RESEARCHERID
THOMSON REUTERS

ISSN: 2277-9655
[Manimekalai* *et al.*, 7(1): January, 2018] Impact Factor: 5.164
IC™ Value: 3.00 CODEN: IJESS7

IJESRT
INTERNATIONAL JOURNAL OF ENGINEERING SCIENCES & RESEARCH TECHNOLOGY

# GROWTH AND CHARACTERISATION OF SACROSINE DOPED POTTASSIUM DIHDROGEN PHOSPHATE CRYSTALS

**K.Manimekalai [*1],R.Rajasekaran [2]**
(Department of Physics, St.Joseph's Institute of Technology,Chennai-119,Tamilnadu,India )
(Department of Physics, Aruna Vidya Arts & Science College,Thiruvannamalai Tamilnadu,India)

**DOI**: 10.5281/zenodo.1147558

## ABSTRACT

Potassium dihydrogen phosphate is a material rich in NLO property with wide range of industrial applications. Certain Amino acids are also rich in NLO properties so they are used as dopants. In the present work Sacrosine one of the twenty amino acid is added in the ratio 1:1 molar percentage to KDP. Single crystals were grown by slow evaporation method. The grown crystals were characterized by powder X-ray diffraction, Single crystal X-Ray diffraction, UV–vis. -spectroscopy, Fourier transform infrared spectroscopy (FTIR), SHG efficiency, Dielectric and Micro hardness studies. The single crystal X-ray diffraction studies reveal the structure and space group of the crystal. The powder X-ray diffraction study shows that the crystalline perfection of grown crystal is good. Fourier transform infrared studies confirm the functional groups of the crystals. It is seen from UV–vis studies that the optical transparency is found to increase much by adding chlorides. SHG efficiency of KDP is found to be slightly increasing with doping of Sacrosine. Dielectric studies show the conductivity and electrical behaviour of the crystal. Micro hardness studies show the mechanical stability of the crystal.

**KEYWORDS**: KDP, FTIR, UV-Vis, NLO, XRD, SHG, Micro hardness

## I. INTRODUCTION

Nonlinear optics is a new frontier of science and technology and the nonlinear optic materials are the precursor of current research playing a vital role in the emerging trend of photonics. Non linear optical processes have applications in the field of telecommunication, optical signal processing and optical switching and laser technology. So extensive studies have been made on the synthesis and growth of NLO materials over the past decades. [1,2] Potassium dihydrogen phosphate (KDP) is an excellent inorganic non-linear optical (NLO) material and has a considerable interest among the researchers due to their extraordinary qualities such as high nonlinear conversion efficiency, wide optical transmission range with low cut off wavelength and high laser damage threshold against the high power laser[3] KDP is an efficient angle tuned dielectric medium for optical harmonic generation in the visible region.[4]. Of all organic materials, amino acids exhibit an extraordinary nonlinear optical properties as they contain both a donor group NH2 and acceptor COOH group and also there is a possibility to transfer intermolecular charge in amino acids.[5] .Amino acids and their compounds belong to a family of organic materials which have wide applications in Sarcosine, also known as N-methylglycine (CH3NH2+CH2OO)−, is a natural amino acid inhibiting two hydrogen atoms which are located at the nitrogen atom. There have been several reports investigating qualitatively the crystal structure of sarcosine in pure and made on several crystalline complexes with organic and inorganic acid derivatives. This amino acid is found naturally in starfish, sea urchins and in the antibiotic actinomycin and is also used in certain cosmetics. It is used in manufacturing bio degradable surfactants [6]
An impurity can suppress, enhance or stop the growth of crystal completely.[7] (Sangwal 1996A lot of research has been undertaken to modify the properties and growth rate of KDP with the addition of suitable impurities.[8] Kumaresan et al(2007) have grown L-glutamic acid, L-Histdine and L-Valine doped KDP crystals. They have shown an improved optical transmission and NLO property and also growth habit modifications. Also they observed an increase in the mechanical hardness with respect to pH variations.[9](Shaikh Kalim shaik Hanif et al 2015)[ reported Glycine doped KDP crytal with enhanced NLO property than pure KDP . So there are so many reports related to doping of amino acids with KDP. With those references the present work is aimed at the doping of amino acid Sacrosine with KDP and their effect and changes in the growth of KDP have been reported.

**ISSN: 2277-9655**
**Impact Factor: 5.164**
**CODEN: IJESS7**

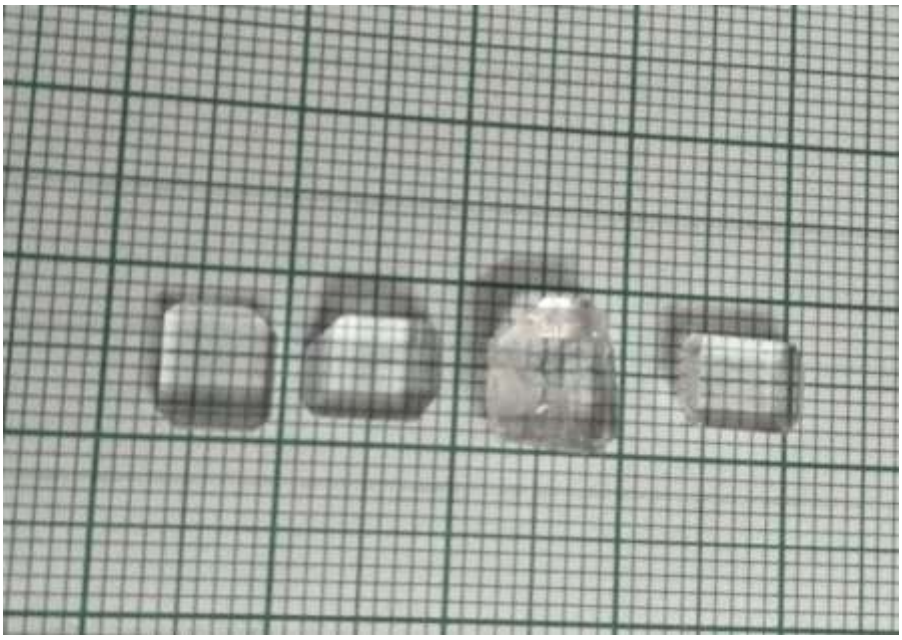
## II. EXPERIMENTAL PROCEDURE

Pure KDP AR grade E-Merck and Sacrosine doped crystals were grown by slow evaporation growth technique at room temperature. The saturated solution is prepared by dissolving the solute of KDP in 30g per 100ml in Millipore water. The doping of Sacrosine was carried out by adding 0.1 weight percentage powder form of Sacrosine into 1 molar 100 ml solution of KDP in millipore water. The mixtures were well stirred for 8 hrs for homogenization .Then it was double times filtered with whatt man filter paper and poured into Petri dishes and covered with perforated polyethylene. The prepared solution was allowed to dry at room temperature and the crystals were obtained by slow evaporation method. In the period of 15-20 days, the crystal had formed as shown in Fig. 1..Then the grown crystals has been subjected various spectral studies to analyze its characteristics . The size of the grown crystal is 8.8*5*2 mm3 and were found to be colour-less and transparent. Figure 1 shows a photograph of 0.1 wt. Sacrosine doped KDP.

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

$$KH_2PO_4 + C_3H_7NO_2 \longrightarrow C_3H_7\,O_4\,NPO^{-}K^{+} + H2O \qquad (1)$$

**Figure**:



**Fig(1) As grown crystals of Sacrosine doped KDP**

### Characterization-

The grown Sacrosine doped KDP crystals were subjected to various characterizations .Single crystal X-ray diffraction studies were carried out using single crystal diffractometer ENRAF NONIUS Cad4 and its lattice parameter volume structure and space group is analysed in given in table. Powder X-ray diffraction studies were carried out using powder X-ray diffraction instrument D8 advanced BRUKER Spectrometer using CuKα radiation source and its wave length (λ=1.54Å), data collected from the 2θ range from 10°to 90° in steps of 0.020 and count time 0.2S.The obtained results are in Fig.2(a) .Identification of functional groups were carried out by FTIR analysis using JASCO 4100 shown in Fig 3.UV-Visible spectral study is carried out using SHIMADZU 2600 in the range 200-1200nm as shown in Fig.4(a) and the results were compared with that of pure KDP and a comparative studies are made between the Sacrosine doped KDP Crystals. The NLO property of the doped crystal is evaluated by the Krutz and Perry (1968) powder technique using a Q-switched, mode locked Nd : YAG laser. Dielectric property of the crystal is carried out for various temperature using **HIOKI MODEL 3532_50 LCR High Tester.** The Vickers micro hardness studies are carried out using Futuretech FM 800 type E series.

RESEARCHERID
THOMSON REUTERS
ISSN: 2277-9655
[Manimekalai* *et al.*, 7(1): January, 2018] Impact Factor: 5.164
IC™ Value: 3.00 CODEN: IJESS7

## III. RESULT AND DISCUSSION

KDP crystal is a promising NLO material with high transparency and frequency doubling property when doped with Sacrosine shows some changes in its Characteristics when subjected to Single crystal X-ray diffraction , powder X-Ray diffraction , Fourier transform Infra red Spectroscopy ,UV Spectroscopy, SHG measurements, Dielectric measurements and Hardness studies.

### 1. Single Crystal XRD Studies:

Single crystal X-ray diffraction analysis was carried out using ENRAF NONIUS Cad4 diffractometer to identify the lattice parameters. The single crystal X-ray diffraction studies confirm the tetragonal structure with the space group of I-42d .The lattice parameters of
Sacrosine doped are; a=b=7.456A ˚ , c=8.75A ˚ , with volume V=389.35A ˚ $^{3.}$ The crystal parameters and cell volume were found to be well in agreement with reported values [11]
as shown in table (1).From the grown doped crystal lattice parameters and space group it is clear that the basic structural property and space group of KDP is not altered by the dopant[12]

| Compoud | Crystal system | Space group | Unit cell parameters |
|---|---|---|---|
| KDP | Tetragonal | I-42d | a=b=7.455Å, c=6.975 Å. α=β=γ=90º |
| KDP +Sacrosine | Tetragonal | I-42d | a=b=7.4565Å,c=8.75 Å. α=β=γ=90º |

**Table-1 Lattice parameters for pure KDP and Sacrosine doped KDP**

### 2.Powder XRD Studies:

The Sacrosine doped KDP crystals when subjected to X-ray diffraction shows pattern as in fig 2 .While comparing with the powder xrd pattern of pure KDP it is found that 2theta values shifted and this suggests that the structure of KDP is slightly disturbed by of Sacrosine which tries to change the transparency.

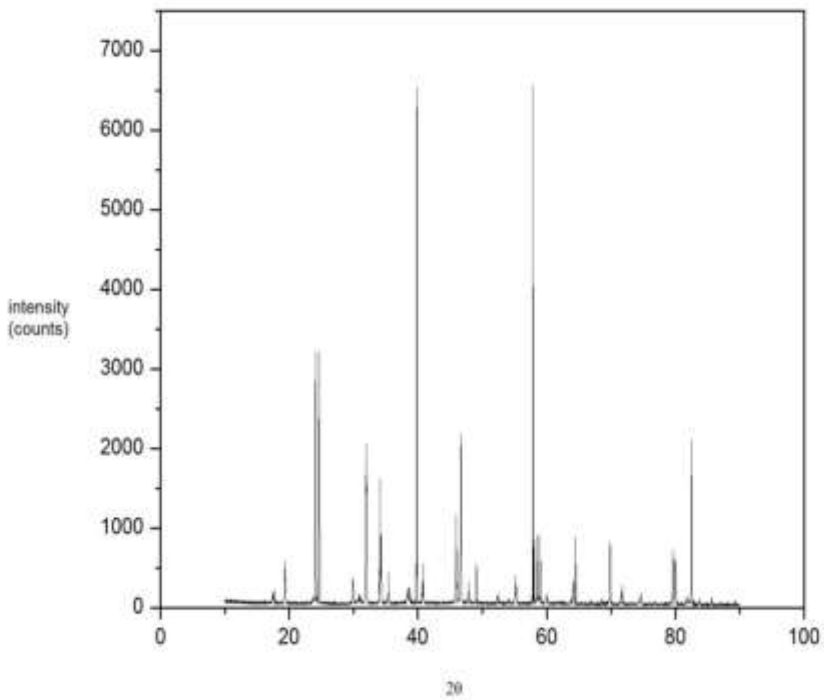



**Fig:2 Powder XRD Pattern of Sacrosine doped KDP**

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

**3.Fourier-Transform Infrared Spectroscopy Studies:**

FTIR is a technique which is used to obtain an infrared spectrum of absorption, emission or photoconductivity of a solid, liquid or gas. It collects high spectral resolution data over a wide spectral range. This analysis has been carried out by recording the spectrum in the range 4000 – 400 cm-1 using KBr pellet method. The spectrum of Sacrosine doped KDP is shown in fig 3.The IR spectra in 450 -600 is called the fingerprint region so it is difficult to assign all absorption bands this region. The already reported pure KDP crystal shows O-H stretching at frequencies 3615 cm-1, 3320 cm-1 and 3155cm-1. P-O-H . Stretching of H2PO4 arises at 2914 cm-1, at 1136 it shows P=O stretching and at 531 shows HO-PO-OH stretching in the spectrum. Table -2 shows the functional group assignments and their frequencies of Sacrosine doped KDP[12]

| Frequency cm-1 | Fuctional group assignments |
|---|---|
| 3437.49 | Asymmetric stretching ofNH3+ |
| 3189 | NH stretching |
| 2963 | C-$H_2$ stretching |
| 2924.52 | C-$H_3$ stretching |
| 2764 | O-H stretching |
| 2460.72 | C=H stretching |
| 1719 | C = O bending |
| 1637.27 | P-O-H bending |
| 1296 | N-H bending of dopants |
| 1096.37 | P=O stretching |
| 904.45 | P=O stretching |
| 536.11 | c-o bending |
| 457.04 | HO-P-OH bending |

**Table:2 Functional groups of Sacrosine doped KDP**

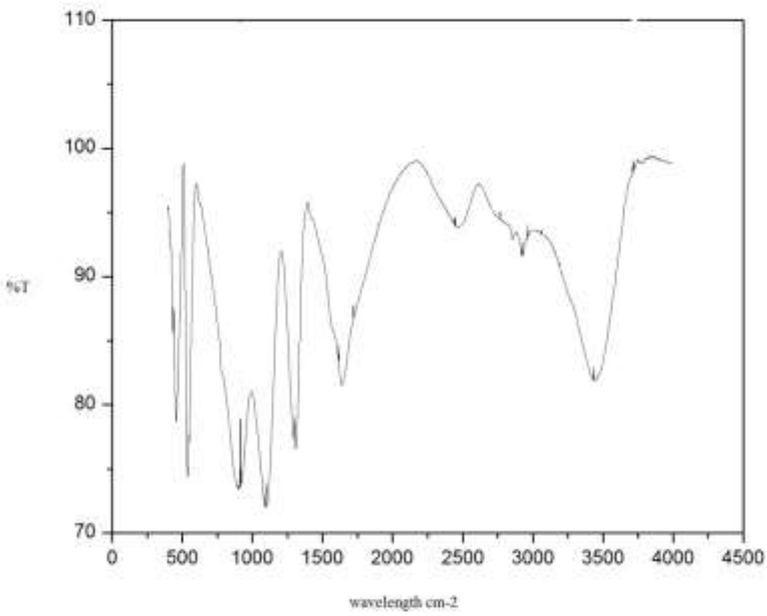



**Fig.3 Shows the FTIR pattern for Sacrosine doped KDP**

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

**4. UV- Visible Spectral analysis:**

The optical transmission spectra has been recorded by using SHIMADZU -2600 spectrometer in the range of 200-1200 nm as shown in fig 4.The crystal is highly transparent in the entire visible region, whereas it has a UV cut off at 260nm. The transmission is uniformly high (73%) for light in the visible region of electromagnetic spectrum, which is useful for nonlinear device application. The resultant spectrum is shown in Fig. 4(a)

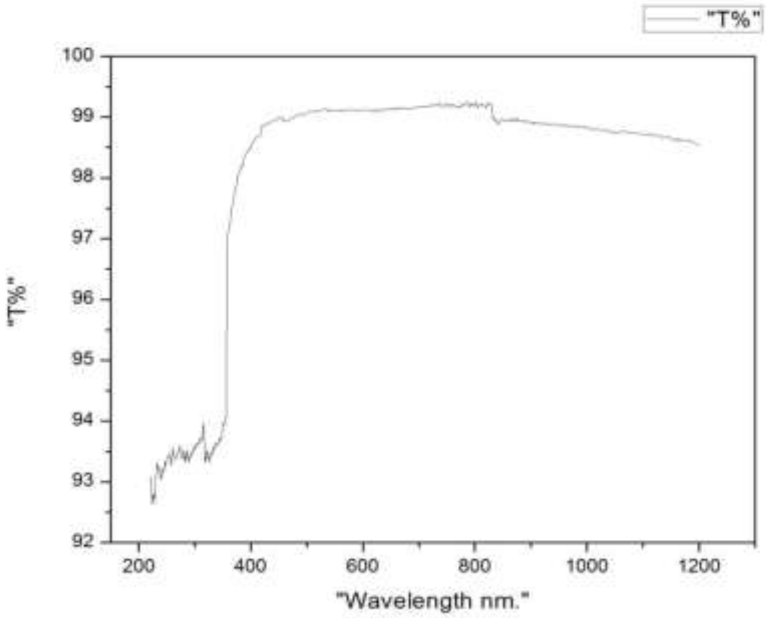



**Fig.4 UV-Spectrum of Sacrosine doped KDP**

The measured transmittance (T) was used to calculate the absorption coefficient (a) using the formula:

$$\alpha = \frac{2.303 \log(\frac{1}{T})}{t}$$

where t is the thickness of the sample[13].

As in indirect band gap semiconductor, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies (hv).

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

Where, A is a constant, Eg the optical band gap, h the Planck's constant and ν the frequency of the incident photons. Optical band gap was calculated from the UV-Visible data. The plot between energy (hν) and $(\alpha h\nu)^{1/2}$ is made as shown in Figure (4.a) (Where α is the absorption coefficient) and the optical band gap energy(Ashour et al 1995) is found to be 2.5 eV by extrapolating the slope region (where it cuts the X-axis) which is shown in Figure( 4.c)The internal efficiency of the device also depends upon the absorption coefficient. Hence by modifying the absorption coefficient and tuning the band gap of the material, one can achieve the desired material.

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

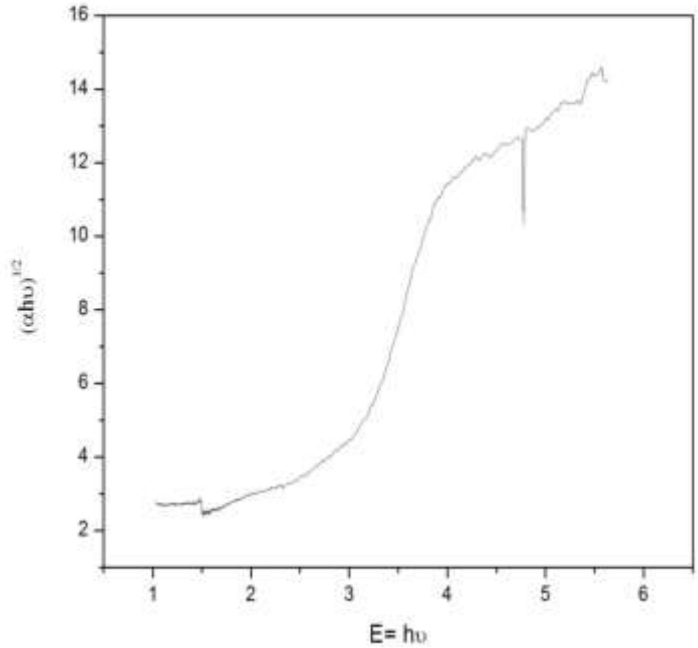



**Fig:4(b) plot of $(\alpha h\upsilon)^{1/2}$ versus photon energy hυ**

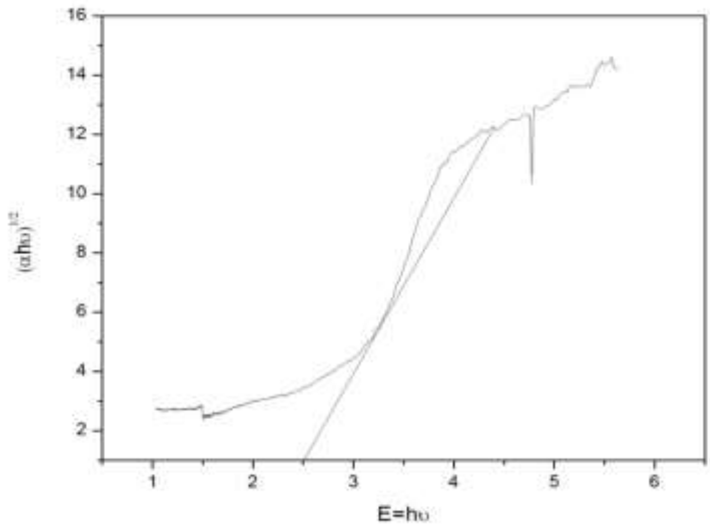



**Fig:4(c) plot of $(\alpha h\upsilon)^{1/2}$ versus hυ showing band gap**

which is suitable for fabricating various layers of the optoelectronic devices
as our requirements.[14].
Extinction coefficient (K) can be obtained from the following equation:

$$k = \frac{\lambda\alpha}{4\pi}$$

The transmittance (T) is given by

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)}$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation. Hence,

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + exp - (2\alpha t)T^2}}{\exp(-\alpha t) + exp - (2\alpha t)T}$$

Refractive index (n) can be determined from reflectance data using the following equation

$$n = -(R+1) \pm 2\frac{\sqrt{R}}{(R-1)}$$

And it found to be 1.02 at wavelength ʎ=1100nm.

**5.Simple Harmonic Studies:**

The pure and doped KDP crystals were made into fine powders of the size of 10 µm. The micro particles were exposed to 1064 nm laser beam from a pulsed Nd: YAG laser to test the second harmonic generation efficiency. An input pulse of 1.9 mJ/pulse was supplied. Signal amplitude in millivolts on the oscilloscope indicates the efficiency of the sample. The pure KDP crystal gave an output 73 mV whereas the Sacrosine doped KDP crystal showed an increase in the SHG efficiency. The Sacrosine doped KDP crystal gave an output of 79mV. Thus, the SHG eficiencies of the doped crystals are 1.084 times greater than the standard KDP crystals respectively[15].

**6. Dielectric study**

The dielectric analysis is an important characteristic that can be used to fetch knowledge based on the electrical properties of a material medium as a function of temperature and frequency. The dielectric studies were measured using **HIOKI MODEL 3532_50 LCR High Tester** .Based on this analysis, the capability of storing electric charges by the material and capability of transferring the electric charge can be assessed.

Dielectric properties are correlated with electro optic property of the crystals, particularly when they are non conducting materials [16]. Microelectronics industry needs low dielectric constant ($\varepsilon r$) materials as an interlayer dielectric[17]

The dielectric constant is calculated using the formula

$$\varepsilon' = \frac{Ct}{\varepsilon o A},$$

where $C$ is capacitance (F), $t$ the thickness (m), $A$ the area($m^2$), and $\varepsilon o$ the absolute permittivity in the free space having a value of 8.854 x $10^{-12}$ $Fm^{-1}$.

Figures5 (a), 5(b) show the variation of dielectric constant and dielectric loss with respect to frequency for all temperatures of Sacrosine doped KDP crystals. Compared to the pure KDP, dielectric constant ($\varepsilon r$ ) value is found to be low for doped KDP[18].

From Figures 5(a) and 5(b), it is clear that dielectric loss is high at low frequency and decreases with high frequencies. The low dielectric loss at high frequency reveals the high optical quality of the crystal with lesser defects, which is a desirable property of NLO applications [19, 20]

dielectric constant and dielectric loss decrease with the increasing frequency. This may be due to the contributions of all the four polarizations such as electronic, ionic, orientation, and space charge, which are predominant in the lower frequency region [21]. The larger value of dielectric constant and dielectric loss at low frequency arises due to the presence of space charge polarization near the grain boundary interfaces, which depends on the purity and perfection of the sample[22].

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

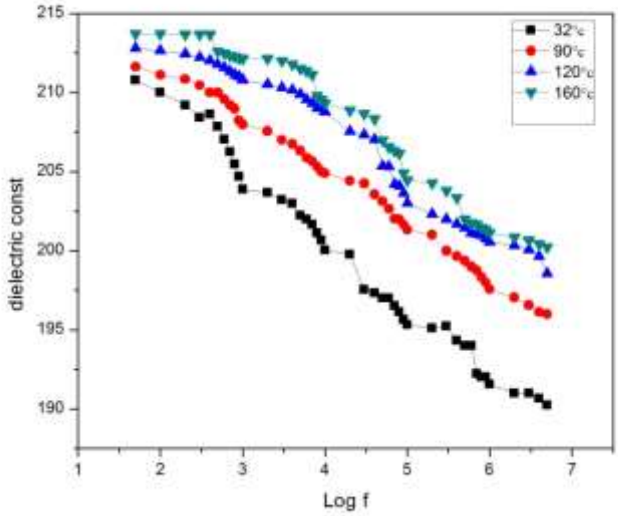



**Fig: 5(a): Variation of dielectric constant with log frequency of the electric field of Sacrosine doped KDP crystals**

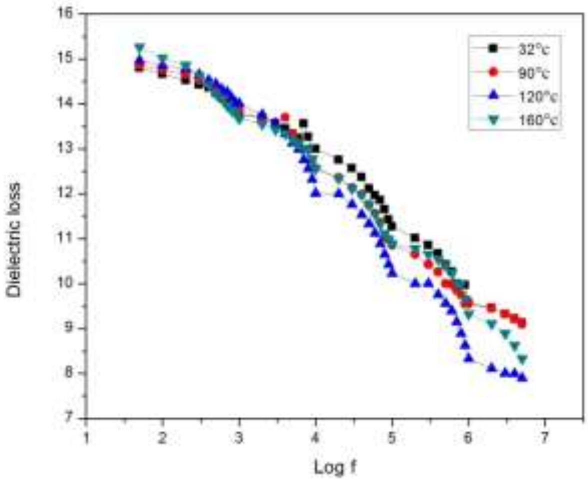



**Fig: 5(b) Variation of dielectric loss with log frequency of the electric field of sacrosine doped KDP crystals**

## 7. Microhardness studies

Microhardness studies have been carried out on sacrosine acid doped KDP using Futuretech FM 800 type E seriesVicker's microhardness tester fitted with Vickers's diamond pyramidal indenter attached to an incident light microscope. The static indentations were made at room temperature with a constant indentation time of 15s for all indentations .The indentation mark were made on the surface by varying the load from 3 to 100g.As micro cracks appeared at higher loads(100g), the load was restricted up to 50gms.The vicker's microhardness number Hv of the crystal was calculated using the relation Hv = 1.8554 P/ $d^2$ Kg $mm^{-2}$ where P is the applied load, d is the diagonal length of the indented impressions in meter.Vicker's microhardness profile as a function of applied load is shown table 3 and in fig.6.It shows that microhardness value of sacrosine acid doped KDP decreases with increase in load, while comparing with pure KDP hardness is low[19,20] Vickers micro-hardness value decreases with comparison to pure KDP. It can be conjectured that the doping of Sacrosine acid softens the KDP crystals.[23]

ISSN: 2277-9655
Impact Factor: 5.164
CODEN: IJESS7

| Load p (gm) | Vicker's Hardness number Hv | |
|---|---|---|
| | Pure KDP | Sacrosine doped KDP |
| 3 | 101.64719 | 87.123 |
| 5 | 130.07932 | 101.021 |
| 10 | 139.6869 | 129.564 |
| 25 | 146.3166 | 135.770 |
| 50 | 152.86302 | 143.214 |

**Table-3 Variation of Hv with load applied for pure and Sacrosine doped KDP**

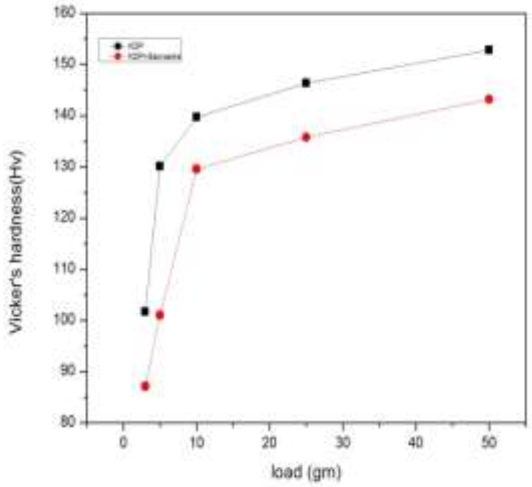



Fig 6 Plot of Hv versus load P for pure Sacrosine doped KDP crystals.

## IV. CONCLUSIONS

Single crystals of Sacrosine acid doped KDP crystals were successfully grown by slow Evaporation method. The Single XRD studies revealed that the crystals are tetragonal and belong to I42d space group. The Powder X-ray diffraction analysis determines the incorporation of Sacrosine Acid into KDP crystal lattice. The Fourier transform infra-red spectroscopy studies carried out confirms the functional groups of dopant present in the grown crystal. The UV-Vis studies reveals that the grown crystals having transmission in the visible range. Then the grown crystals subjected to Kurtz Perry powder method to test the efficiency of the relative second harmonic generation reveals the moderate NLO property of the grown crystal and the results were compared to standard KDP. From the Dielectric studies of the sample it was noticed that dielectric constant and dielectric loss decreases with increasing frequency. Hardness studies reveals it is a soft material and Hardness (Hv) was found to decrease by addition of Sacrosine acid in pure KDP and proves to be good material for photonic device fabrication.

## V. ACKNOWLEDGMENT

The Authors are thankful to Dr.N.P.Rajesh (SSN College of Engineering, Kalavakkam,Chennai) for providing Lab facilities for the crystal growth., to management of Loyola College - Times of India Major Research Project (3LCTOI14PHY002)., Chennai – 34 for providing hardness study and to SAIIF IIT Chennai for single crystal XRD.

## VI. REFERENCES

1. S. Dhanuskodi, P.A. Angeli Mary, Jr.Cryst. Growth 253 ,424-428,(2003).
2. P.N. Prasad, D.J.Williams, Introduction to Non-linear Optical effects in Molecules and Polymers, Wiley – Interscience, New York(1991)

3. N.Kangathara, G.Anbalagan, "Growth, Optical and Dielectric studies on Pure anmd L-Lysine Doped KDP crystals", International Journal of Optics, (2012).
4. N.A.Booth, A.A.Chernov, P.G.Vekolow, Jr.Crystal growth 237-239,1812,( 2002).
5. Shaikh Kalim Shaikh Hanif, A.B.Lad and B.H. Pawar, " Efect of low anmd high concentration of Glycine of properties of KDP Crystals", Pelagia Research Library, Advances in Applied Research, (2015).
6. K. Sangwal, Prog. Cryst.Growth Charact. Mater.,Vol. 32, 3-43(1996).
7. P.Kumaresan, S.Moorthy Babu, P.M. Anbarasan, Optical studies on pure and amino acids doped KDP Crystal", Journal of Optoelctronics and adcanced materials Vol 9,(2007).
8. Shaikh Kalim Shaikh Hanif, A.B.Lad and B.H. Pawar, " Efect of low anmd high concentration of Glycine of properties of KDP Crystals", Pelagia Research Library, Advances in Applied Research, (2015).
9. Study on Growth Habit, SHG and Thermal Properties of Urea Phosphate Doped KDP Crystals G. G. Muley Department of Physics, Sant Gadge Baba Amravati University, Amravati, 444602, (MS) India Science and Technology 2012, 2(5): 109-113 DOI: 10.5923/j.scit.20120205.01
10. Effect of Zinc chloride on the growth and characterization of L-proline Cadmium chloride monohydratesemiorganic NLO single crystal S.vetrivel*,P.Anandan,K.Kanagasabapathy,Suman battacharya,S.Gopinath,R,Rajasekaran Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 110(2013) 317-323
11. Synthesis, crystalgrowthandcharacterizationofasemiorganicmaterial:Calcium dibromidebis(glycine)tetrahydrate P.V.Dhanaraj,T.Suthan,N.P.Rajesh Current AppliedPhysics10(2010)1349e1353
12. Anbu Chudar Azhagan, S., Ganesan, S. Effect of zinc acetate addition on crystal growth, structural, optical, thermal properties of glycine single crystals. Arabian Journal of Chemistry(2013),http://dx.doi.org/10.1016/j.arabjc.2013.09.041 many decades is understanding and controlling solution
13. Effect of KDP on the growth,thermal and optical properties of L-alanine single crystals T. Thilak ,M.Basheer Ahamed,G.Maruthu,G.Vinitha Arabian journal of chemistry(2013)
14. S. Boomadevi, H. P. Mittal, and R. Dhansekaran, "Synthesis,crystal growth and characterization of 3-methyl 4- nitropyridine 1-oxide (POM) single crystals," *Journal of Crystal Growth*, vol. 261, no. 1, pp. 55–62, 2004.
15. B. T. Hatton, K. Landskron, W. J. Hunks et al., "Materials chemistry for low-k materials," *Materials Today*, vol. 9, no. 3,pp. 22–31, 2006.
16. S. Goma, C. M. Padma, and C. K. Mahadevan, "Dielectric parameters of KDP single crystals added with urea," *MaterialsLetters*, vol. 60, no. 29-30, pp. 3701–3705, 2006
17. S. Suresh, A. Ramanand, D. Jayaraman, and P.Mani, "Growth,photoconductivity and dielectric properties of triglycine sulfate (TGS) single crystals," *Optoelectronics and Advanced Materials*, vol. 4, no. 11, pp. 1763–1765, 2010.
18. C. Balarew and R. Duhlew, "Application of the hard and softacids and bases concept to explain to ligand coordination in double salt structures," *Journal of Solid State Chemistry*, vol.55, no. 1, pp. 1–6, 1984.
19. M. Meena and C. K. Mahadevan, "Growth and electrical characterization of L-arginine added KDP and ADP single crystals," *Crystal Research and Technology*, vol. 43, no. 2, pp.166–172, 2008
20. S. Aruna, G. Bhagavannarayana,M. Palanisamy, P. C. Thomas,B. Varghese, and P. Sagayaraj, "Growth, morphological,mechanical and dielectric studies of semi organic NLO single crystal: l-argininium perchlorate," *Journal of Crystal Growth*, vol. 300, no. 2, pp. 403–408, 2007.
21. Vickers Microhardness Studies of Pure and Amino Acids Doped Potassium Dihydrogen Phosphate Crystals K. D. Parikh1,∗, D. J. Dave 2, B. B. Parekh3, and M. J. Joshi4 Journal of Advanced Physics Vol. 5, pp. 1–6, 2016