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Investigation on the Growth and Characterization of Pure and Oregano Extract Doped Kip Single Crystals

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Abstract: In the present investigation, pure KDP and Oregano extract doped KDP (OKDP) crystals were grown from aqueous solution by the slow evaporation technique. The incorporation of dopant was confirmed by powder X-ray diffraction analysis and FT-IR technique. The range of optical transmission was ascertained using UV–vis–NIR studies. Theoretical calculations were carried out to determine the linear optical constants such as extinction coefficient and refractive index. The refractive index of the crystal is found to be 1.31. Second harmonic generation efficiency of the crystal is found to be 2.3 times that of potassium dihydrogen orthophosphate. The experimental results evidence the suitability of the grown crystal for optoelectronic applications.
Keywords:Single crystal growth;Growth from solutions; Powder X-ray diffraction; Dielectric analysis; Nonlinear optic materials.

I. INTRODUCTION

Nonlinear optics (NLO) is a forefront of current research because of its importance in providing the key functions of frequency conversion, light modulation, and optical memory storage for the emerging technologies in the areas of telecommunications, signal processing and optical interconnections. In recent years, there has been extensive research on the growth of nonlinear optical materials because of their wide applications in optoelectronics. Potassium dihydrogen phosphate (KDP) is one of the best known NLO material and is being used for laser frequency conversion, harmonic generation for high pulse energy, and electro-optical modulation. KDP and Deuterated potassium dihydrogen phosphate (DKDP) crystals are still the only nonlinear optical crystals which can be applied to laser radiation conversion in laser fusion systems. These crystals are required to have good optical property and high laser damage threshold [1].In recent years, many studies have proved that the incorporation of impurities on inorganic crystals provides visible changes in their habits [2,3]. An impurity can suppress, enrich or stop the growth of crystal completely [4,5]. The impurity effect depends on the impurity concentration, supersaturation, temperature and pH of the solution. Organic doping improves the nonlinear optical properties of the grown crystals for the second harmonic generation in comparison to pure crystals [6-8].Aromatic plants like basil, thyme, oregano etc. are an excellent source of secondary metabolites, in particularly phenolic compounds (phenolic acids derivates, flavonoids) that are associated with antioxidative and antimicrobial action in all biological systems. In recent years, due to their diverse biological functions, phenols have received great attention [9]. Oregano is rich in phenolic acids. Its scientific name is origanum vulgare and the molecular formula is $C_{10}H_{14}O$.In the present work pure and oregano extract doped KDP crystals were grown by slow evaporation technique and the grown crystals were subjected to X-ray diffraction, FTIR –spectroscopy, UV visible spectral analysis and second harmonic generation measurements.

II. EXPERIMENTAL PROCEDURE

Commercially available KDP was used for the growth. Without any further purification, KDP was dissolved in double distilled water. After obtaining the saturation, the solution was stirred well for two hours, filtered and kept separately for slow evaporation. A similar procedure is followed for the addition of oregano extract to the saturated solution of KDP. Within 15 days, transparent crystals of both pure (14mm x 6mm x 2mm) and oregano extract doped KDP (11mm x 5mm x 1.8mm) crystals were grown. The photographs of the grown crystals are shown in Fig. 1.

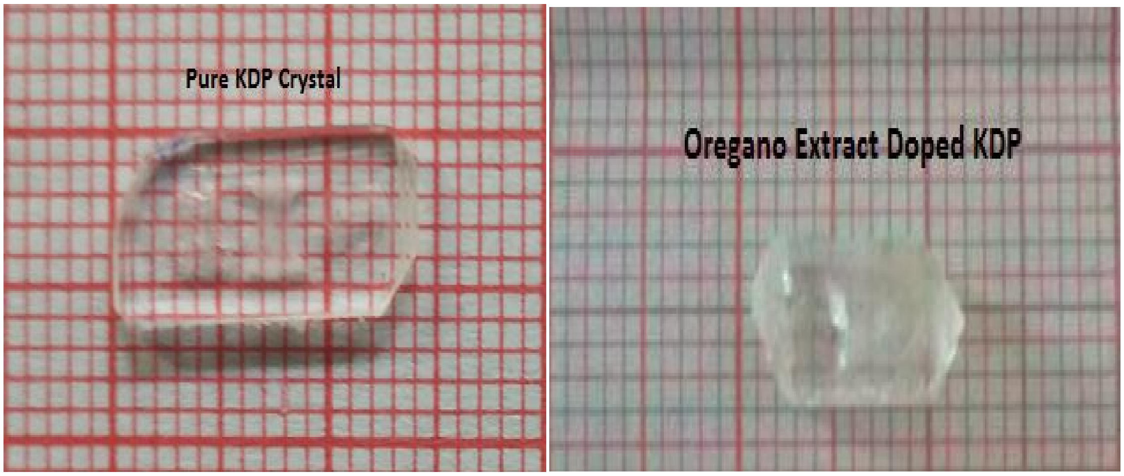

Fig 1. The photograph of the grown crystals of pure and oregano extract doped KDP single crystals.

III. RESULTS AND DISCUSSION

A. Powder X- Ray diffraction

X-ray diffraction technique is a powerful tool to analyze the crystalline nature of materials. Powder X-ray diffraction analysis was carried out by using PANalytical X-Ray diffractometer with CuKα radiation (λ=1.5406 Å). The samples were scanned over the range 10° - 80° at a rate of 1^o per minute. The XRD pattern of pure KDP & oregano extract doped KDP is shown in Fig. 2.Powder XRD results shows that the presence of the dopant has not altered the basic structure of KDP crystal. The prominent peaks observed in the diffraction pattern of pure and OKDP confirm the single crystalline nature of the crystals.The most prominent peaks, with the maximum intensity of the XRD patterns of pure and doped specimens, are quite different. These observations could be attributed to strains in the lattice. Peak intensity is a reflectance of both absorption and amount of phase in the mixture. Asymmetry is comprehensively due to the geometrical conditions of the sample and instrument, the aberrations of diffraction angle and scattering of reflection plane.The calculated cell parameters are discussed in Table 1. The studies confirmed the tetragonal structure of pure and doped KDP crystal and the slight changes observed in cell parameters indicate the influence of dopant on crystal lattice of KDP, the results are in good agreement with literature [10,11]

Table 1

Crystal	Crystal System	Space group	Volume$(Å)^3$	Cell Parameters
KDP	Tetragonal	I-42d	385.92	a =b =7.436Å c = 6.979 Å
OKDP	Tetragonal	I-42d	387.81	a = b =7.448Å c = 6.991 Å

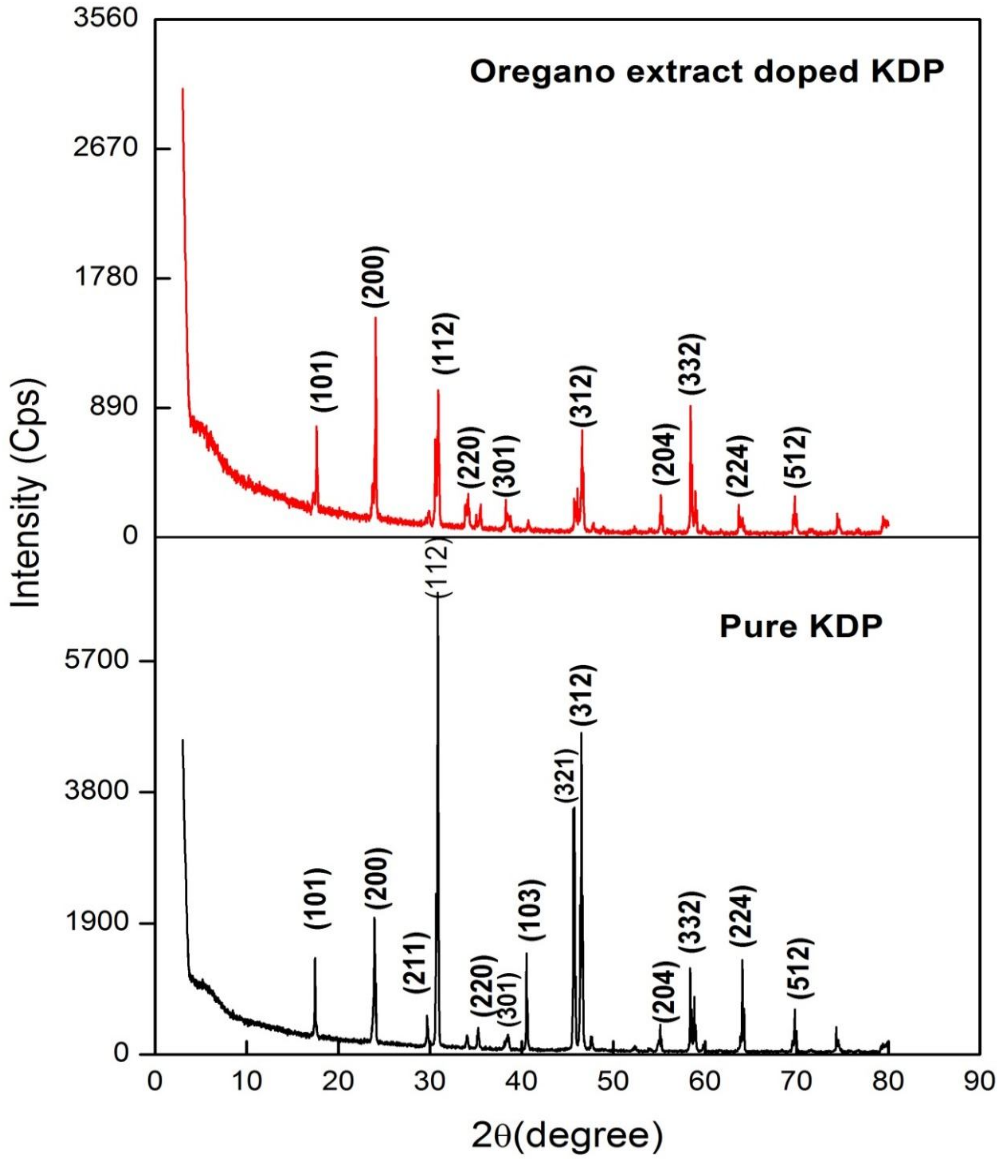

Fig 2. Powder X-ray diffraction pattern of pure and Oregano extract doped KDP single crystals.

B. FTIR analysis

The qualitative aspects of infra-red spectroscopy are one of the most powerful attributes of this diverse and versatile analytical technique. FTIR spectral analyses of pure and doped crystals were carried out in the mid IR range (400–4000 cm^{-1}). The spectrum is shown in Fig. 3. The presented IR-absorption spectrum of pure KDP crystal clearly coincides with known literature data [12]. There is a minor change in peak positions on doping with oregano extract which confirms the incorporation of dopant into the KDP lattice.

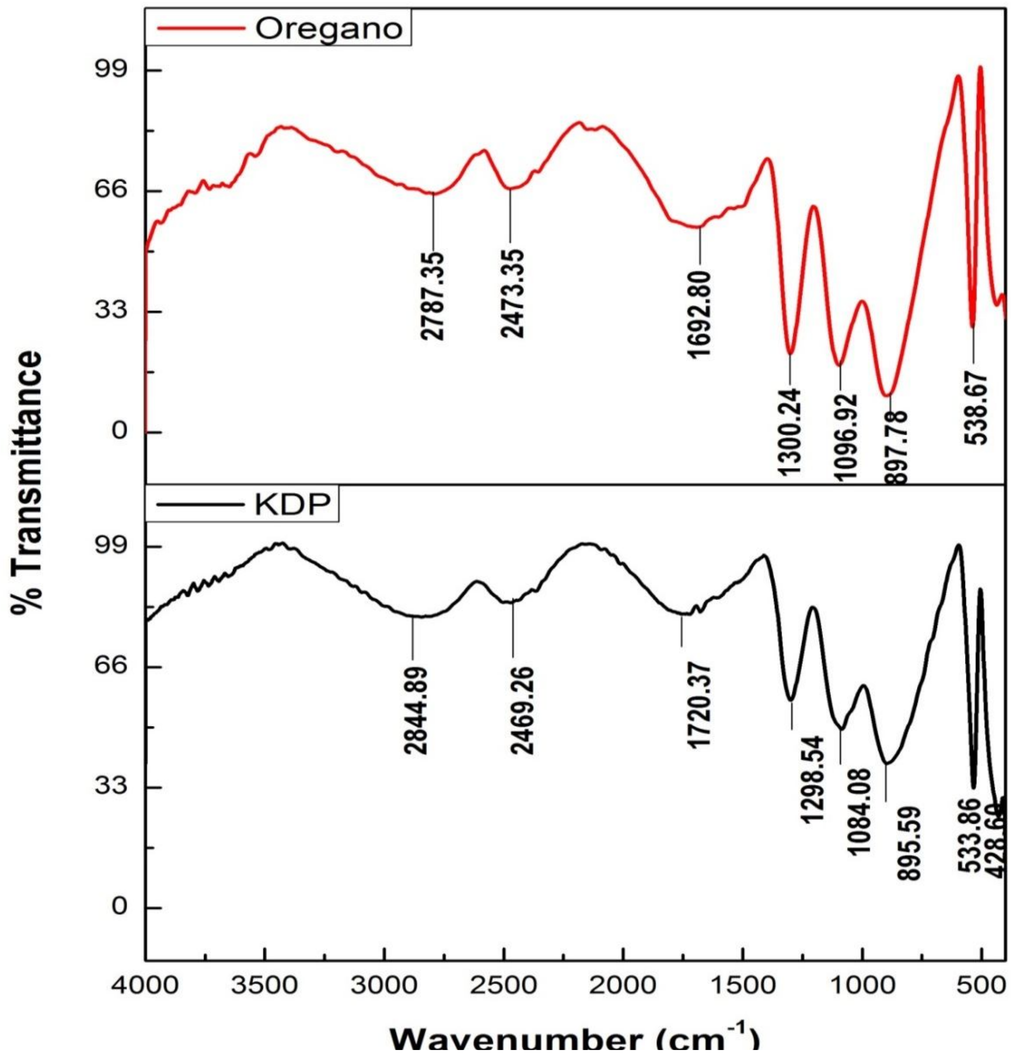

Fig 3. FTIR spectrum for pure and oregano extract doped KDP single crystals.

C. UV-Vis Analysis

The absorption coefficient (α), refractive index (n) and extinction coefficient (k) are the important optical properties of any material. These optical properties are influenced as a result of oregano extract doping in KDP crystal because of modifications in their dependence on electromagnetic radiation. Moreover, the evaluation of optical constants is an important factor for the design and analysis of optoelectronic devices and laser frequency conversion applications in industry. Information of refractive indices and extinction coefficients at energies other than the fundamental absorption edge guides in understanding the electronic band structures of materials.Also, a preferred lower cut-off in the transmittance analysis in the range between 200 and 300 nm is considered effective for optical applications.

Fig. 4 shows the UV-vis transmittance spectra of pure and oregano doped KDP recorded in the wavelength range 200-1200 nm. The cut-off wavelength for pure KDP was observed to be 252 nm for pure KDP but with doping, it shifted to 270 nm. A broad absorption peak at 498 nm was observed for OKDP. This may be due to the presence of phenolic acids and their derivatives in oregano [13]. The cut-off wavelength suggests the usefulness of these crystals in several optoelectronic applications.

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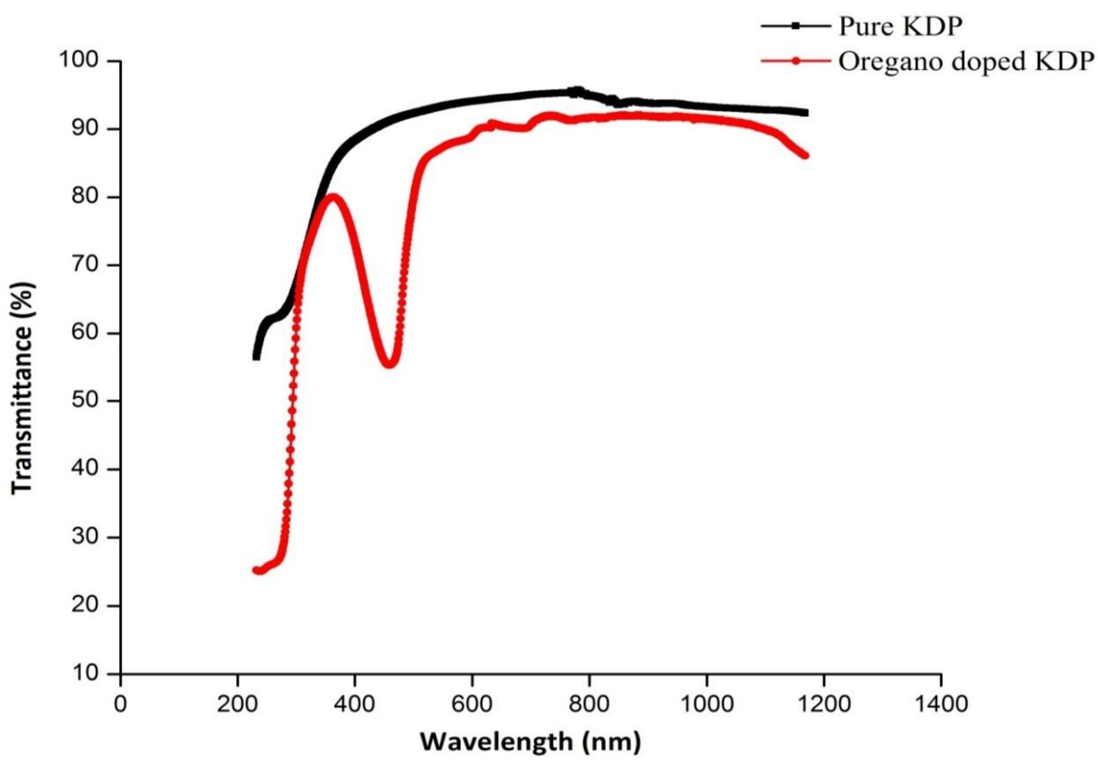

Fig 4. UV-Visible transmission spectra of pure and oregano extract doped KDP single crystals.

1) *Optical absorption coefficient:* The optical absorption coefficient (α) is a function of incident photon energy that increases exponentially and then saturates, a behaviour typically governed by the density of states in the conduction band. It can be calculated using transmittance data from the following relation [14,15].

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

Wheret is the crystal thickness and T is the transmittance. According to the Tauc relation, the absorption coefficient is related to the photon energy (hν) in the grown crystals as:

$$\alpha hv = A(hv - E_g)^{1/2}$$

Where is the optical band gap and A is a constant, indicating the allowed direct inter band transition.

The Talc's graph[16] plotted between the product of absorption coefficient and the incident photon energy $(\alpha h\nu)^2$ with the photon energy (hν) at room temperature shows a linear behavior that can be considered as evidence of the direct transition. Fig. 5shows the plot of $(\alpha h\nu)^2$ vs photon energy for pure and oregano extract doped KDP crystals, where the energy band gap was evaluated by extrapolating the linear portion of the curve to $(\alpha h\nu)^2 = 0.0$ and was found to increase with doping in the KDP crystal.

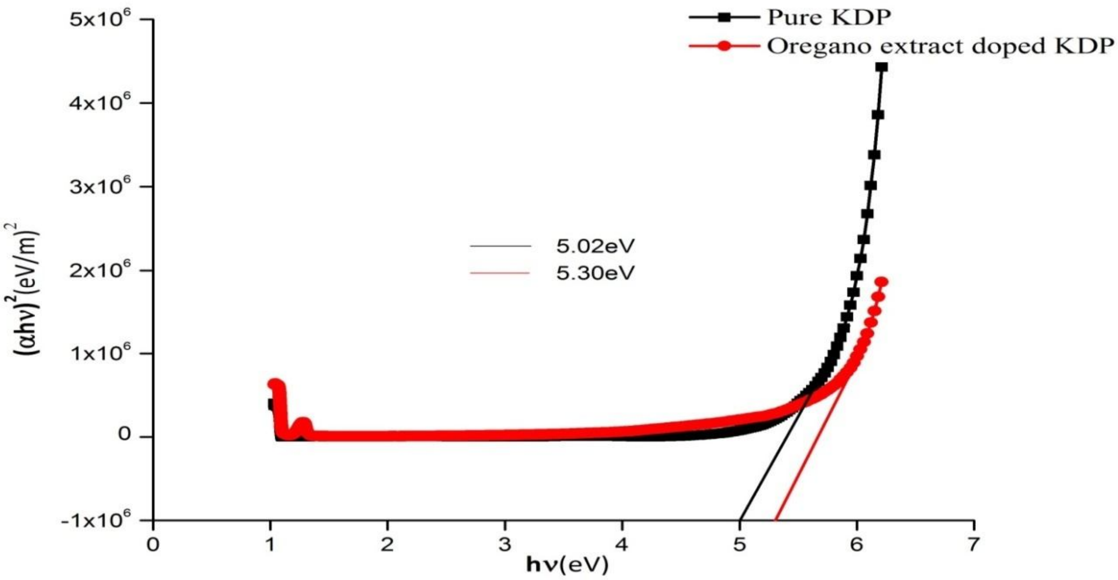

Fig 5. $(\alpha h\nu)^2$ vs. hν spectra of pure and oregano extract doped KDP single crystals.

2) Optical properties and constants

The reflectance (R) in terms of the absorption coefficient can be written as[17]

$$R = 1 \pm \sqrt{\frac{1 - \exp(-\alpha t) + \exp(\alpha t)}{1 + \exp(-\alpha t)}}$$

The reflectance vs wavelength for pure and oregano extract doped KDP crystal is shown in Fig.6. The reflectance of the oregano doped crystals was nearly reduced by half as compared to that of pure KDP, suggesting high transmittance in the case of doped crystal.

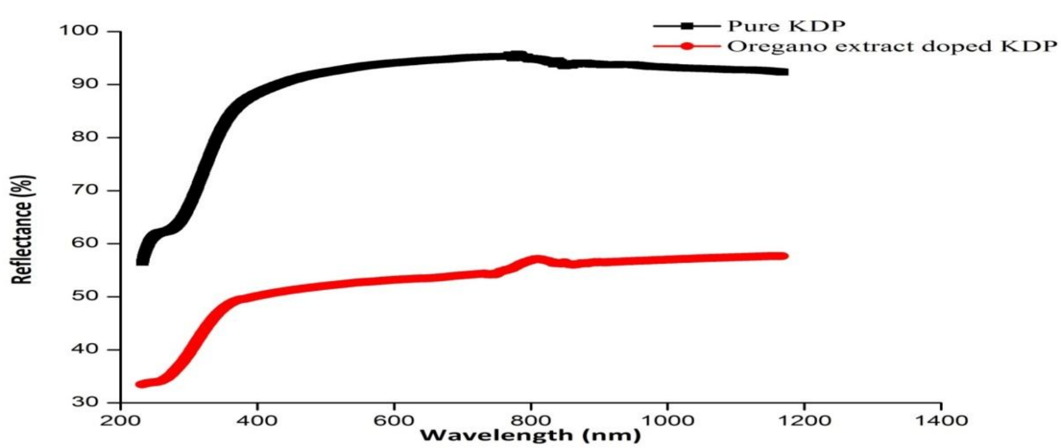

Fig 6. Reflectance vs wavelength for pure and oregano extract doped KDP single crystals.

The optical properties of the crystals are governed by the interaction between the crystal and the electric and magnetic fields of the electromagnetic waves. Extinction coefficient is the fraction of light lost due to scattering and absorption per unit distance in a participating medium. In electromagnetic terms, the extinction coefficient can be explained as thedecay or damping of the amplitude of the incident electric and magnetic fields. The extinction coefficient (k) shown in Fig. 7 can be obtained from the equation:

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

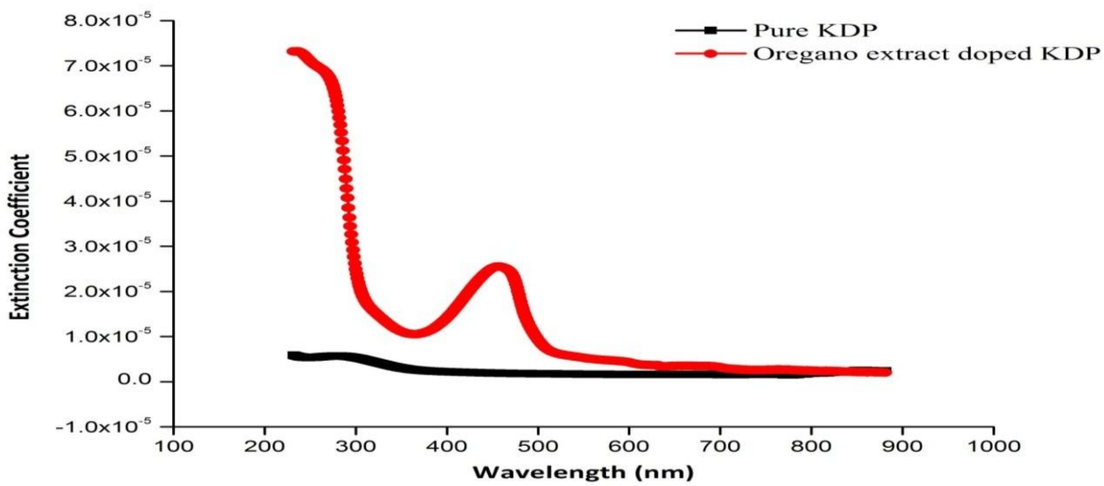

Fig 7. Extinction coefficient vs hν for pure and oregano extract doped KDP single crystals.

The refractive index (n) can be determined from reflectance (R) data using the following relation

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

The wavelength dependence of n for pure and doped KDP crystal in the range 200–1200 nm is shown in Fig. 8. Initially the refractive index decreases with increasing wavelength, then it becomes constant.

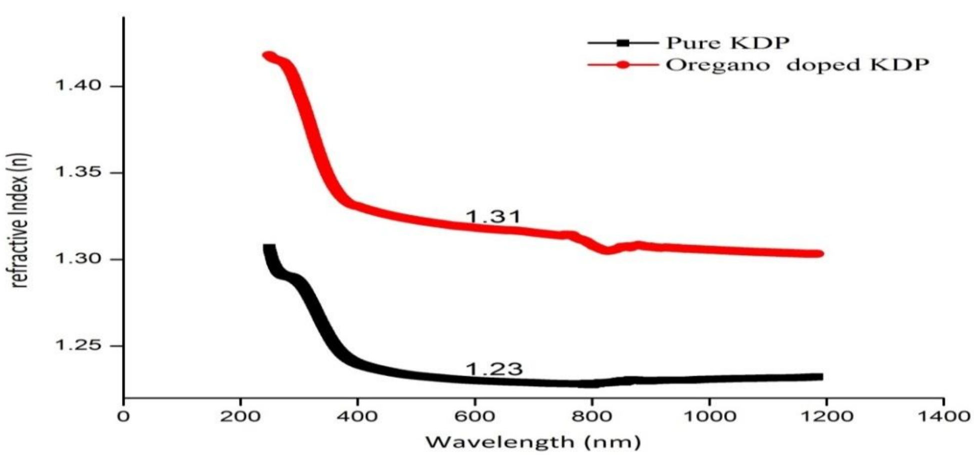

Fig 8. Refractive index vs wavelength for pure and oregano extract doped KDP single crystals.

From the optical constants, the electric susceptibility (χ_c) can be calculated using the following relation [18].

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_c = n^2 - k^2$$

Hence,

$$\chi_c = \frac{n^2 - k^2 - \varepsilon_0}{4\pi}$$

Where ε_0 is the dielectric constant in the absence of any contribution from free carriers. The real part of dielectric constant ε_r and imaginary part of dielectric constant ε_i can be calculated following the relation[19]

$$\varepsilon_r = n^2 - k^2 \text{and} \varepsilon_i = 2nk$$

The calculated values are given in Table 2.

The optical conductivity (σ) of the grown crystals was determined[20] using the following equation

$$\sigma = \frac{\alpha n c}{4\pi}$$

where c is the velocity of light. The variation of optical conductivity with photon energy is given in Fig.9. From the graph, it was observed that the optical conductivity remains constant until the photon energy of 4 eV, beyond which it increases linearly. As a consequence of its increased band gap and other calculated optical constants like extinction coefficient, refractive index, optical conductivity, etc., the oregano extract doped crystals can be of potential interest for optical applications.

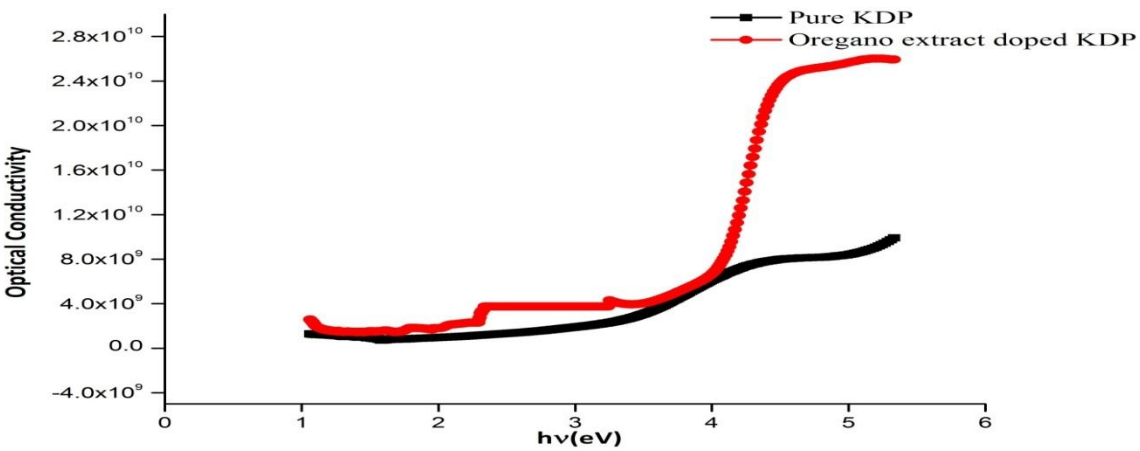

Fig 9. Optical conductivity vs photon energy for pure and oregano extract doped KDP single crystals.

D. Second Harmonic Generation Efficiency Measurements

The first and the most widely used technique for confirming the SHG from prospective second order NLO materials is the Kurtz powder technique [21] to identify the materials with non- centrosymmetric crystal structures. The SHG conversion efficiency of oregano extract doped KDP crystal was studied using a 1064 nm Nd: YAG laser. The samples of oregano extract doped KDP were made in powder form. To make relevant comparisons with known SHG materials, KDP was also ground and sieved into the same particle size range. The powdered samples were filled air-tight in separate micro-capillary tubes of uniform bore of about 1.5mm diameter. A Q-switched, A fundamental laser beam of 1064 nm wavelength from a Nd: YAG laser was made to fall normally on the sample cell. The power of the incident beam used was 1.1mJ/pulse. The input laser beam was allowed to pass through an IR reflector and then directed on the micro-crystalline powdered samples packed in a capillary tube. The photodiode detector and oscilloscope arrangements measured the light emitted transmitted by the sample. The SHG radiations of 532nm (green light) transmitted through the sample were collected by a photomultiplier tube (PMT-Hamamatsu-model R 2059). The optical signal incident on the PMT was converted into voltage output at the CRO (Tektronix-TDS 305213).The output intensity of SHG gives relativevalues of NLO efficiency of the material. It is found that the efficiency of SHG for oregano extract doped KDP is 2.3 times of that of standard KDP. A similar effect was observed in literature when KDP crystals were doped with neem leaves extract [7]and ginger extract [8].

IV. CONCLUSION

Pure and oregano extract doped KDP single crystals have been grown by slow evaporation method. The incorporation of oregano extract in KDP crystal has been identified by FT-IR spectral analysis. The powder XRD studies confirmed the cell parameters and improved crystalline nature of oregano doped KDP crystal. The crystals were found to show good transparency in the UV-visible region with increased band gap and enhanced optical constants making them useful for photonic device applications. The SHG efficiency measurements were carried out for the grown crystals and found that the SHG efficiency for oregano extract doped KDP is 2.3 times of that of standard KDP.The OKDP crystal with improved crystalline perfection and good optical properties is desirable material for NLO device applications.

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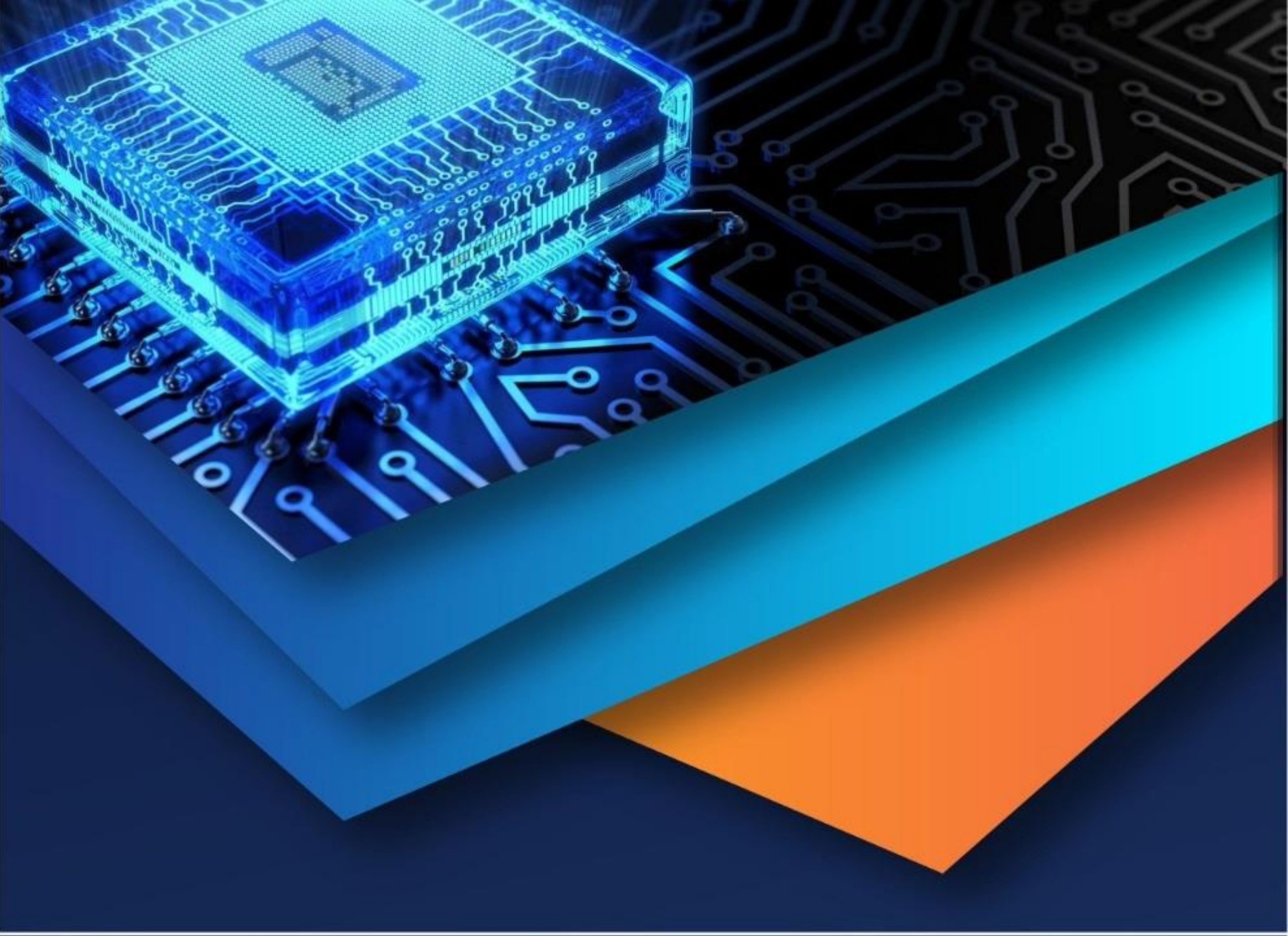

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