

OPTICAL, MECHANICAL AND THERMAL PROPERTIES OF DYE DOPED VANILLIN SINGLE CRYSTAL

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Abstract

A crystal of vanillin doped with rhodamine dye was grown using solution growth technique. Dyeing of crystals is a practice developed particularly for quantum optics applications, because of the very significant increase in surface area achieved in growing crystals. The lattice parameters of the grown dye doped vanillin crystal were studied using single crystal XRD analysis. The optical properties of the doped vanillin crystal were analyzed to understand the second harmonic generation efficiency of the material in the UV-Vis.IR region. FTIR analysis gives the detail of the functional groups present in the grown crystal. The dielectric study of the grown crystal was carried out to establish the dielectric behavior of the material in the frequency range from 50 Hz to 5 MHz at different temperatures. The thermal properties of the crystal were studied by using TGA/DTA analysis. The mechanical stability of the dye doped vanillin crystal was studied by Vicker's Microhardness test. The SHG efficiency of the DV single crystal was tested to assess by using Kurtz-Perry powder method.

INTRODUCTION

The nonlinear optical materials has developed due to their potential applications in the areas of optical computing, optical data storage and signal processing [1-3]. The photonic device depends mainly on the development of NLO materials with maximum second harmonic generations' efficiency (SHG). The organic NLO materials with small organic molecules have a large dipole moment and a chiral structure. The presence of impurity molecules, even at lower concentrations in the solution, may have considerable effect on their properties [4,5]. The Urea (N_2H_4CO) and Thiourea (N_2H_4CS) are simple organic molecules with large dipole moment and have the ability to form an extensive network of hydrogen bonds. If added as a dopant, it is expected to occupy the interstitial positions of the lattice and in turn this may lead to various changes in the physical properties [6-8].

Vanillin is an organic compound with molecular formula $C_8H_8O_3$, also known as 4- hydroxy 3-methoxy benzaldehyde having the structure 4-(HO) $C_6H_3 - 3 - (OC H_3) CHO$. It is one of the organic nonlinear optical materials which exhibit a good Second Harmonic Generation (SHG). The crystal growth and NLO properties of vanillin crystal was studied by several researchers.

Crystalline Vannlin occurs naturally in cured vanilla pods, in potato parings, and in Siam benzoin [9]. Isolated Vannilin appears as white needle-like crystalline powder with an intensely sweet and

very retentive creamy vanilla-like odor. Vanillin is a substance generally recognized safe (FDA-Code of Federal Regulations, 2002) and is one of the most important flavour-active additives used as a sweetener in foods, confectionery, and beverages, as aroma in the production of balsams, cosmetics, perfumes, fragrances, deodorants, candles, incense, and air fresheners. VAN is also used as reagent in analytical chemistry and in the manufacture of agrochemical products and pharmaceuticals [10,11]. Single crystals of VAN are useful in non-linear optics [12-17].

EXPERIMENTAL

For the present study, the pure form of Vanillin (Merck GR) and commercially available Rhodamine B was taken to crystallize the new doped single crystal of vanillin. The pure form of vanillin was dissolved in ethanol and stirred continuously for 6 hours. The Rhodamine B also dissolved in ethanol and added to the stirred solution. The mixed solution was filtered using ultra micro-pore filter paper. Then the saturated solution was kept in a vibration free area with a tightly closed plastic cover. Good quality single crystals of rhodamine doped vanillin were collected from the mother solution in a time span of 10 days. The photographs of the as grown crystal doped vanillin (DV) are shown in Fig. 1.

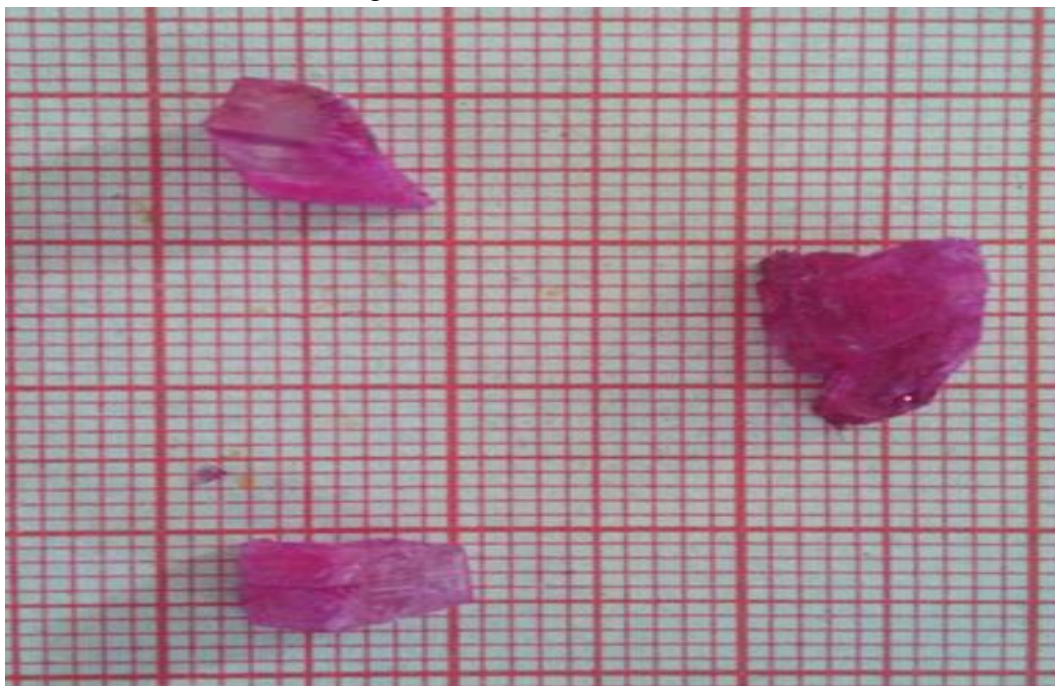


Fig. 1 single crystal of doped vanillin

CHARACTERISTIC STUDIES

Single-crystal X-ray Diffraction

Single crystal X-ray diffraction analysis are used to find the cell dimensions of the grown crystal. The cell parameters of DV (Dye doped vanillin) was carried out using BrukerKappa Apex II single-crystal X-ray diffractometer. The unit cell parameters of the DV crystal $a = 14.056(4) \text{ \AA}$, $b = 7.853(1) \text{ \AA}$, $c = 14.987(5) \text{ \AA}$, $\text{Alpha} = 90.00(0)^\circ$, $\text{Beta} = 115.53(2)^\circ$, $\text{Gamma} = 90.00(0)^\circ$ and volume $V = 1492.8(8) \text{ \AA}^3$. These values agreed well with the pure vanillin crystals, the grown crystal retains its original structure. This result reveals that, the Rhodamine B has entered into the lattice sites of vanillin.

Fourier Transform Infra-Red Spectroscopy

KBr pellet technique is used to record the Fourier transform infrared spectrum at room temperature in the range of $4000\text{--}400 \text{ cm}^{-1}$. The effect of Rhodamine B on the functional groups of the pure Vanillin crystal has been identified by the FTIR spectrum. The recorded FTIR Spectrum of Doped Vannillin are shown in Fig. 2, exactly matches with each other due to overlapping of bonds although there is a change in organic elements percentage due to the addition of dopants. The frequencies with their relative intensities obtained in FTIR spectrum of dye doped vanillin crystal. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and from the literature data.

The Peak observed at $3173, 2955, 2913 \text{ cm}^{-1}$ are mainly due to C-H stretching mode of vibrations. Similarly the band appears at $1263, 1158, 811$ and 728 cm^{-1} are assigned to C-H in plane and out of plane deformations respectively. The band appears at 3558 cm^{-1} mainly due to O-H stretching mode of vibration. The C-C stretching mode of vibrations occurs at 1511 and 1458 cm^{-1} . The peak at 1520 and 1610 cm^{-1} are due to C-O and C=O stretching mode of vibrations. The major peaks the intense absorption at 1649 cm^{-1} is attributed to C=O stretching vibrations of COOH group. Aromatic ketones have absorption band due to the in-plane deformation vibration of C-CO group at 588 cm^{-1} . $\text{CH}_2\text{-CO}$ deformation at 1429 cm^{-1} supported the presence of methyl group.

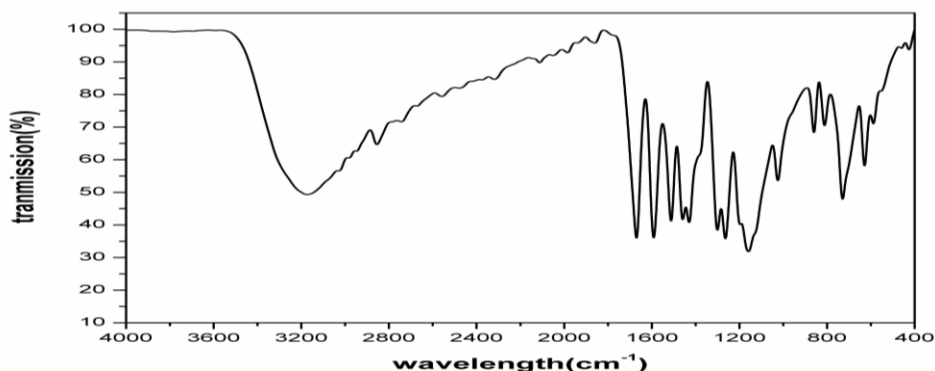


Fig. 2 FTIR spectrum of doped vanillin

Table 1: FTIR Assignments of Doped Vannilin

Peak (cm-1)	Assignment
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3558	O-H Stretching
3173	C-H Stretching
2955	C-H Stretching
2913	C-H Stretching
1649	C=O stretching
1610	C-O stretching
1520	C-O stretching
1511	C-C stretching
1458	C-C stretch (in ring)
1429	CH ₂ -CO deformation
1263	C-H ₂ in plane bending
1158	C-H in plane bending
859	CH ₂ out of plane wag
811	=C-H wag
728	=C-H bend
588	C-CO deformation

Optical Studies

The linear optical studies of the materials may be characterized by UV-Vis.-NIR analysis. The linear optical studies of the present compound dye doped vanillin crystals was recorded using Lamda35 model Perkin-Elmer double beam UV-Vis- NIR spectrophotometer in the wavelength between 110-1100 nm. In transmittance spectrum of the DV crystal, the transmittance occurred in the visible region exactly at 552 nm. Absence of absorption in the region between 560 and 960 nm, is shown in Fig. 3. From the UV-Visible-NIR Spectrum analysis, the Doped Vanillin single crystals are suitable for the NLO materials because near the infrared region there is no absorption. The NLO property of the grown single crystal DV were confirmed by the SHG analysis.

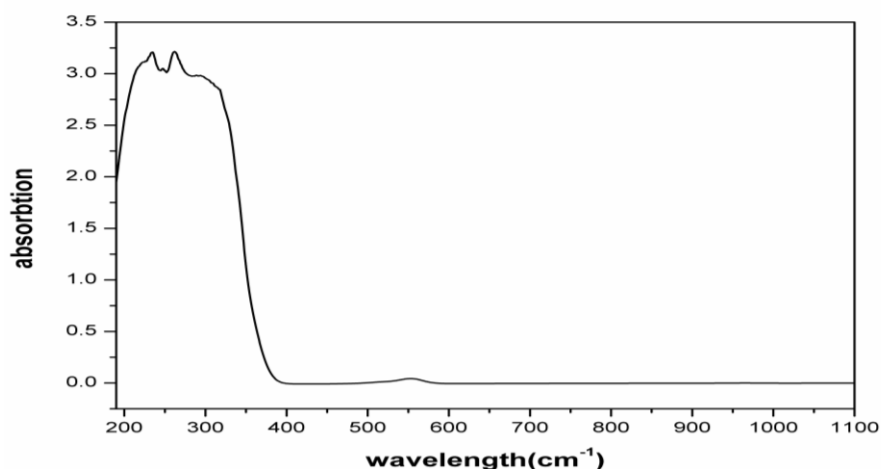


Fig. 3 UV-Visible spectrum of doped vanillin

SHG Efficiency Studies

The nonlinear optical properties of the grown crystals were identified by the second harmonic generation efficiency. The characterization studies of SHG efficiency of the grown crystal has been carried out using the modified experimental setup of Kurtz and Perry technique [18]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm, pulse width of 8 ns and with a repetition rate of 10 Hz was used. The confirmation of the generation of the second harmonics efficiency of the grown crystal by the emission of green light. The input energy applied to measure the SHG efficiency of the crystal is 0.70 joule and the output energy measured from the crystal is 5.87 milli Joule. The output energy of the reference sample KDP is 5.82 milli Joule. The SHG conversion efficiency of grown crystal DV is found to be about 1.1 times that of KDP.

Thermogravimetric Analysis

The thermal stability of the grown crystal was studied by the thermo gravimetric analysis (TGA) and DTA using Perkin Elmer Thermal Analysis Instrument and Netzsch Instrument. The TGA was carried out in nitrogen atmosphere at a heating rate of 5⁰ C/min in the temperature range of 50–800⁰C. The TGA curve area and DTA curves are shown in Fig.4. Thermal decomposition of DV crystal begins at 90⁰ C and ends at 220⁰ C. The grown crystal gets fully decomposed at 220⁰ C. A slight increment is observed in first stage of decomposition temperature of doped crystals, suggesting that Rhodamine B has modified the thermal stability of the crystals. A sharp endotherm at about 88.5⁰C for the grown crystal is due to the melting point of DV crystals. The second endothermic peak at 211.2⁰C. The melting point and the thermal stability of the doped crystals were found to be varying from pure vanillin crystals [15]. The changes in the parameters are due to the incorporation of Rhodamine B atoms into the lattice and it clearly indicates that these materials are suitable for NLO applications. The sharpness of this peak shows the good degree of crystallinity of the sample.

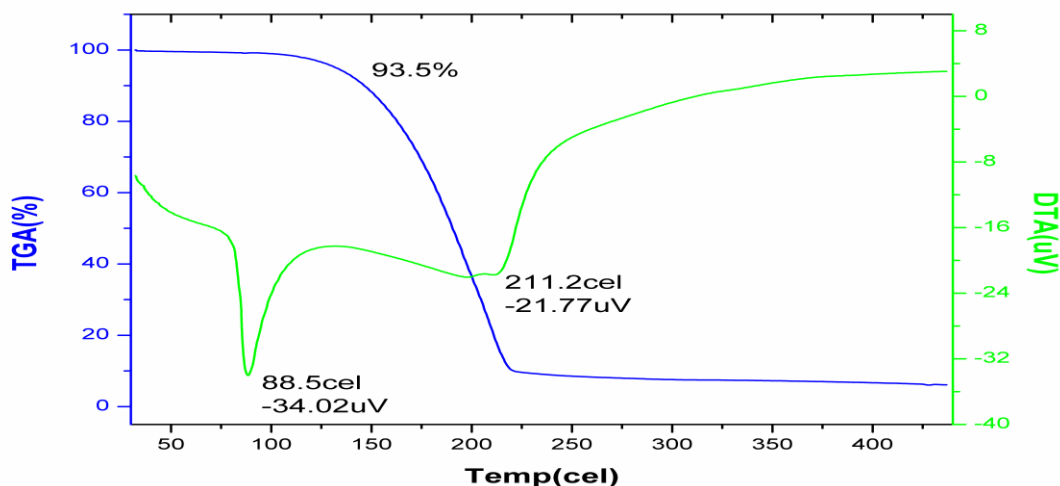


Fig. 4 TGA/DTA analysis of doped vanillin

Dielectric Studies

A study of the dielectric properties of solids gives information about the electric field distribution within the solid. The dielectric constant of a material is composed of four contributions, they are electronic, ionic, Orientation and space charge polarizations. All these are active at low frequencies. The nature of the variation of dielectric constant with frequencies indicates which contributions are present.

Dielectric permittivity and loss

The dielectric constant and dielectric loss were measured using the conventional parallel plate capacitor method using HIOKI 3532 -50 LCR meter in the frequency range of 50 Hz and 5MHz at various temperatures ranging from 323 to 373 K. The crystal sample was electroded on either side with graphite coating to make it behave like a parallel plate capacitor. The variation of dielectric constant and dielectric loss with frequency at different temperatures is shown in Figs. 5 and 6 respectively. The dielectric constant decreases very rapidly at low frequencies, and then slowly at higher frequencies. It also indicates that the value of dielectric constant increases with increase in temperature. The same trend is observed in the case of variation of dielectric loss with frequency at different temperatures. This is normal dielectric behavior that both dielectric constant and dielectric loss decrease with increase in frequency. This can be understood on the basis that the mechanism of polarization is similar to the conduction process [20,21]. Dielectric loss ($\tan \delta$) is the loss of energy that goes into heating a dielectric material in a varying electric field. The behavior of low dielectric loss with high frequency for the sample suggests that the crystal possess enhanced optical quality with lesser defects and this parameter plays a vital role for the fabrication of nonlinear optical devices [22,23].

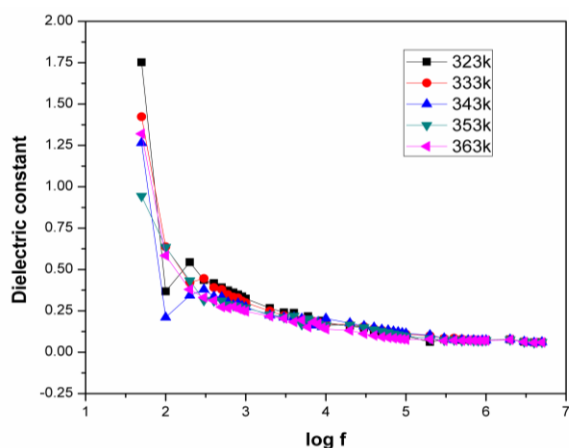


Fig. 5 Dielectric constant Vs log F of DV

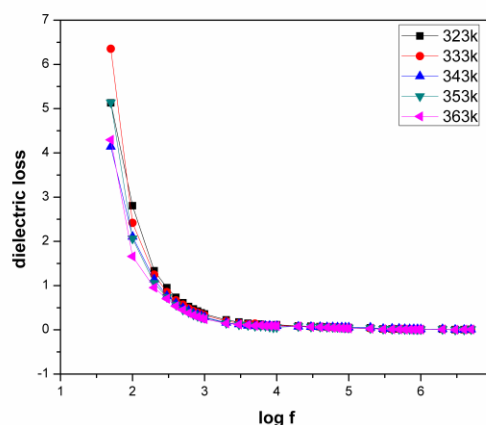


Fig. 6 Dielectric loss Vs log F of DV

A material must have low dissipation factor for device fabrication. It is observed that the dielectric loss decreases with increasing frequency. The larger values of dielectric loss at lower frequencies may be attributed to space charge polarization owing to charged lattice defects [24]. The very low dielectric loss reveals the very high purity of the crystals [25]. These curves suggest that dielectric loss is also strongly dependent on the frequency of the applied field.

Vicker's Microhardness Measurement

The microhardness characterization is extremely important as far as the fabrication of devices is concerned. Hardness of a material is a measure of the resistance it offers to local deformation. Vickers microhardness measurements of doped vanillin crystal were made using Leitz-Wetzlar microhardness tester fitted with a Vickers diamond pyramidal indenter. The measurements were made at room temperature and the indentation time was kept at 10 s. Microhardness value was taken as the average of the several impressions made.

The Vicker's hardness was calculated using the standard formula

$$H_v = 1.8544P/d^2 \quad \text{Kg/mm}^2$$

Where H_v is the Vickers hardness number in Kg/mm^2 , P is the applied load in Kg , d is the diagonal length in mm .

A graph plotted between hardness number (H_v) and applied load (P) as shown in Fig.7. From the graph it was observed that Vickers hardness number (H_v) increases with in increases load.

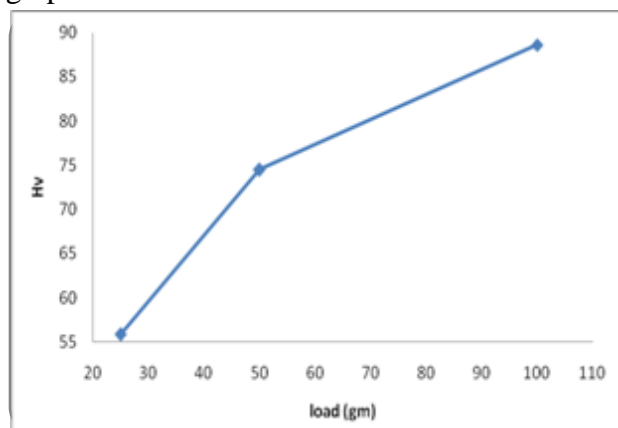


Fig. 7 Load vs Hardness of doped vanillin

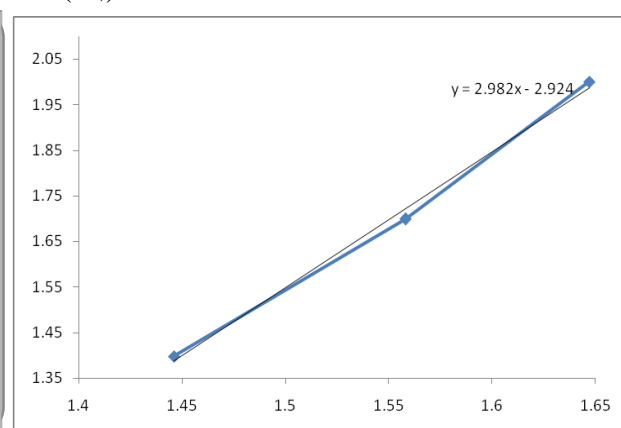


Fig. 8 log P vs log d of doped vanillin

It shows that hardness value increases rapidly with increase of load up to 50 g and beyond which it increases slowly. At low loads, the indenter penetrates only the top surface layers generating dislocations, which results in the increase of hardness in this region. The slow increase of hardness at higher loads can be attributed to the mutual interaction or rearrangement of dislocations [26].

Elastic Stiffness and Yield Strength

The microhardness value correlates with other mechanical properties namely yield strength (σ_y) and elastic stiffness constant (CII). Yield strength is a point at which material exceeds the elastic limit and will not return to its origin shape or length if the stress is removed. Yield strength is one of the important properties for device fabrication which can be calculated by the relation,

$$\sigma_y = H_v / 3$$

The elastic stiffness constant gives an idea about tightness of bonding between neighbor atoms and it was calculated using Wooster's empirical relation as [27-30]

$$C_{11} = H_v^{7/4}$$

The elastic stiffness constant and yield strength are tabulated in Table.2

Table 2: Elastic stiffness and Yield strength of DV

Load (P) g	Hv (kg/mm ²)	C ₁₁ (x10 ⁻³ M Pa)	σ _v (M Pa)
25	55.85	11.190	182.573
50	74.5	18.527	243.54
100	88.6	25.093	289.633

Meyer Index (n)

The materials are classified by the Meyer's index number. The Meyer's index number is calculated from the Mayer's law, which relates the load and indentation diagonal length.

$$P=kd^n$$

Where k is the material constant and n is the Mayer's index (or work-hardening coefficient). The above relation indicates that H_v should increase with the increase in P if $n > 2$ and decrease with P when $n < 2$. The ' n ' value is determined from the plot of $\log P$ vs. $\log d$, as shown in Fig.8. The slope of the plot of $\log P$ versus $\log d$ gives the work hardening index (n) and that is found to be 2.982. The material is confirmed as hard material with amount of mechanical strength which is better for device fabrications [31].

CONCLUSION

Rhodamine Doped Vanillin was grown by slow evaporation method. The unit cell dimensions of DV crystal were calculated from the single crystal XRD analysis. The functional groups presence in the crystals have been studied by FT-IR analysis. Its optical behavior has been assessed by UV-Vis. Spectroscopy. The thermal stability of the doped crystals has been confirmed by TGA and DTA studies. It is observed that DV crystal has 1.1 times relative SHG efficiency than that of KDP. The mechanical stability of the grown DV crystal has been confirmed by Vicker's hardness test, from the value of the hardening number (n) the crystal belongs to hard material.

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