iJRASET
International Journal For Research in
Applied Science and Engineering Technology


# INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY

**Volume:** 5 **Issue:** XII **Month of publication:** December 2017

**DOI:**

www.ijraset.com

Call: 08813907089 | E-mail ID: ijraset@gmail.com

# Structural Analysis of Pure and Nickel Sulphate Doped KDP Crystals Grown by Gel Medium

M.P. Rameela[1], T.H. Freeda[2], T. Asaithambi[3]
[1]*Dept. of Physics Sarah Tucker College for Women, Tirunelveli*
[2]*Dept. of Physics S.T. Hindu College Nagercoil*
[3]*P.G and Research Department of Physics, Alagappa Govt Arts , College., Karaikudi.*

***Abstract: Optically good quality pure and metal doped KDP crystals have been grown by microbial free gel growth method at room temperature and their characterization have been studied. Gel method is a very simple method and can be utilized to synthesize crystals which are having low solubility. Potassium dihydrogenorthophosphate KH2PO4 (KDP) continues to be an interesting material both academically and industrially. KDP is a representative of hydrogen bonded materials which possess very good electro – optic and nonlinear optical properties in addition to interesting electrical properties. Due to this interesting properties, we made an attempt to grow pure and Nickel sulphate doped KDP crystals in various concentrations (0.002, 0.004, 0.006, 0.008 and 0.010) using gel method. The grown crystals were collected after 15 days. We get crystals with good quality and shaped. The dielectric constants of metal doped KDP crystals were slightly decreased compared to pure KDP crystals. FTIR, XRD analyses also done . Results were discussed in detail.***

## I. INTRODUCTION

Potassium dihydrogen orthophosphate (KDP) $KH_2PO_4$ continues to be an interesting material both academically and industrially. KDP is a representative of hydrogen bonded materials which possess very good electro – optic and nonlinear optical properties in addition to interesting electrical properties. The demand for high quality large single crystals of KDP increase due to the application as frequency conversion crystal in inertial confinement fusion [1-2]. The piezoelectric property of KDP crystal makes it useful for the construction of crystal filters and frequency stabilizers in electronic circuit's .

The excellent properties of KDP include transparency in a wide region of optical spectrum, resistance to damage by laser radiation and relatively high non- linear efficiency, in combination with reproducible growth to large size. Therefore, it is commonly used in several applications such as laser fusion, electro-optical modulation and frequency conversion. Many studies on the growth and properties of KDP crystals in the presence of impurities have been reported [3 - 4]. Potassium dihydrogen phosphate (KDP) crystal draws persistent attention of scientists due to its excellent quality and possibility of growing large- size crystals [5 - 6]. Microscopically, crystal growth includes crystal morphology, crystal defects, and growth rate, which are all related to the constituent growth units and their chemical bonding process [7 - 8]. KDP, ADP and DKDP are the only nonlinear crystal currently used for these applications due to their exclusive properties. The grown crystals were characterized using dielectric constant, electrical properties, optical transmittance, for pure and $NiSO_4$ doped KDP crystals.

## II. MATERIALS AND METHODS

Pure and $NiSO_4$ doped KDP single crystals are grown in sodium meta silicate gel medium using analar grade KDP and NiSO4 with in concentrations of 0.002, 0.004, 0.006, 0.008 and 0.010 of dopant and sodium meta silicate ($1.08 g/cm^3$ ). During the process pH was maintained at 5-6 at room temperature figure (1). Ethyl alcohol of equal volume is added over the set gel without damaging the cell surface .When the alcohol diffuses into the set gel, it reduces the solubility. This induces nucleation and the nuclei are grown into the single crystals. The crystal growth was carried out at room temperature. The growth period was about 20 days for pure and $NiSO_4$ doped KDP crystals. Pure and KDP doped crystals are shown in the figure.

International Journal for Research in Applied Science & Engineering Technology (IJRASET)
*ISSN: 2321-9653; IC Value: 45.98; SJ Impact Factor :6.887*
*Volume 5 Issue XII December 2017- Available at www.ijraset.com*

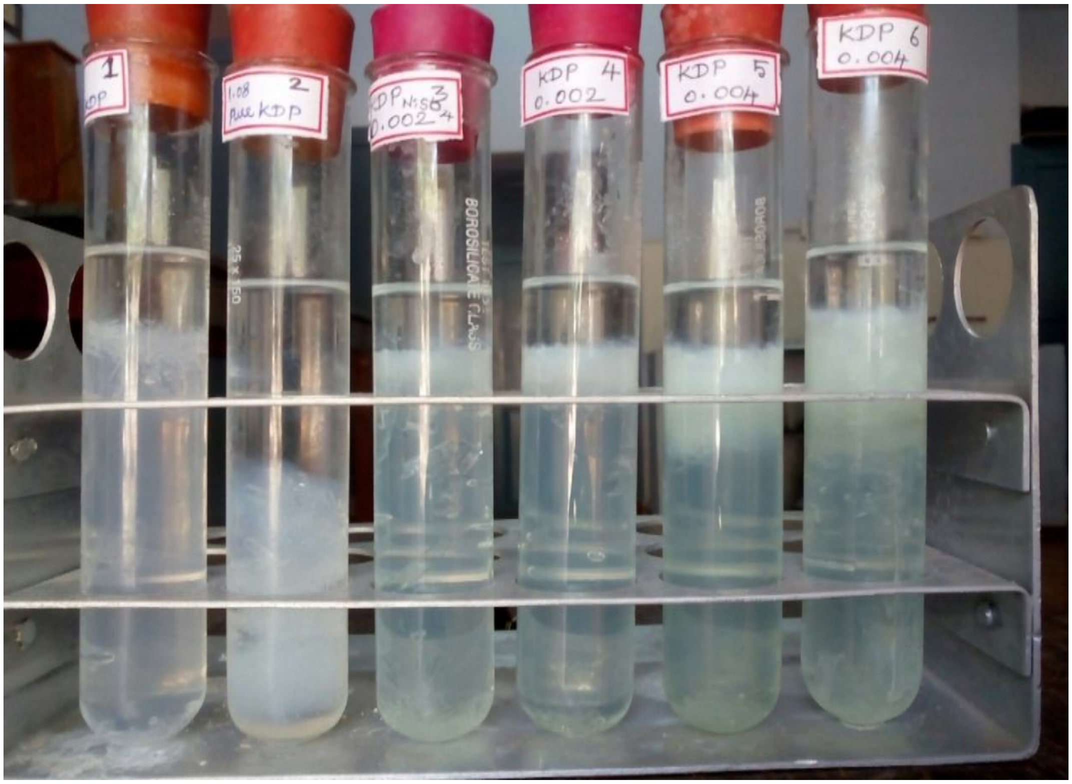



Figure.1 Growth of pure KDP doped with $NiSO_4$ with various concentrations

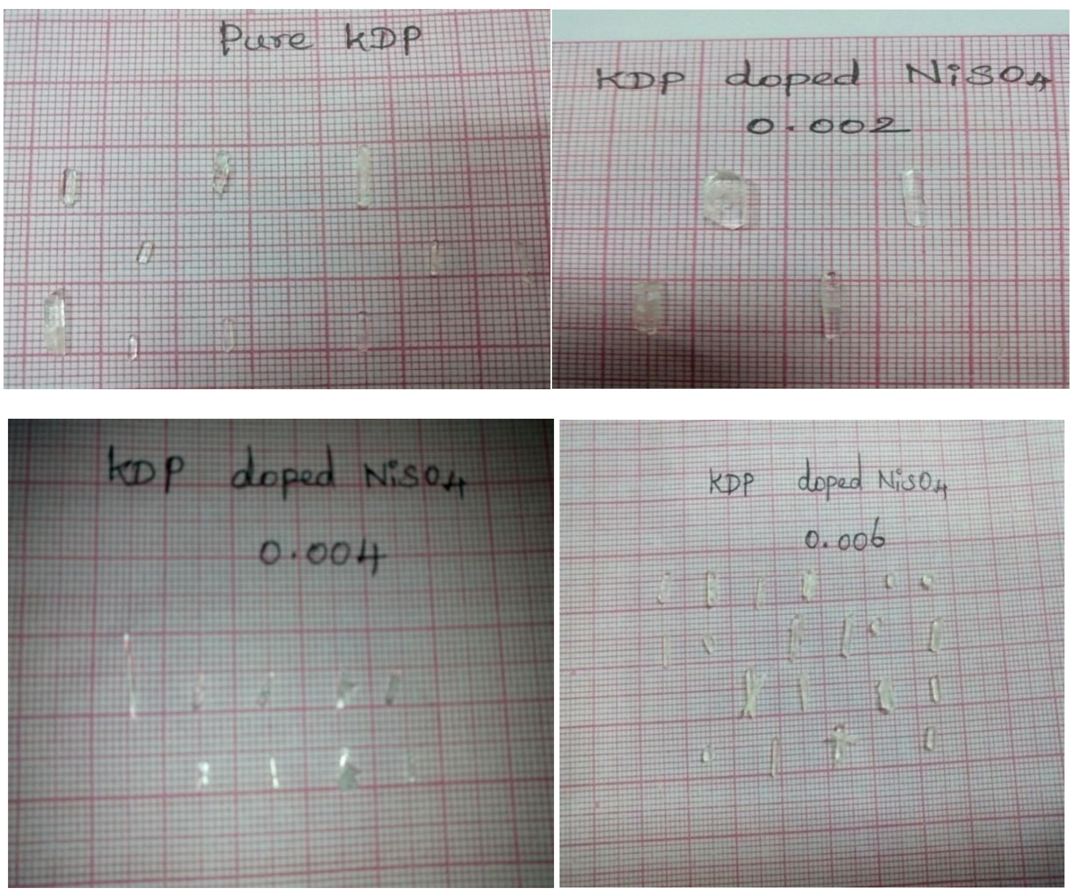



Fig. 2. Gel grown Pure KDP and NiSO4 added KDP crystals

### A. *Doping*

Doping means adding impurity to the known pure crystal .To prepare a doped crystal a required amount of dopant solute is also mixed along with the pure solute.

Table 1: Doping concentrations of impurities

| Doping ratio | Mass of $NiSO_4$ Added in gm |
|---|---|
| 1 : 0.002 | 0.06571 |
| 1 : 0.004 | 0.13143 |
| 1 : 0.006 | 0.19714 |

An impurity can suppress, enhance or stop the growth of crystal completely. It usually acts on certain crystallographic faces. The effects depend on the impurity concentration, super saturation, temperature and pH of the solution.

## III. RESULTS AND DISCUSSIONS

### A. *Dielectric constant and electrical conductivity studies:*

Dielectric properties are correlated with electro- optic properties of the crystals particularly when they are non- conducting materials. Due to the incorporation of metal ions polarization increases and the electrical conductivity increases. The magnitude of dielectric constant depends on the degree of polarization, charge displacement in the crystal. The dielectric constant of materials is due to the contribution of electronic, ionic, dipolar and space charge polarizations which depends on the frequencies [5]. At low frequencies, all these , polarization are active lower frequencies and high temperatures [6], in KDP crystals, many reports are available about its dielectric behavior and in our present work the measured dielectric constant values are in good agreement with the reported results [7-8]. The temperature dependence of dielectric constant at frequency 100Hz to 1KHz is shown in fig. 3,4. Even though KDP has many reports on dielectric loss, the study clearly ensures the crystalline perfection of crystals in our present case; it is observed that the dielectric loss decreases with increasing frequency and low dielectric losses were observed for the gel method crystal compared to the solution growth. The lower value of dielectric constant is a suitable parameter for the enhancement of SHG signals. The measurement of dielectric constant and loss as a function of frequency at different temperatures give an idea about the electrical processes that are taking place in materials and these parameters were measured on the polished (010) face of the pure and metal doped KDP crystals. Frequency dependences of dielectric constant of these crystals at room temperature are observed from the figures and it is observed that dielectric constant of KDP and $NiSO_4$doped KDP crystals are high at low frequencies and they decreases with increase in frequency. The very high value of $\boldsymbol{\varepsilon_r}$ at low frequencies may be due to the presence of all four polarizations namely space charge, orientation, electronic and ionic and its low values at higher frequencies may be due to the loss of significance of these polarizations gradually. The nature of decrease of $\boldsymbol{\varepsilon_r}$frequency suggests that pure and $NiSO_4$ doped KDP crystals contain dipoles of continuously varying relaxation times.

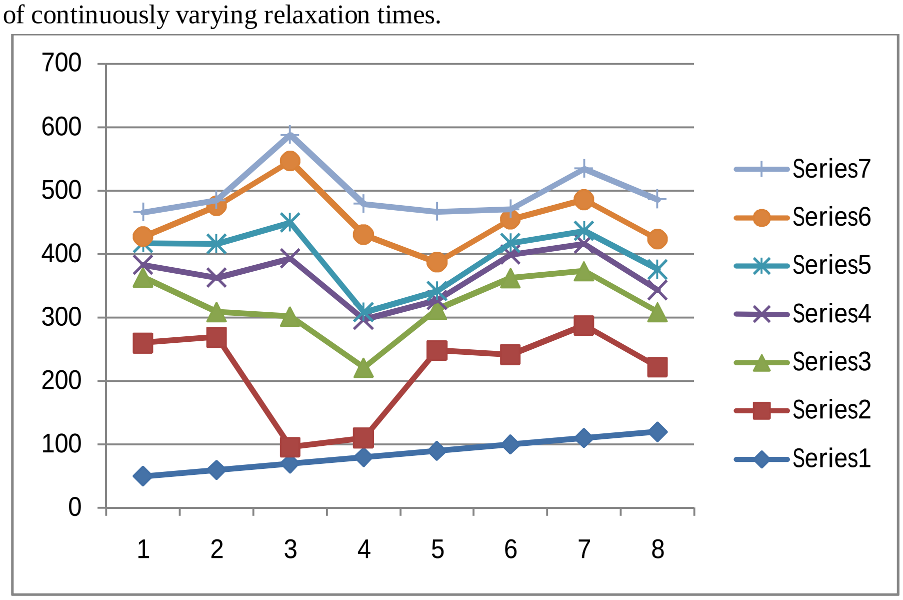



Fig.3. Variation of dielectric constant ($\varepsilon_r$) with temperature at frequency of 100Hz for pure and $NiSO_4$ doped KDP crystals

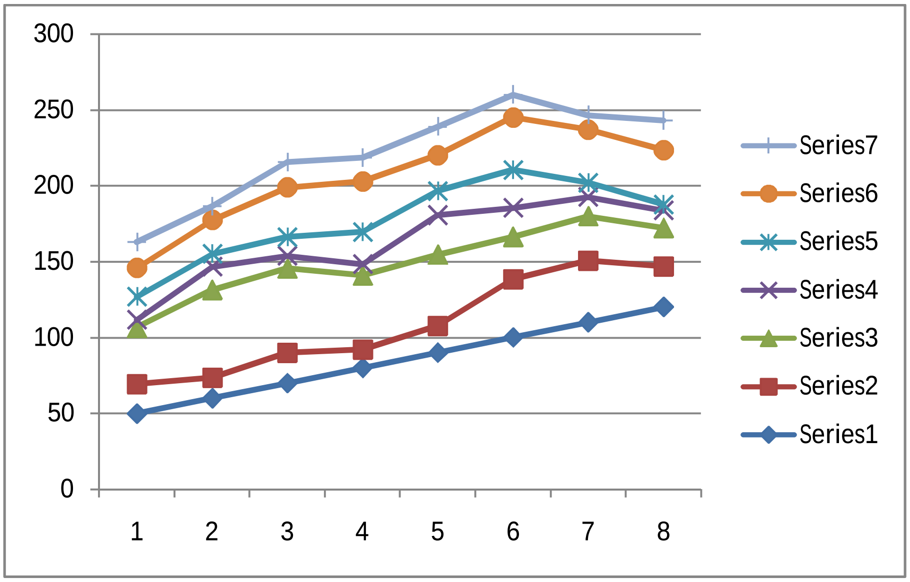



Fig.4. Variation of dielectric constant ($\varepsilon_r$) with temperature at frequency of 1KHz for pure and $NiSO_4$ doped KDP crystals

*B.FT- IR studies on pure and $NiSO_4$ doped KDP crystals*

The observed FT-IR spectra of pure and $NiSO_4$ doped KDP crystals are shown in figure

From FT-IR spectra ,the broad band which appears in the range 3261 to2922 $cm^{-1}$ is due to free O-H stretching of KDP . It is seen that these are very weak bonds. The peak at2922$cm^{-1}$ is due to P-O-H asymmetric stretching. The strong intensity band at 2433$cm^{-1}$ is due to one of the P-O-H bending of KDP. The sharp and strong intense bands appearing at around 1300$cm^{-1}$ and 1147 $cm^{-1}$ were due to P=O symmetric stretching . The sharp bands at around 1147 $cm^{-1}$ was due to symmetric P=O stretching in KDP and appeared at 1300$cm^{-1}$ in the doped KDP. The spectrum shows an additional peak at 905 $cm^{-1}$ . This is attributed to P-O-H stretching of KDP. Another sharp band at 543 $cm^{-1}$ was due to HO-P-OH bending. A detailed assignment of the frequencies observed in FTIR spectrum is given table

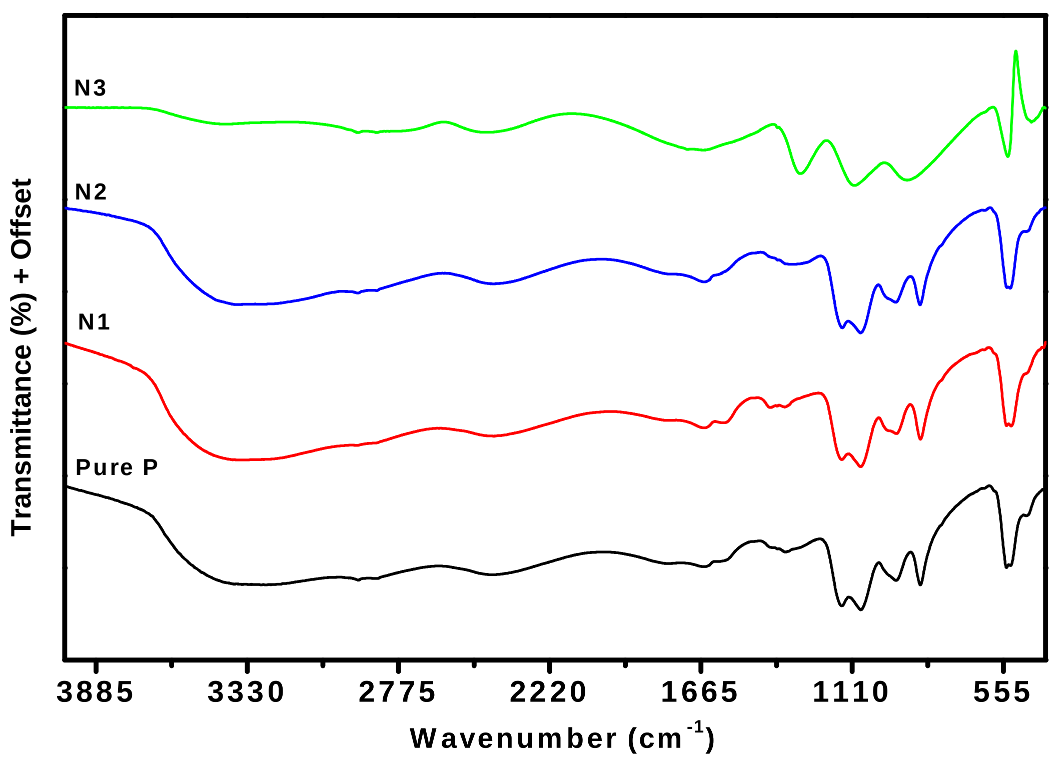



Fig.5 Shows the FTIR pattern of (a) Pure KDP and(b)N1 (c) N2 (d) N3 are doped Nickel Sulphate in different concentration.

| .Pure KDP | (b) N1 | (c) N2 | (d) N3 | Assignments |
|---|---|---|---|---|
| 3261 vw | 3422 vw | 3419 vw | 3408 vw | Free –O-H stretching |
| 2922 s | ----- | 2923s | 2923 s | P-O-H symmetric stretching |
| 2433 | 2424 | 2427 | 2454 | P-O-H bending of KDP |
| 1147 vs | 1147vs | 1148vs | 1101vs | P=O stretching of KDP |
| 948 vs | 947vs | 950vs | 908vs | P-O stretching |
| 859 s | 859s | 860 s | ------ s | P-O-H stretching of KDP |
| 543 sh | 543sh | 529sh | 538sh | Presence of metal ions (Nickel) |

vs –very strong s- strong vw –very weak sh- sharp

### *C. Powder XRD Studies*

The powder X-ray Diffractometer analysis (XPERT-PRO) has been carried out for the rapid identification and quantification of grown crystal at 2 theta position of 10° to 80°. At maximum intensity the various structure parameters like the crystalline size, micro strain and dislocation density has been calculated by Debye – Scherer's formula and tabulated below [9-10].

$D = 0.9\ \lambda / \beta \cos\theta$

where $\lambda$ is wavelength of the X-ray radiation, $\beta$ is full width at half maximum (FWHM) of diffraction peak (in rad), and $\theta$ is scattering angle.

Further, the dislocation density (δ) and micro strain (ε) was estimated by the relation

$\delta = 1/D^2$ and $\varepsilon = \beta\cos\theta / 4$

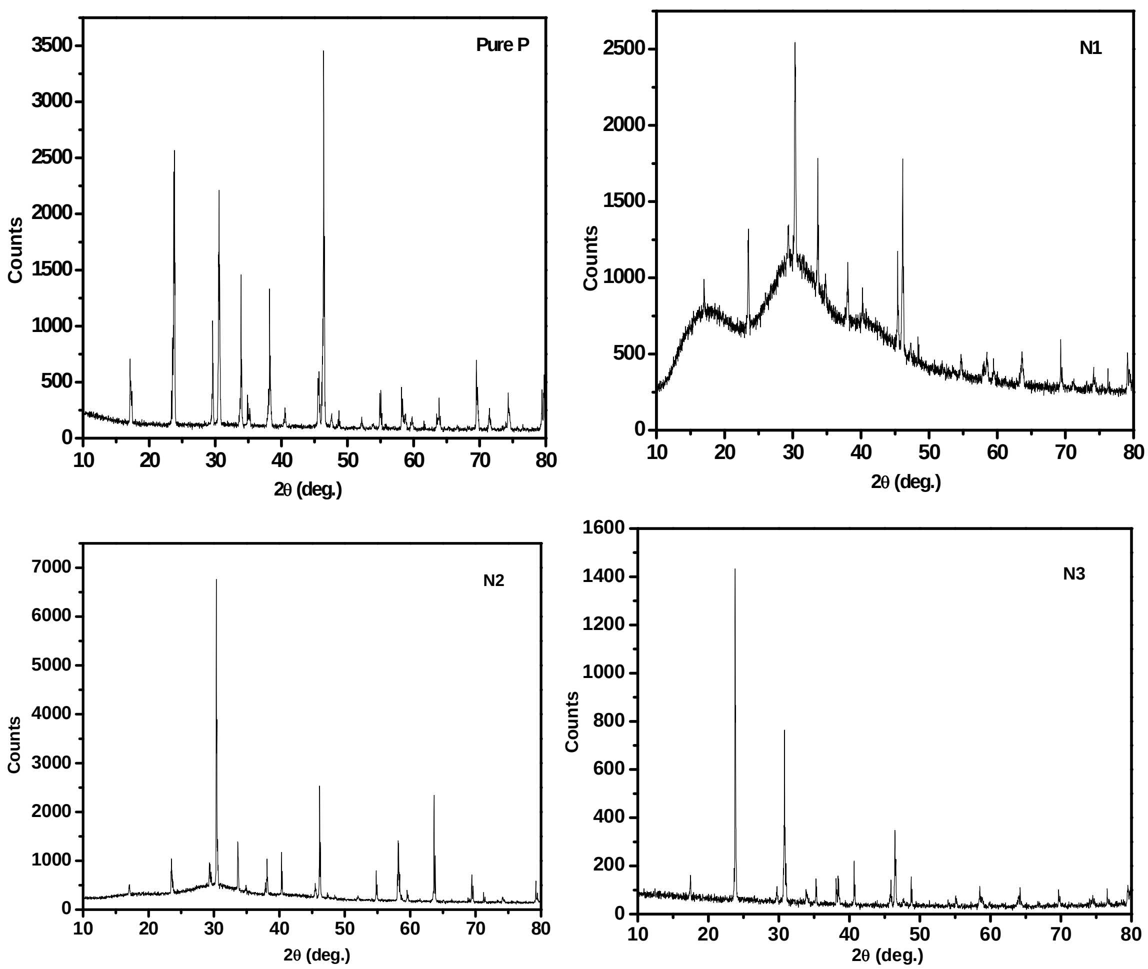



Fig6. Shows the Powder XRD pattern of (a) Pure KDP and (b) N1 (c) N2 (d) N3 are doped Nickel Sulphate in different concentration.

*D. X-Ray Diffraction data ( crystalline size, micro strain and dislocation) for KDP doped with N1- 0.002,N2- 0.004, N3- 0.006, concentration of Nickel Sulphate*

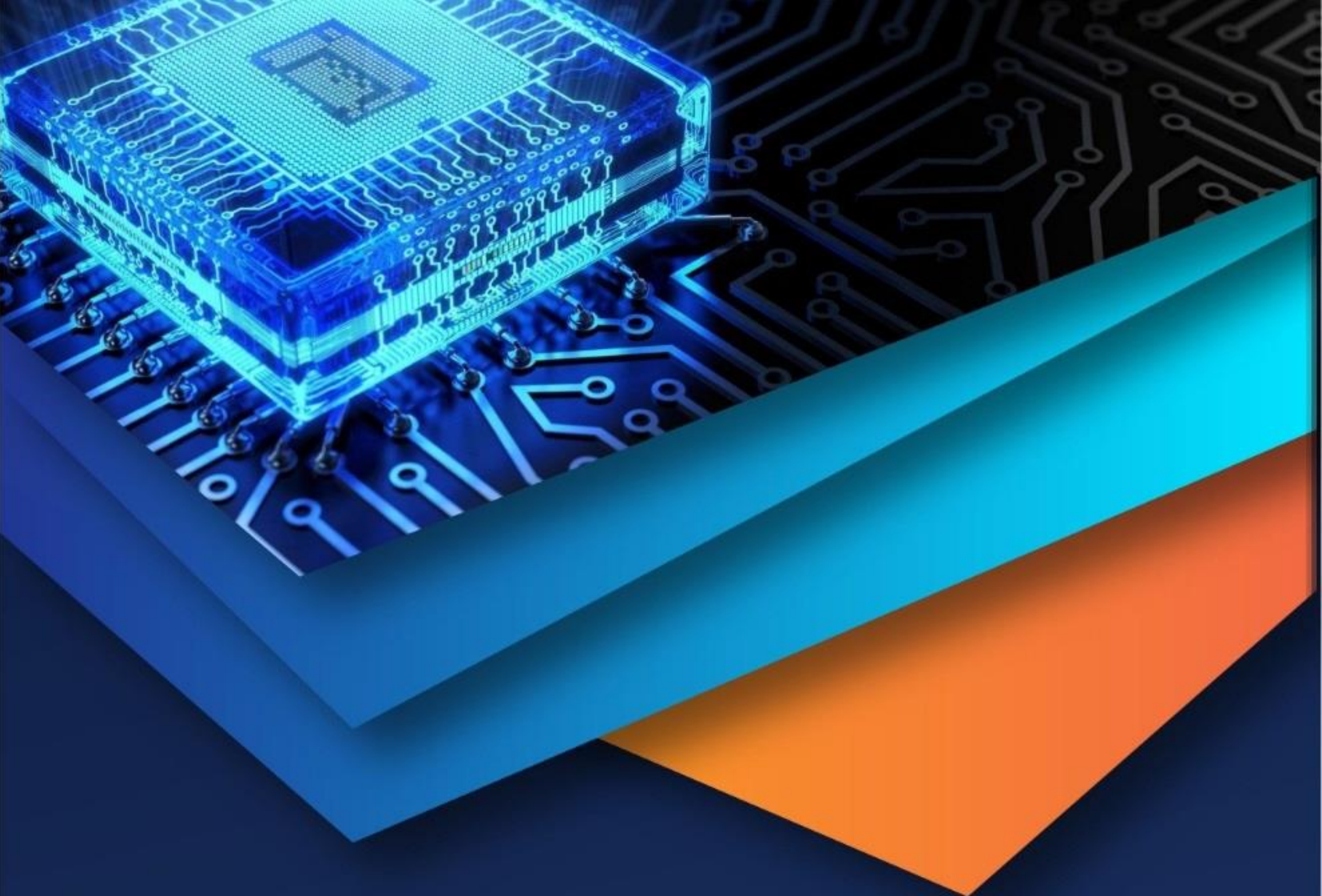
| Sample | d spacing | 2θ | FWHM - β | Crystalline Size nm | Dislocation $10^{14}$ 1/m$^2$ | Microstrain $10^{-4}$ |
|---|---|---|---|---|---|---|
| Pure KDP | 2.92106 | 30.580 | 0.0040 | 36.6262 | 7.4544 | 9.6460 |
| KDP+ N1 | 2.93174 | 30.434 | 0.0047 | 30.5727 | 10.6987 | 11.337 |
| KDP+ N2 | 2.93824 | 30.397 | 0.00185 | 77.6645 | 1.6578 | 3.7803 |
| KDP+ N3 | 2.90267 | 30.8047 | 0.00087 | 165.3095 | 36.5935 | 2.0968 |

## IV. CONCLUSION

Pure KDP crystals and metal doped KDP crystals are grown by gel method. In gel growth, due the three dimensional structures, the crystals are free from microbes. The capacitance and dielectric constant and electrical conductivity were measured at different frequencies of pure and $NiSO_4$doped KDP crystals. The capacitance and dielectric constants of metal doped KDP crystals were slightly decreased compared to pure KDP crystals. The lower the value of dielectric constant more is the enhancement of SHG signals. The electrical conductivity (σ) of the pure KDP and $NiSO_4$ doped KDP crystals were found to be increase with increase of temperature and frequencies. The FT-IR spectral studies confirm the presence of all the functional groups and also the presence of $NiSO_4$ in the grown crystals. The presence of additional peaks in the XRD spectrum of doped KDP crystals shows the presence of additional phases due to doping.

## REFERENCES

[1] X.Sun, X, Xu, Z.Gao, Y.Fu, S.Wahg, H.Zong, Y.Li, J.Cryst.Growth.,217(2000) 404
[2] N.Zaitseva, L.Carman, I.Smolsky, J.Cryst.Growth.,241 (2002) 363.
[3] Bo Wang. Chang –shuiFang.Sheng –Iai Wang, Xun Sun, Quing-tianGu,Yi-ping Li, Xin-guangXu, JianqinZhang,BingLiu,with potassium carbonate as additives .J.Cryst.Growth.,310, (2008) 5341-5346.
[4] N.Pattanaboonmee, P.Ramasamy, P.Manyumprocedia Engineering., 32 (2012) 1019-1025.
[5] DongliXu, DongfengXue. J.Cryst. Growth .,310 (2008) 1385
[6] DogliXu, DongfengXue, J.Alloys Compd., 449 (2008) 353
[7] DongliXu, DongfengXue. J.Cryst. Growth .,310 (2008) 1385
[8] S.Balamurugan, P.Ramasamy, SpectrochimicaActa., Part A 71 (2009) 1979-1983
[9] Jingran Su, Youting Song, Daofan Zhang and Xinan Chang, Powder diffraction, 24, (2009) pp. 234.
[10] James R. Connolly, Introduction to X-Ray Powder Diffraction, Spring EPS400-002 (2007).




10.22214/IJRASET

45.98

IMPACT FACTOR: 7.129

IMPACT FACTOR: 7.429


# INTERNATIONAL JOURNAL FOR RESEARCH

IN APPLIED SCIENCE & ENGINEERING TECHNOLOGY