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# Studies on Linear and Nonlinear Optical Properties of Vanillin

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**Abstract:** Vanillin, an organic material, was grown as single crystal by solution growth technique using a mixed solvent methanol and chloroform. XRD study confirms that the grown crystal belongs to monoclinic system with space group $P2_1$. The surface features of the crystal were analyzed with Atomic Force Microscope (AFM). The important optical parameters such as absorption coefficient, extinction coefficient, refractive index, optical band gap, optical conductivity and electrical conductivity were estimated from UV–vis–NIR spectral analysis to study the linear optical behavior of the material. The dielectric studies of the sample were carried out in the frequency range from 50 Hz to 5 MHz. The second harmonic generation efficiency (SHG) was evaluated both theoretically and experimentally to analyses the NLO behavior of the material.
**Keywords**: solution growth technique, lattice parameters, optical parameters, polarizability, atomic force microscope, nonlinear optical material.

## 1.Introduction

The field of nonlinear optics has developed considerable amount of interest among the researchers to synthesis new nonlinear optical materials due to their potential applications in the areas of optical switching, optical data storage for the developing technology in telecommunication and signal processing [1-3]. The fabrication of optoelectronic and photonic devices depends mainly on the development of NLO materials with maximum second harmonic generations efficiency (SHG). There are some interesting organic materials like amino acids which can be used for NLO applications. These organic materials possess high optical nonlinearity and chemical flexibility. Vanillin is an organic compound with molecular formula $C_8 H_8 O_3$, also known as 4-hydroxy 3-methoxy benzaldehyde having the structure 4-(HO) $C_6H_3$ – 3 – (OC $H_3$) CHO. In the present investigation, vanillin was first grown using solution growth technique. The linear and nonlinear optical properties were analyzed to understand the second harmonic generation efficiency of the material in the near infrared region. The surface structure of the vanillin crystal was studied using atomic force microscope. The dielectric study of the grown crystal was carried out to establish the dielectric behavior of the material. Finally NLO property was tested to assess the SHG efficiency of the material.

## 2. Synthesis and growth of vanillin

The solubility of vanillin in water was found to be low. Hence, water is not a good solvent for growing large size vanillin crystals [4]. When the solvent like methanol or mixed solvent methanol-acetone or methanol-chloroform was used, the solubility of vanillin was found to be considerably enhanced. The solubility of vanillin was found to be 89.4g in 50ml of methanol-chloroform (4:1 ratio) at room temperature. A saturated solution of vanillin was prepared using the solvent methanol. The solution was continuously stirred with magnetic stirrer to ensure homogeneity of the solution. The solution was filtered and covered with a perforated lid. The solution was allowed to evaporate gradually and isothermally. This led to supersaturation resulting in the formation of tiny crystals. The size and purity of the crystal were improved due to the repeated crystallization process. The crystal thus obtained has the dimensions of 7.86 × 6.59 × 2.21 $mm^3$ and is shown in Fig.1.

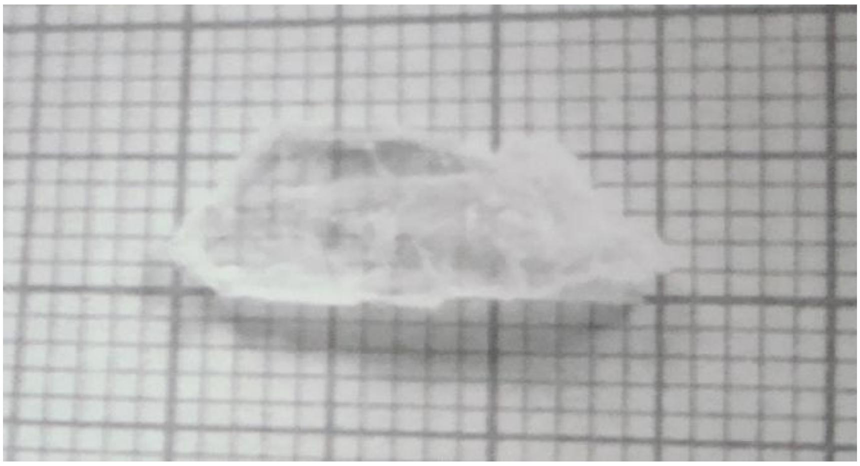

**Fig. 1 Photograph of as-grown vanillin crystal**

## 3. Characterization technique

Single crystal XRD study was carried out using Enraf Nonious CAD4 single crystal diffractometer to determine the lattice parameters and the space group of the grown crystal vanillin. The surface morphology of the crystal was analyzed using Atomic Force Microscope (Digital Instrument Dimensions 3100 AFM). The absorption spectrum was recorded with the help of VARIAN CARY 5E UV-vis-N IR spectrometer in the wavelength range 200-1200 nm to analyses the linear optical property of the material. The dielectric property was analyzed using a HIOKI 3532 - 50 LCR HITESTER in the frequency range 50 HZ to 5 MHz Nonlinear optical property was tested by Kurtz and Perry powder technique (QUANTA RAY model LAB-170-10) and the SHG efficiency was assessed.

## 4. Results and discussion

### 4.1 Single crystal XRD analysis

Single crystal XRD was studied for the grown crystal using Engraft Nonie's CAD 4 / MACH3 single crystal diffractrometer coupled with space group $P2_1$.The calculated unit cell parameters are found to be a=14.07Å, b=7.87Å and c=15.01Å; $\alpha=\gamma=90^o$, $\beta=115.14^o$ and volume V=1498 $(Å)^3$. These values are found to be in good agreement with the reported values [5, 6]. The space group is recognized as non-centrosymmetric which fulfills the condition for the material to exhibit NLO behavior.

### 4.2 Atomic microscopy analysis

Vanillin single crystals were subjected to surface analysis using Atomic Force Microscope. The flat surface of the as-grown crystal was scanned by AFM with scan and rate of scanning maintained at 5 $\mu m$ and 1052 Hz respectively. Figs 2(a) and (b) show the surface topology of the crystal with two and three dimensional views under tapping amplitude mode. Figs. 3(a) and (b) show the surface topology of the crystal with two and three dimensional views under tapping phase mode. The photographs (Figs. 2 (a) and (b)) clearly reveal the smooth surface of the grown crystal with more transparency. The photographs (Figs 3 (a) and (b)) reveal the existence of steps provided by the growth spirals. The grown spirals can be detected using SEM images. AFM study confirms the formation of ordered terraces due to diffusion of adsorption of molecules over the steps provided by the growth spirals.

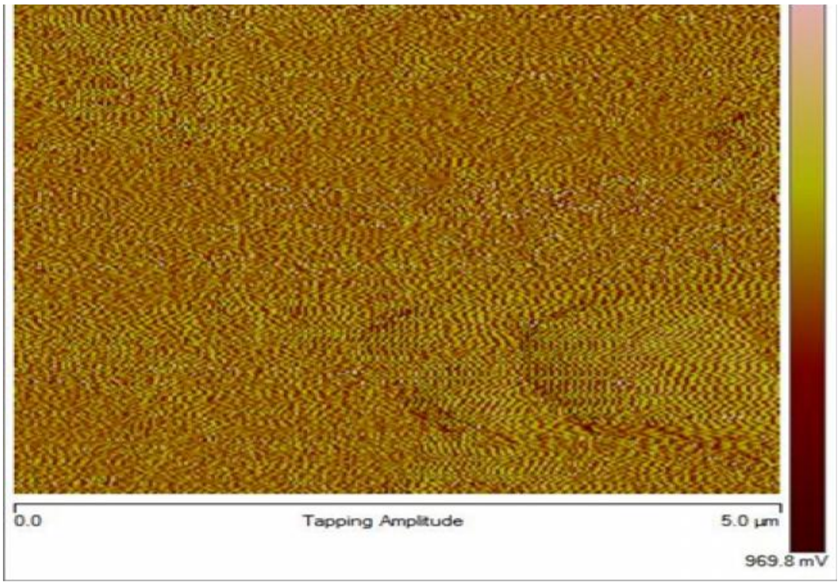


**Fig. 2(a) Two dimensional view of the surface topology of vanillin crystal**

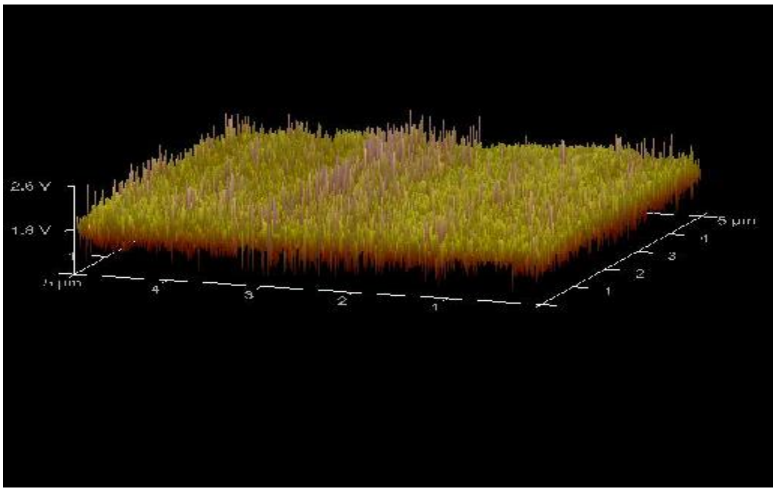


**Fig. 2(b) Three dimensional view of the surface topology of vanillin crystal (Tapping Amplitude)**

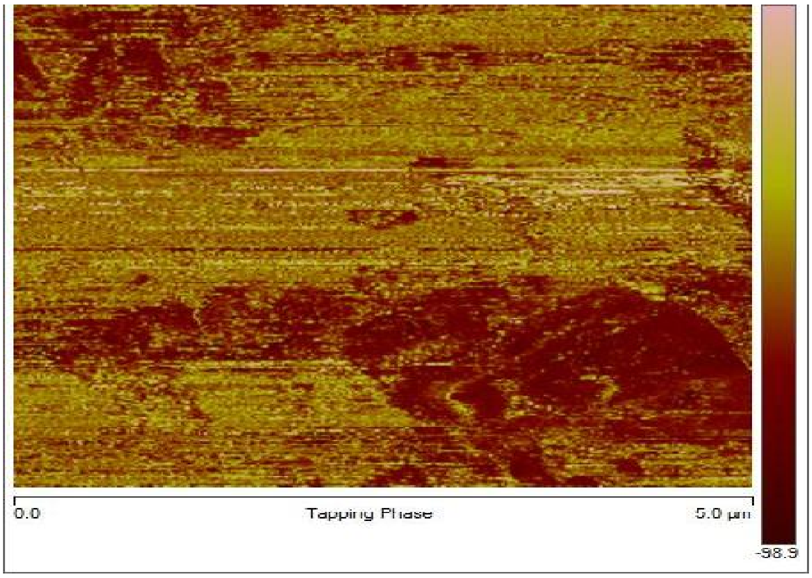


**Fig. 3(a) Two Dimensional view of the surface topology of vanillin crystal**

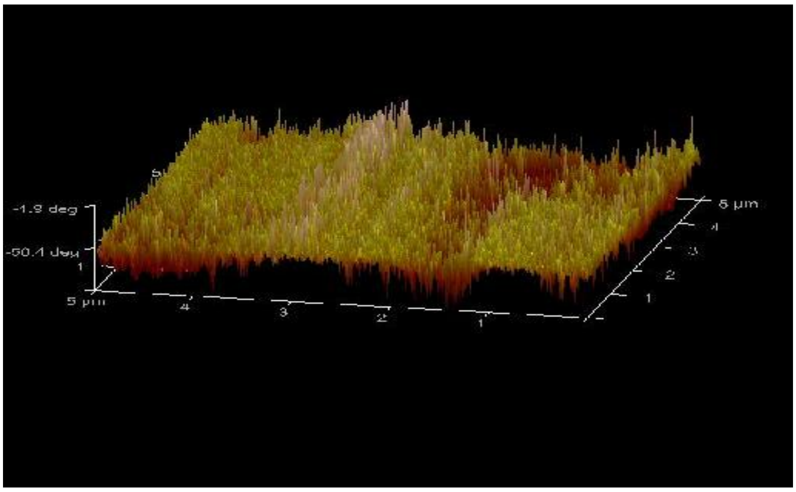


**Fig. 3(b) Three Dimensional view of the surface topology of vanillin crystal (Tapping Phase)**

### 4.3 Linear optical property

Fig.4 shows UV–vis–NIR absorption spectrum of vanillin recorded in the wavelength range of 300 – 1200 nm. The material shows the transparent nature from 380 nm onwards. It is observed that the material can readily transmit the laser beam of wavelength 1064 nm in the infrared region for analyzing the NLO activity of the crystal. The material can therefore be used for fabricating NLO devices.

The optical absorption coefficient (α) was calculated using the following relation

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

where T is the transmittance and d is the thickness of the crystal. The other optical parameters such as band gap ( $E_g$), extinction coefficient (K), reflectance (R), linear refractive index (n), complex dielectric constant ($\varepsilon_c$), optical conductivity ($\sigma_{op}$) and electrical conductivity ($\sigma_c$) were calculated from the following relations.

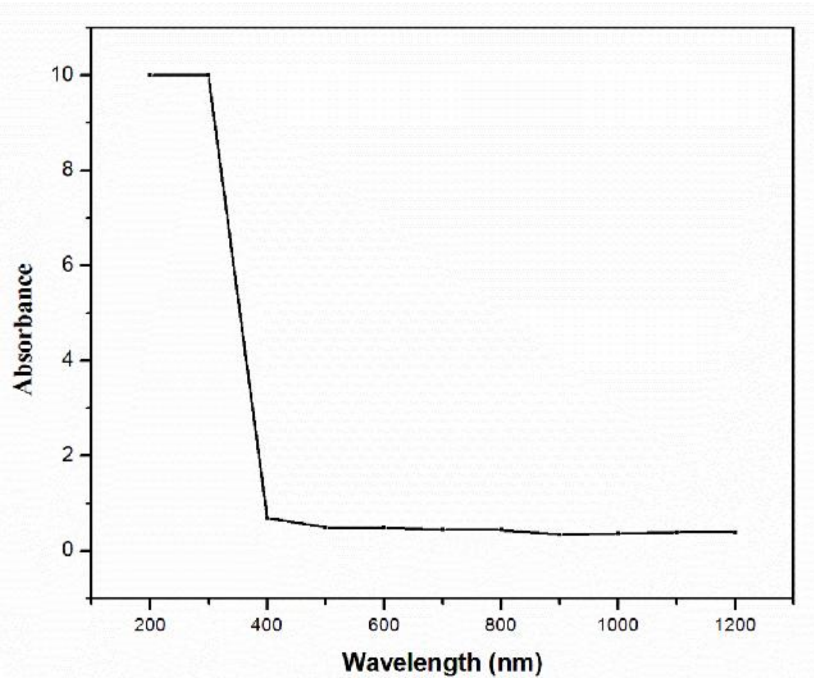


**Fig. 4 Plot of absorbance against wavelength**

The energy band gap ($E_g$) of the material has been estimated using the Tauc's [7] relation given by

$$\alpha = \frac{(h\upsilon - E_g)^{\frac{1}{2}}}{h\upsilon} \qquad (2)$$

where hν is the photon energy (eV). The band gap was calculated from the linear part of the plot of $(\alpha h\nu)^2$ versus hν as shown in the Fig 5. The value of $E_g$ is found to be 1.79 eV which confirms the wide transparency and dielectric behavior of the materials. The extinction coefficient (K) is expressed as

$$K = \frac{\lambda\alpha}{4\pi} \qquad (3)$$

where λ is the wavelength of the incident radiation. The relation connecting transmittance (T), reflectance (R) and refractive index (n) are given as follows using the expression T+R=1

Hence, $T = \frac{4n}{(n+1)^2}$ (4)

$$\mathbf{R} = \left(\frac{n-1}{n+1}\right)^2 \qquad (5) \text{ and}$$

$$n = \frac{-(T-2) \pm \sqrt{4-4T}}{T} \qquad (6)$$

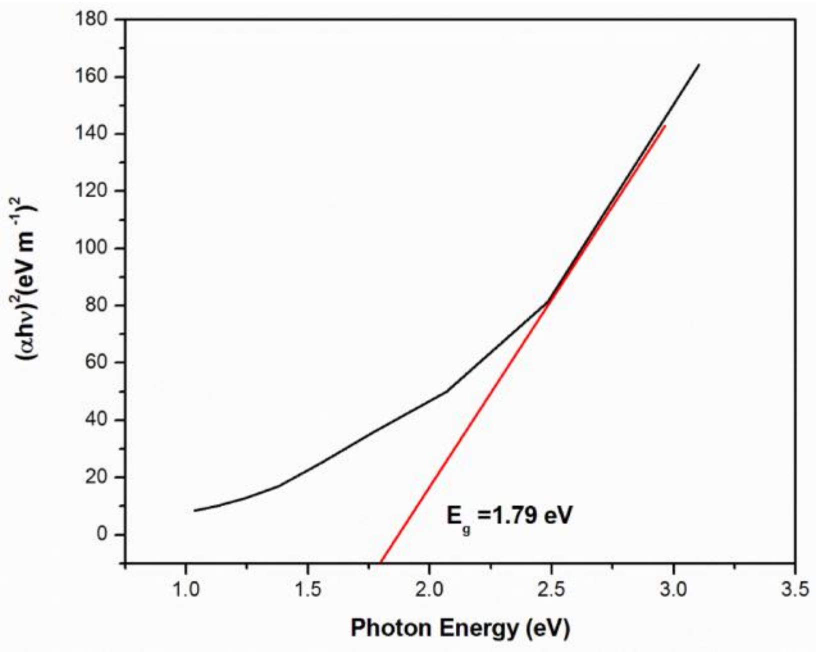


**Fig. 5 Plot of (α hν )$^2$ versus photon energy (hν)**

The complex dielectric constant $\varepsilon_c$ is written in terms of real εr and imaginary (εi) parts of dielectric constant as,

$$\varepsilon_c=\varepsilon_r+\varepsilon_i \quad (7)$$

$$\varepsilon_r = n^2 - K^2 \quad (8)$$

and

$$\varepsilon_i = 2nk \quad (9)$$

Since K is negligibly small,

$$\varepsilon_c = \varepsilon_r = n^2 \quad (10)$$

The optical conductivity $\sigma_{op}$ of the material is related to the absorption coefficient and refractive index as

$$\sigma_{op} = \frac{\alpha n c}{4\pi} \quad (11)$$

where c is the velocity of light. The electrical conductivity of the material is expressed as

$$\sigma_e = \frac{2\lambda\sigma_{op}}{\alpha} \quad (12)$$

The high transmittance and the low absorbance and reflectance of the material over a wide range of wavelength suggest that the material vanillin can be used as anti-reflection coating in solar thermal devices and nonlinear applications [8,9]. The variation of extinction coefficient is found to be linear with respect to wavelength even for low values of absorbance. The refractive index (n) is found to vary from 1.44 to 1.35 over the wavelength range of 400 -1200 nm. The lower range of complex dielectric constant (0.97-1.81) over the transmission range of the material really counts for the induced polarization in the material to exhibit NLO activity due to incident radiation on the material.

The higher order of optical conductivity at higher photon energy (Fig. 6) confirms the better conversion efficiency of the material vanillin for second harmonics generation [8]. The lower value of electrical conductivity at higher photon energy (Fig. 7) is a clear manifestation of dielectric nature of the material.

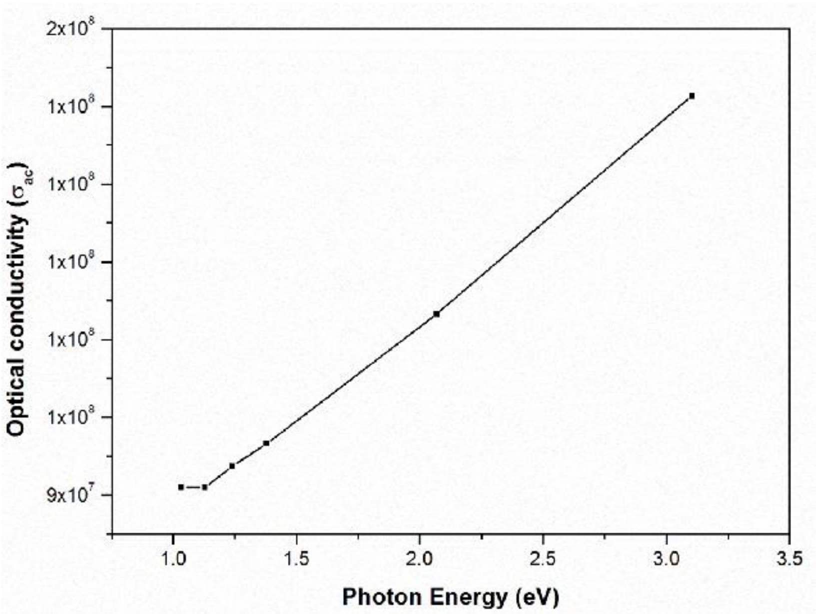


**Fig. 6 Plot of optical conductivity versus Photon energy (hν)**

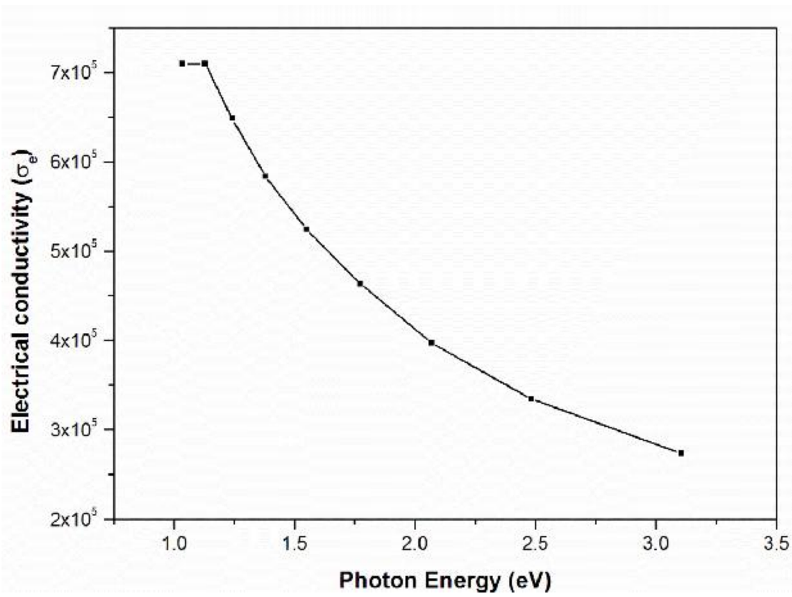


**Fig. 7 Plot of electrical conductivity versus photon energy (hν)**

**4.3 Dielectric studies**

Single crystals of vanillin were subjected to dielectric studies at room temperature for the frequency range from 50 Hz to 5 MHz. Good quality crystal was used for this study. The dielectric constant ($\varepsilon'$) and dielectric loss ($\varepsilon''$) were calculated by using the relations

$$\varepsilon' = \frac{Cd}{\varepsilon_0} \qquad (13) \text{ and}$$

$$\varepsilon'' = \varepsilon_r D \qquad (14)$$

where C is the capacitance, d is the thickness, A is the area of the grown crystal $\varepsilon_0$ is the permittivity of free space and D is the dissipation factor. It is observed from the Figs. 8 and 9 that the value of dielectric constant and dielectric loss are high in the lower frequency region. The larger value of dielectric constant at lower frequencies is due to the contribution from all the four polarization viz. electronic, ionic, dipolar and space – charge polarizations. The low value of dielectric constant and dielectric loss at higher frequencies suggest that the grown crystal contains minimum density of defects with high optical quality [9].

**4.4 Nonlinear optical property**

Dielectric studies of the crystal are more useful to establish the dielectric behavior of the material and to estimate the polarizability of the material to assess the SHZ efficiency of the material. The polarizability of vanillin and KDP were calculated using Clausius – Mosotti relation

$$\alpha = \frac{3M}{4\pi\rho N_A}\left(\frac{\varepsilon' - 1}{\varepsilon' + 2}\right) \qquad (15)$$

where $N_A$ is Avogadro number, M is the molecular weight, ρ is the density and $\varepsilon'$ is the dielectric constant. The calculated values of polarizability for both vanillin and KDP are given as $4.82 \times 10^{-23}$ cm$^3$ and $2.15 \times 10^{-23}$ cm$^3$ respectively. Since the polarizability of vanillin in found to be larger than that of KDP, the SHG of vanillin is theoretically interpreted as larger than that of KDP.

The nonlinear optical property and the efficiency were tested using Kurtz and Perry powder technique. The grown crystal vanillin was crushed to fine powder and placed in a micro capillary of uniform bore [10]. A high intensity of laser radiation from Nd: YAG laser source of wavelength in the NIR region was passed through the sample. The output was measured as 13.8 mV for an output 4.2 mJ/ pulse. The sample was replaced by KDP crystal and the output was measured as 6.8 mV without changing the input. Therefore, the SHG efficiency of vanillin is found to be twice that of KDP. Hence the experiment is found to be in good agreement with the theoretically predicted result from the calculated polarizability value. It is concluded that the grown crystal vanillin is an excellent material showing higher SHG efficiency for NLO applications.

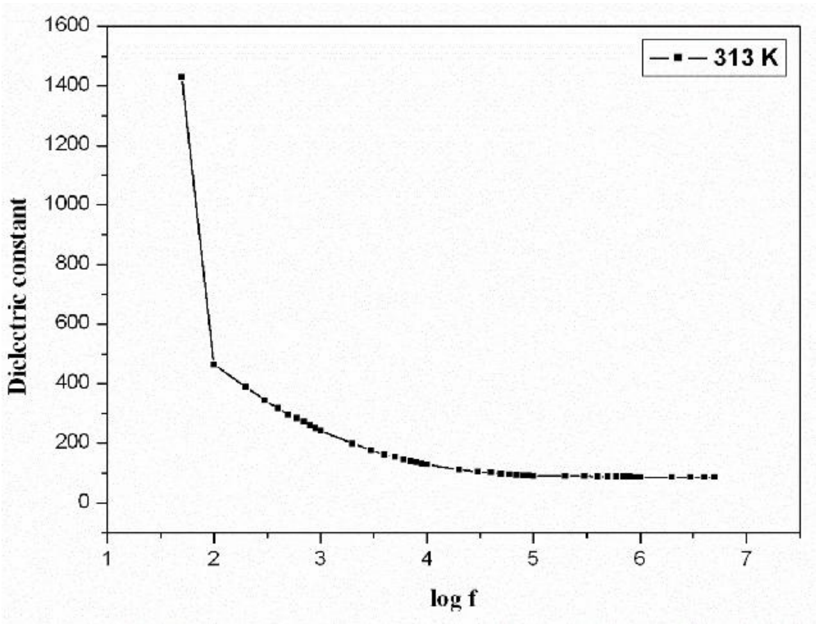


**Fig .8 Plot of dielectric constant versus log f**

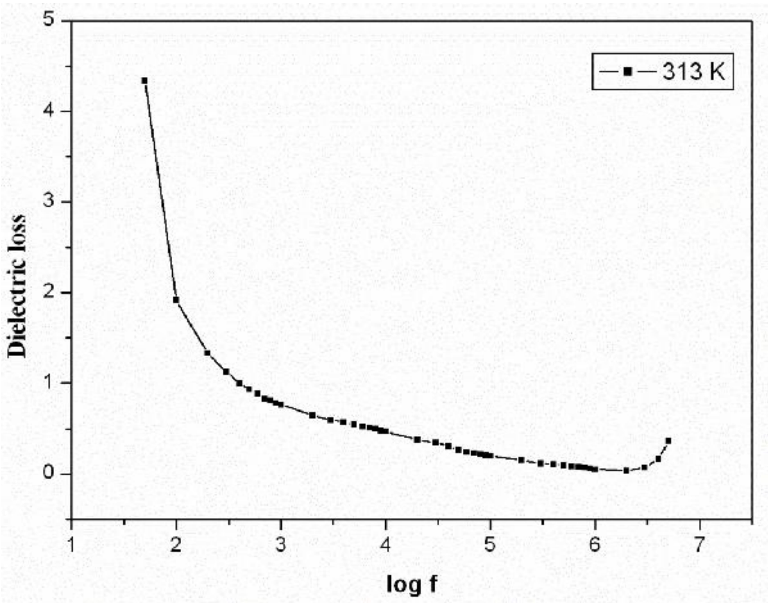


**Fig. 9 Plot of dielectric loss versus log f**

## 5. Conclusion

Good quality vanillin single crystals were grown by slow evaporation technique. Single crystal XRD analysis has confirmed that the grown crystal belongs to monoclinic system with space group $P2_1$. The surface topology was analyzed using AFM study. The linear optical properties such as transparent range, optical band gap, extinction coefficient, refractive index, complex dielectric constant, optical conductivity and electrical conductivity were discussed using UV –vis –NIR spectrum. Dielectric studies established the dielectric behavior of the grown crystal. NLO property was tested using Kurtz and Perry powder technique. The SHG efficiency of vanillin is found to be twice that of KDP. Therefore, vanillin is an excellent material with higher second harmonic generation efficiency required for optical device fabrications.

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