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

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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 KH_2PO_4 (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 $NiSO_4$ with in concentrations of 0.002, 0.004, 0.006, 0.008 and 0.010 of dopant and sodium meta silicate ($1.08g/cm^3$). 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.



Figure.1 Growth of pure KDP doped with NiSO₄ with various concentrations

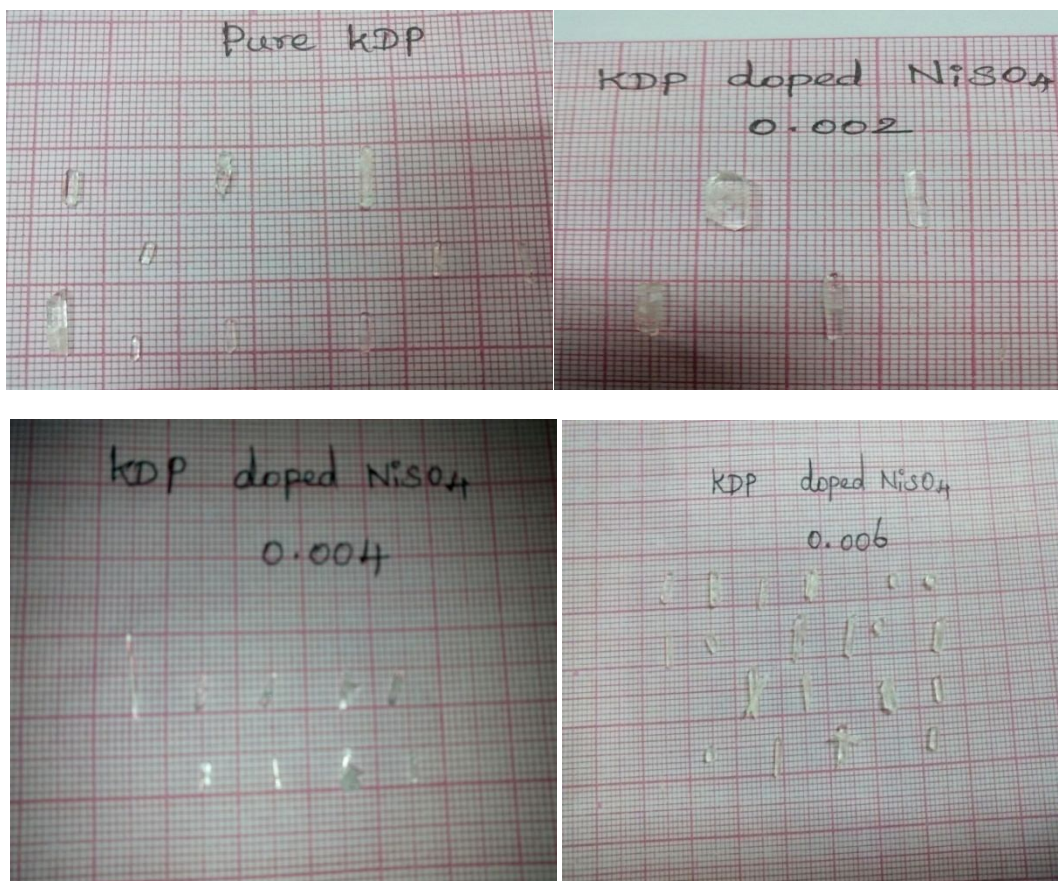


Fig. 2. Gel grown Pure KDP and NiSO₄ added KDP crystals

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 NiSO₄doped KDP crystals are high at low frequencies and they decreases with increase in frequency. The very high value of ϵ_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 ϵ_r frequency suggests that pure and NiSO₄ doped KDP crystals contain dipoles of continuously varying relaxation times.

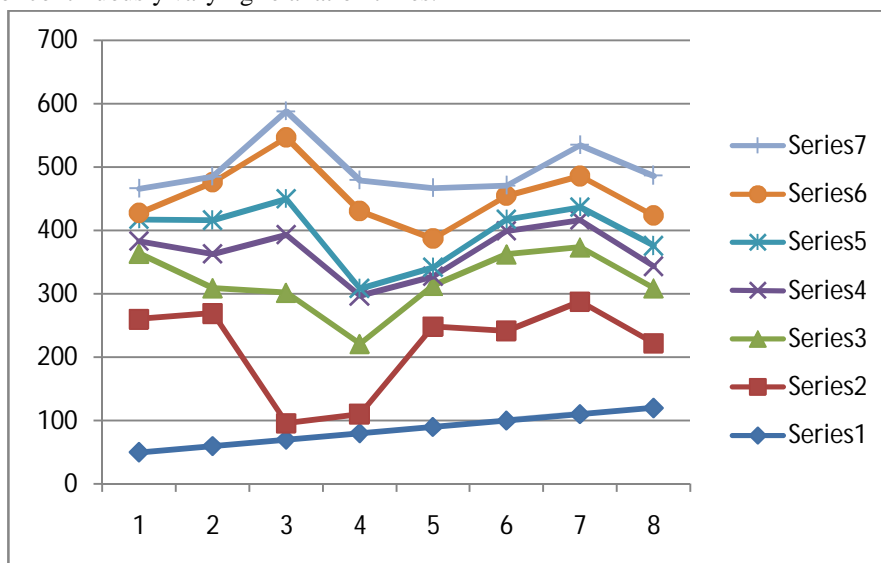


Fig.3. Variation of dielectric constant (ϵ_r) with temperature at frequency of 100Hz for pure and NiSO₄ doped KDP crystals

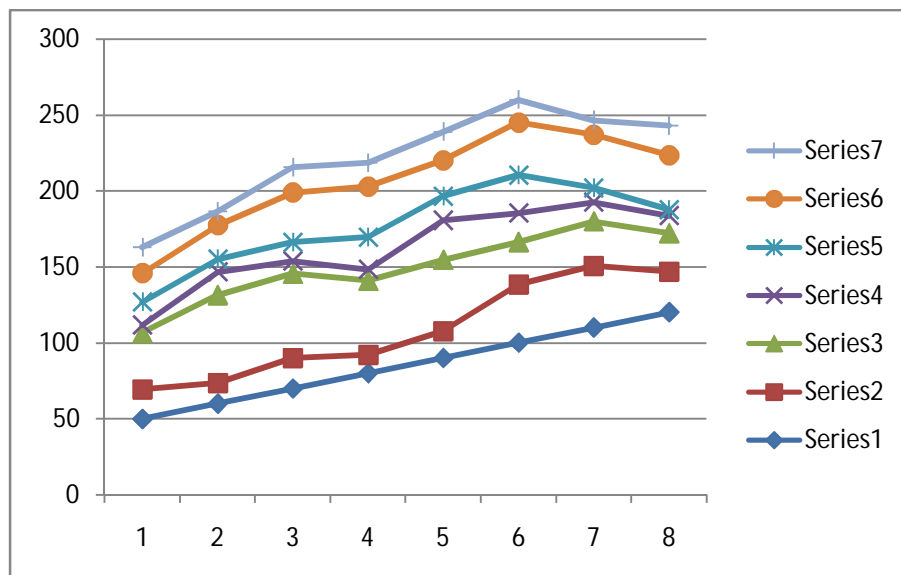


Fig.4. Variation of dielectric constant (ϵ_r) with temperature at frequency of 1KHz for pure and NiSO_4 doped KDP crystals

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 to 2922 cm^{-1} is due to free O-H stretching of KDP. It is seen that these are very weak bonds. The peak at 2922 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

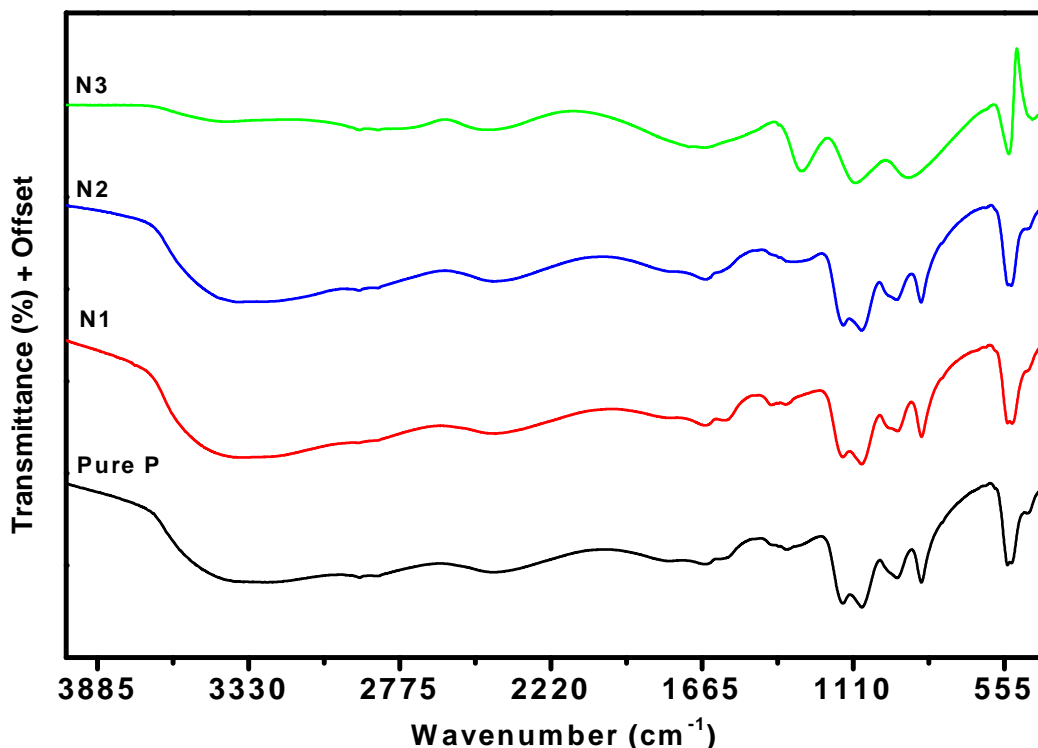


Fig.5 Shows the FTIR pattern of (a) Pure KDP and (b) N1 (c) N2 (d) N3 are doped Nickel Sulphate in different concentration.

.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 λ is wavelength of the X-ray radiation, β is full width at half maximum (FWHM) of diffraction peak (in rad), and θ is scattering angle.

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

$$\delta = 1/D^2 \quad \text{and} \quad \epsilon = \beta \cos\theta / 4$$

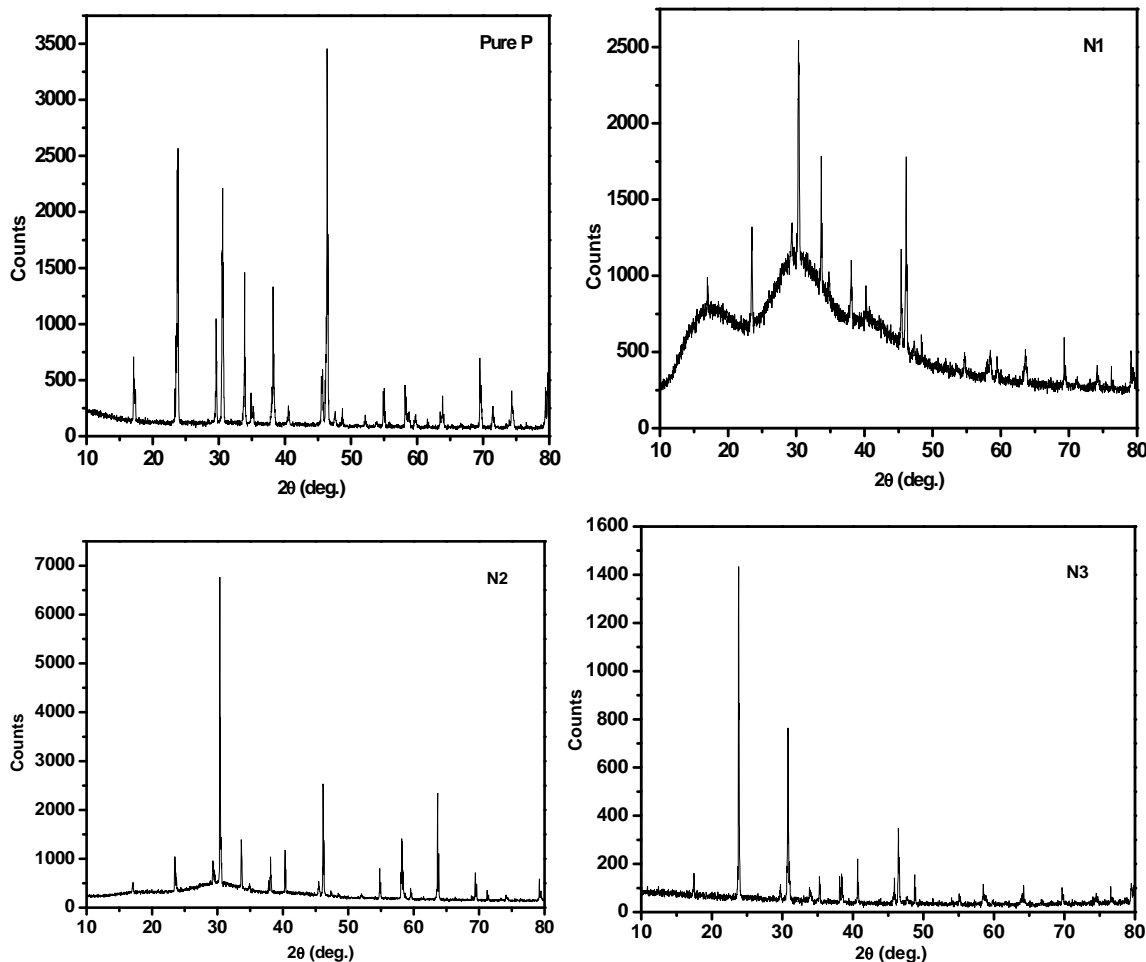


Fig6. Shows the Powder XRD pattern of (a) Pure KDP and (b) N1 (c) N2 (d) N3 are doped Nickel Sulphate in different concentration.

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 NiSO₄doped 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 NiSO₄ 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 NiSO₄ 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.

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