air-tight container maintained at a constant temperature [9, 10] with continuous stirring. After reaching saturation, the equilibrium concentration of the solute was analysed gravimetrically. The solubility of doped KDP was measured for each dopant and was found to be 32.5-grams/100 ml at 40 °C for Glutamic acid, 31.5 grams/100 ml at 40 °C for L-Histidine and 32.75 grams/100 ml at 40 °C for L-Valine. The seed crystals are prepared at low temperature by spontaneous nucleation. Seed crystals with perfect shape and free from macro defects were used for growth experiments. Large single crystal KDP and doped KDP (L-Glutamic acid, L-Histidine, L-Valine) were grown using a constant temperature bath (CTB), controlled with an Indtherm temperature programmer/controller. The mother solution was saturated using the initial pH values, 4.5, 4.6 and 4.8 for L-Glutamic acid, L-Histidine, and L-Valine dopants respectively. The growth was carried out for more than 20 days by keeping the bath at a temperature of 38 °C.

A few nuclei of doped KDP had appeared at the bottom of the beaker and grew for a few days. The change of super saturation was greater than 15 % of the critical

super saturation during the growth of doped of a few doped KDP crystals. Constant temperature bath is used for the bulk growth of aminoacid doped KDP crystals. Transparent good quality crystals were obtained after 20 days. The hardness measurements of the grown crystals were carried out with Vickers Pyramidal indenter and using the Leitz Metallux II microscope.

All three aminoacids used as dopants are colorless in crystalline state. They melt with decomposition at high temperature. They are soluble in polar solvents. They possess asymmetric carbon atoms. Therefore, they are optically active.

The partial substitution of potassium ions may be explained as the consequence of following chemical reactions.



3. Characterisation studies

3.1 FT-IR spectral studies

The FTIR spectra of all the samples were recorded from solid phase samples on a Bruker IFS 66V model spectrophotometer using 1064 nm output of a cw diode pumped Nd:YAG laser as a source of excitation in the region $400 - 4000 \text{ cm}^{-1}$ operating at 200 mW power on the samples, with a spectral resolution of 2 cm^{-1} . The IR spectra [11-14] were also recorded on Shimadzu-800, FTIR spectrometer series of Japan in the region $400 - 4000 \text{ cm}^{-1}$. The frequencies for all sharp bands are accurate within $\pm 1 \text{ cm}^{-1}$. The observed FT-IR spectra of single and doped KDP are shown in Fig. 2.



Fig. 1.(a) As grown L-Valine:KDP crystal.

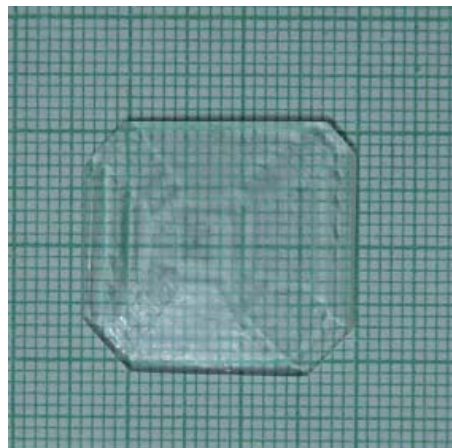


Fig. 1.(b) Seed crystals of L-Glutamic acid doped KDP.

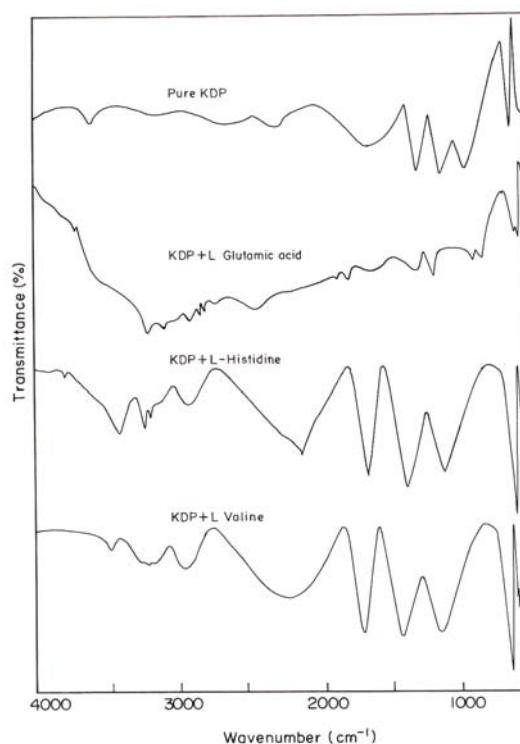


Fig. 2. FT-IR spectra recorded for the pure and amino acids doped KDP crystal.

The values of bond length and bond angles were taken from Sutton's table. Internal co-ordinates for the out of plane torsional vibrations are defined as recommended by IUPAC. The general quadratic valence force was adopted for both in plane and out of plane vibrations.

The frequencies with their relative intensities obtained in FTIR of pure and doped KDP and their most probable assignments are presented in Table 1. The observed spectra are explained on the C_3 point group symmetry for potassium dihydrogen phosphate and C_{2v} point group symmetry for potassium hydrogen phthalate ion. The 11

optically active fundamental vibrations belong to C_3 point groups are

$$\begin{aligned}\Gamma &= \Gamma_{\text{tra}} + \Gamma_{\text{rot}} + \Gamma_{\text{vib}} \\ \Gamma &= 5A + 10E \\ \Gamma_{\text{tra}} &= A + E \\ \Gamma_{\text{rot}} &= A + E \\ \Gamma_{\text{vib}} &= \Gamma - \Gamma_{\text{tra}} - \Gamma_{\text{rot}} \\ &= 5A + 10E - 2A + 2E \\ \Gamma_{\text{vib}} &= 3A + 8E\end{aligned}$$

The 42 active vibrations of C_{2v} point groups are distributed as

$$\begin{aligned}\Gamma &= 16A_1 + 8A_2 + 16B_1 + 8B_2 \\ \Gamma_{\text{rot}} + \Gamma_{\text{transl}} &= A_1 + A_2 + 2B_1 + 2B_2 \\ \therefore \Gamma_{\text{vib}} &= 15A_1 + 7A_2 + 14B_1 + 6B_2\end{aligned}$$

Table 1. Observed and calculated IR frequencies (cm^{-1}) of Pure KDP and KDP doped with L(+) Glutamic Acid, L(-) Histidine and L(+) Valine.

Species	Calculated Frequencies (cm^{-1})	Observed IR frequencies and intensities				Assignments
		Pure KDP	KDP doped with L(+) Glutamic Acid	KDP doped with L(-) Histidine	KDP doped with L(+) Valine	
A/E	3605	3600 VW	—	—	—	Free O—H stretching hydrogen bonded of KDP
	3333	3340 W	3350 VW	3435 M	3425 VW	O—H stretching hydrogen bonded of KDP
	2919	2924 W	2950 M	2923 M	2923 M	C—Haliphatic stretching superimposed with N—H stretching
	2839	2844 VW	—	2852 VW	2853 VW	P—O—H symmetric stretching
	2461	2466 W	2418 M	2465 M	2460 M	NH_3^+ bending superimposed with P—O—H stretching
	2358	2362 VW	—	—	—	P—O—H bending of KDP
	—	1725 M	—	1713 M	1713 M	C=O stretching
	1650	1655 VS	1648 VS	1641 VS	—	Stretching of KDP
	1295	1299 S	1303 S	1303 S	1303 S	P=O stretching of KDP
	904	908 S	—	908 S	907 S	P—O—H stretching of KDP
	—	—	878 M	—	—	N—H wagging
	535	539 S	—	534 S	535 S	HO—P—OH bending
	—	—	487 S	487 S	486 S	N—H torsional oscillation
	—	—	480 S	481 S	479 S	N—H torsional oscillation

VS – Very Strong S – Strong M – Medium W – Weak VW – Very Weak

All these modes are active in Infrared except A_2 mode, which is Infrared inactive for C_{2v} group. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and from the literature data.

The bands appeared at 3600 cm^{-1} in pure KDP, KDP doped with L-Glutamic acid, L-Histidine, L-Valine were assigned to free O—H stretching. The very weak bands indicate its presence in low concentration. The absence of even such a weak band in the case of KDP doped with L-Glutamic acid indicated the strong interaction of L-Glutamic acid with O—H groups. The broad absorption band appeared at 3340, 3296, 3255 were assigned to hydrogen bonded O—H stretching frequencies in pure

KDP, KDP + L-Glutamic acid and KDP + L-Histidine respectively. The absence of this peak in KDP doped with L-Valine supported again the strong interaction of L-Glutamic acid with O—H groups and the possible entry of these ions in the lattice site of KDP crystal. This leads to the decrease in the frequency of O—H stretching and confirms the non-linear optical property of pure and doped. This property is also reflected in the P=O, P—O, P—OH stretching and HO—P—OH bending vibrations (see Table 1).

Our present IR study on pure and doped KDP clearly indicated the effect of dopants on the crystal structure of pure KDP, which leads to the change in the absorption of

IR frequencies and the non-linear optical property of both the crystals. The study also confirmed that the dopants had entered the lattice sites of tetragonal KDP.

3.2. TGA and DTA studies

To analyse the thermal stability [4-5] and to confirm the melting point of the material, the thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out using PL-STA 1500 thermal analyzer at a heating rate of $20^{\circ}\text{C min}^{-1}$ in air (Fig. 5).

The DTA curve shows that doped (L-Glutamic acid) KDP melts at a temperature around 25°C and it undergoes an irreversible endothermic transition around 236°C followed by another endothermic peak at 295°C . The TGA curve shows that there is a weight loss of about 66.8% in the temperature range $236^{\circ}\text{C} - 325^{\circ}\text{C}$ due to the release of volatile substances, probably carbon dioxide or ammonia. Prolonged heating up to 900°C does not produce any exothermic or endothermic peaks in the DTA curve whereas TGA shows almost complete weight loss and the residual weight obtained at 900°C is 13.24 %.

TGA and DTA studies were carried out on pure and doped KDP single crystals. Powder samples were prepared by crushing single crystal using mortar and pestle. Experiments were performed using simultaneous TG-DTA (SETARAM STA 409°C) analysis by heating the sample at 10 Kelvin/min in the temperature range between 25 and 900°C under nitrogen atmosphere. The DTA curves of pure KDP samples show 5 major endothermic peaks at 156, 192, 272, 559 and 798°C respectively (Fig. 5a). In TG curve the mass loss begins at about 190°C with a major event at 273°C , which corresponds very well with the DTA result. The total mass loss is 2.795 % and the saturation occurs at 350°C i.e., above 350°C the TG curve return to its baseline and a constant weight obtained. However, the DTA curve reveals two more events at 560 and 798°C , respectively, and these peaks are not accompanied by the weight loss. They might be attributed to high temperature phase transition of KDP [4]. In addition, a significant splitting appears in the DTA peak at 272°C . This possibly indicates the decomposition of KDP into $\text{K}_2\text{H}_2\text{P}_2\text{O}_7$ and water as $2\text{KH}_2\text{PO}_4 \rightarrow 2\text{KPO}_3 + 2\text{H}_2\text{O}$. The satellite peak might correspond to the low temperature structural phase transition of KDP. TGA&DTA results of L-Histidine-doped (0.1 mol%) KDP samples are very much comparable with the pure KDP results except small deviations in the peak positions. Another significant observation is that the intensity of the major peak (274.6°C) which splits in two peaks is reversal when compared to pure samples. The results suggest that the phase stability of the L-Histidine -doped KDP might have been improved when compared to the pure KDP sample that results in a higher decomposition temperature. The total mass loss is 2.774 % and is comparable to pure KDP sample. Contrary to the above results, the L-Valine doped KDP sample do not show any splitting in the major DTA peak (272°C) at least up to the resolution limit of the instrument. It can be noticed that the intensity of satellite

peak (at 227°C) is very low when compared to those for the other two samples. This result is very significant in two different aspects: (i) the result indicates that the dopant L-Valine is actually substituted in the crystal lattice (ii) the result suggests the KDP phase stability improves in the presence of L-Valine. However, further studies with various doping level is required for confirming these observations. The TGA results are similar to other two samples with a load mass loss of 2.699 %. Fig. 5b shows that loss of water occurs at 150°C , the reaction is exothermic and at 274.6°C occurs the crystallization of salt. At 380°C takes place the loss of CO_2 , which is an exothermic reaction.

3.2 Dielectric and linear optical property studies

The extended portions of the crystals were removed completely and the crystals were ground to proper thickness and polished. Each sample was electroded on either side with air-drying silver paste so that it behaved like a parallel plate capacitor. A4279A, multi frequency LCR meter (Hewlett-Packard) was used to measure capacitance (C) of the sample as a function of frequency. Fig. 4 shows the variation of dielectric constant with frequency measured at room temperature for L-Glutamic acid doped crystal grown at an optimized pH value of 4.2. The dielectric constant is maximum at low frequency and decreases with increase in frequency. The increase in the dielectric constant [18] at low frequency is attributed to space-charge polarization. Variation of dielectric loss as a function of frequency is depicted in figure. The low value of dielectric loss at pH 4.2 indicates that the L-Glutamic doped KDP crystals possess fewer defects. The UV visible spectra recorded on the L-Glutamic doped KDP crystals, L-Histidine doped KDP crystals and L-Valine doped KDP crystals in the range 200-1200 nm show that the transmission is higher for L-Valine doped KDP grown crystal at an optimized pH value of 4.2 (Fig. 3).

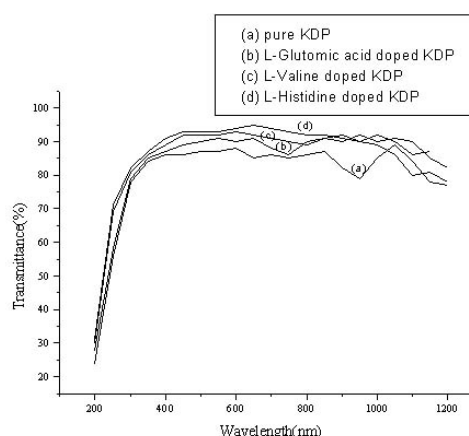


Fig. 3. UV-visible transmission spectra of (a) Pure, (b) L-Glutamic acid (c) L-Histidine, (d) L-Valine doped KDP crystal.

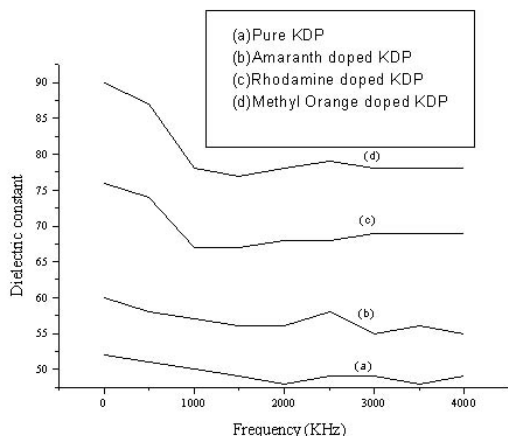


Fig. 4. Dielectric studies on amino acids doped KDP crystal.

3.3 NLO properties

In order to confirm the NLO property the doped KDP crystal has been tested using the Nd-YAG laser. Small crystals of aminoacids doped KDP was placed on the sample holder and the red color laser beam was made to pass through the crystal and the incoming beam passing through the crystal converted into the green light. The efficiency of doped KDP crystals were compared with pure KDP and also shows that L-Valine doped KDP crystal have higher efficiency.

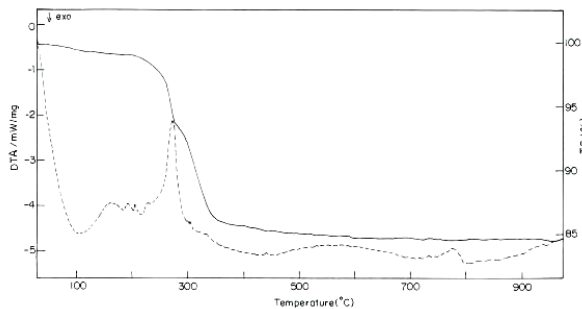


Fig. 5. TGA-DTA spectra of pure KDP crystal.

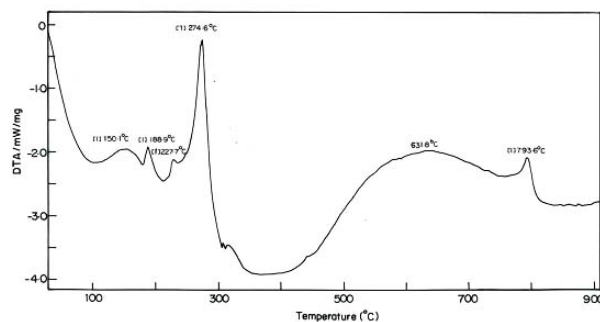


Fig. 5(a) TGA-DTA spectra of amino acid (L-Glutamic acid) doped KDP crystal.

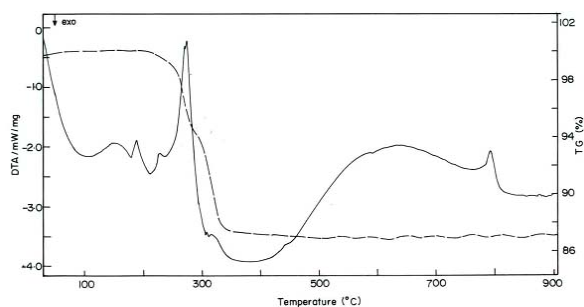


Fig. 5(b) TGA-DTA spectra of amino acid (L-Histidine) doped KDP crystal.

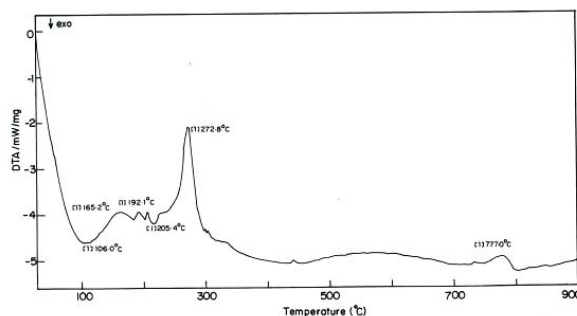


Fig. 5(c) TGA-DTA spectra of amino acid (L-Valine) doped KDP crystal.

4. Results and discussion

The dopants L-Glutamic acid, L-Histidine and L-Valine are expected to substitute the potassium ions in the KDP lattice due to their valency as well as proximity of ionic radius. KDP was doped with L (+) Glutamic acid and IR spectrum was recorded for the range from 4000 cm^{-1} to 400 cm^{-1} . The absorption frequencies of KDP + L (+) glutamic acid and pure KDP are compared. The O-H stretching OH-P-OH bending vibrations appeared at 3600(vw) cm^{-1} and 539(s) cm^{-1} in pure KDP were found to be missing in the IR spectrum of KDP doped with L (+) glutamic acid. It clearly indicated that the O-H group of KDP might have reacted with COOH group of L (+) glutamic acid. The dopant glutamic acid consists of two COOH and one NH_2 group. One of the COOH groups has been converted into COO^- and NH_3^+ (zwitter ion) by reaction with NH_2 group. The second COOH group of L (+) glutamic acid might have reacted with OH group of KDP [12]. The P=O stretching usually appear at 1152 cm^{-1} and 1190 cm^{-1} in oxides of phosphorous appeared at 1299 cm^{-1} in pure KDP and at 1303 cm^{-1} in KDP doped with L (+) glutamic acid revealed the etherification of P-O-H group of KDP with one of the COOH group of L (+) glutamic acid. This is further confirmed by the increase in the P=O stretching frequency of KDP doped with L (+) glutamic acid. This increase is due to the electronegativity of the alkoxy group of L (+) glutamic acid. The change in the structure of the pure KDP when it is doped with L (+) glutamic acid results in the change in the interaction of IR

radiation with sample and confirms the non-linear optical property of the KDP with dopant L (+) glutamic acid.

The comparison of IR spectrum of pure KDP and KDP doped with L (-) histidine and L (+) valine revealed that no much change in the frequencies absorbed for pure KDP and KDP doped with L (-) histidine and L (+) valine except some additional IR frequencies appeared at 2852 cm^{-1} and 2465 cm^{-1} due to the interaction of the N-H stretching frequency of aminoacids with P-O-H symmetric stretching of KDP [15-17]. The very low intensity of O-H stretching frequency in the KDP doped with L (-) histidine revealed the involvement O-H in hydrogen bonding with ring nitrogen of L (-) histidine. This was further confirmed by high intensity O-H stretching band at 3435 cm^{-1} in KDP doped with L (-) histidine compared to free O-H stretching frequency band at 3600 cm^{-1} in the case of the pure KDP. Further the decrease in the O-H hydrogen bonded stretching frequency by 165 cm^{-1} in the case of KDP doped with L (-) histidine compared to free O-H of pure KDP revealed the extend of hydrogen bonding between H^+ of KDP with ring nitrogen of L (-) histidine and in weakening the O-H bond strength of pure KDP.

It was found that the optical property of pure and doped KDP changed not only due to the weakening of the bond between O-H and C=O due to hydrogen bonding but also due to the substitution of metal ions in the crystal lattice of tetragonal KDP crystals which increased the bond strengths [19-21]. Since H^+ ion having the radii of only $0.3\text{ \AA}$ is being replaced by amino acids there must be a strain in the accommodation of these ions instead of H^+ . Hence, only a limited number of ions can diffuse into the lattice sites of tetragonal KDP crystals. The adsorption of impurities on prismatic faces retards the growth velocity of the prismatic face and induces many tiny imperfections. The adsorption of silica clusters under high super saturation results in growth centers, which are effectively blocked, and this causes subsequent growth of islands. This is supported by observations that inclusions including tiny ore minerals and Brazil twins are concentrated in the growth sectors of prism and tapered faces and the impurities are riched in the prism sectors. As a result, the growth hillocks change form from rectangular to square-like on the prismatic faces of crystals grown from solution with impurities [20-23]. A large number of tiny growth islands elongated in the x-direction are formed on the tapered faces of KDP crystals.

5. Conclusion

A new nonlinear optical material, aminoacids (L-Glutamic acid, L-Histidine and L-Valine) doped KDP crystals have been grown by slow evaporation technique at room temperature. The functional groups present in the grown crystals have been confirmed by FTIR spectral analysis. The observed frequencies were assigned on the basis of symmetry operation on the molecule and normal coordinate analysis. The study not only confirmed the strong interaction amino acids of the dopants with the -OH group of KDP but also the entry of these ions in the

crystal lattice of tetragonal KDP crystal. All three aminoacids used as dopant are colourless crystalline. They melt with decomposition at high temperature. They are soluble in polar solvents. They possess asymmetric carbon atom. Therefore, they are optically active. TGA and DTA show that the material is thermally stable until it melts at 225°C . The NLO property the doped KDP crystal has been tested using the Nd-YAG laser.

The presence of dopants in the crystal was qualitatively investigated by the FTIR studies. The doping with L-Glutamic acid, L-Histidine and L-Valine causes much broadening of the peaks in the spectra when compared to the pure KDP crystal. The spectra also reveal reduction in the crystal hardness as a result of dopant incorporation-this has been evident in the hardness measurements for pure and doped KDP crystals. It is inferred that the modes due to polar groupings, for example COOH, COO- are more broadened compared to the modes of non-polar groupings illustrating that the doped crystals reject more degree of interaction for the polar groupings rather than for non-polar groupings. The capacitance and dielectric loss were measured at different temperatures for pure and aminoacid doped KDP crystals at different frequencies and subsequently the permittivity (ϵ_r) and loss factor (ϵ'') were calculated. The dielectric loss was higher for pure crystals than for pure crystals than the doped crystals.

References

- [1] Tiffany N. Thomas, Terry A Land, Michael Johnson, William H Casey, *Journal of Colloid and Interface Science* **280**, 18-26 (2004).
- [2] H. F. Robey, *J. Crystal Growth* **259**, 388-403 (2003).
- [3] H. V. Alexandru, S. Antohe, *J. Crystal Growth* **258**, 149-157 (2003).
- [4] Jong-Ho Park, *Solid-state communications* **123**, 291-294 (2002).
- [5] Byoung-Koo Choi, *Journal of Physics and Chemistry of solids* **56**, 1023-1030 (1995).
- [6] J. Podder, *Journal of Crystal Growth*, **237-239**, 70 (2002).
- [7] Sonal S. Gupte, Ranjit D. Pradhan, *J. Appl. Phys.* **91**, 3125 (2002).
- [8] Shukin Lin, Liting Li, *J. Cryst. Growth*, **249**, 341 (2003).
- [9] N. Zaitseva, L. Carman, I. Smolsky, *J. Cryst. Growth* **241**, 363 (2002).
- [10] N. Y. Garces, K. T. Stevens, L. E. Halliburton, M. Yan, N. P. Zaitseva, J. DeYoreo, *J. Cryst. Growth*, **225**, 435 (2001).
- [11] J. H. Schachtschneider *Tech Rep Shell Development Company Emeryville CA, USA*, (1969).
- [12] G. Ravi, K. Srinivasan, S. Anbukumar, P. Ramasamy, *J. Cryst. Growth*, **137**, 598 (1994).
- [13] S. Hirota, H. Miki, K. Fukui, K. Maeda, *J. Cryst. Growth*, **235**, 541 (2002).
- [14] Tanusri Pal, T. Kar, Xin-Qiang Wang, *J. Cryst. Growth*, **235**, 523 (2002).

- [15] S. Anbukumar, S. Vasudevan, P. Ramasamy, *J. Mater. Sci.* **5**, 223 (1986).
- [16] P. M. Ushasree, R. Jayavel, P. Ramasamy, *Mater. Chem. Phys.* **61**, 270 (1999).
- [17] Silverstein, Bassler and Morrill, *Spectrometric identification of organic compounds*: by John Wiley & Sons, Inc., Fourth Edition, Page 176, (1981).
- [18] Mirosława Rak, N. N. Eremin, T. A. Eremina, V. A. Kuznetsov, T. M. Okhrimenko, N. G. Furmanova, F. P. Efremova, *Journal of Crystal Growth* **273**, 577-585 (2005).
- [19] Mirosława Rak, N. N. Eremin, T. A. Eremina, V. A. Kuznetsov, T. M. Okhrimenko, N. G. Furmanova, F. P. Efremova, *Journal of Crystal Growth* **273**, 586-593 (2005).
- [20] N. Kubota, J. Fukazawa, H. Yashiro, J. W. Mullin, *J. Crystal Growth* **143**, 487 (1994).
- [21] J. F. Jurado, A. Garcia, R. A. Varas, *Solid State Ionics* **136-137**, 985-989 (2000).
- [22] N. P. Rajesh, V. Kannan, P. Santhanaraghavan, P. Ramasamy, *Materials Letters* **52**, 326-328 (2002).
- [23] V. I. Bredikhin, G. L. Galushkina, A. A. Kulagin, S. P. Kuznetsov, O. A. Malshakova, *J. Crystal Growth* **259**, 309-320 (2003).

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