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Multifunctional Characterization Of Oxalic Acid Crystal For Optical Applications Grown In Presence Of Nickel Nitrate

Sujata B. Bade, Atul Birajdar, Y. B. Rasal, S.S. Hussaini
Crystal Growth Laboratory, Department Of Physics, Milliya Arts, Science And Management Science College, Beed-431122, Maharashtra, India
Shri Chhatrapati Shivaji College Omerga, Dist. Dharashiv Maharashtra, India.

Abstract: -
The slow evaporation solution technique has been effectively employed to grow single crystals of oxalic acid, with dimensions reaching up to 15×8×6 mm³. A single crystal X-ray diffraction examination unveils the lattice parameters of the grown crystal. FTIR analyses the vibration modes of various molecular groups in the crystal. The presence of various functional groups was confirmed using FT-IR spectroscopy. UV-visible spectroscopy was employed to determine key optical parameters of the crystal in the range of 200-800 nm. A Second harmonic study was carried out for grown crystal by Kurtz's Perry Powder technique. The sample is also tested for antimicrobactarial properties. Optical absorption response is scrutinized through UV-visible, Photoluminescence, and NLO studies. Thermal studies indicate the crystal's stability up to 210 °C.

Keywords: *Organic Single Crystal; Nonlinear Optics; UV-visible; X-ray diffraction; PL*

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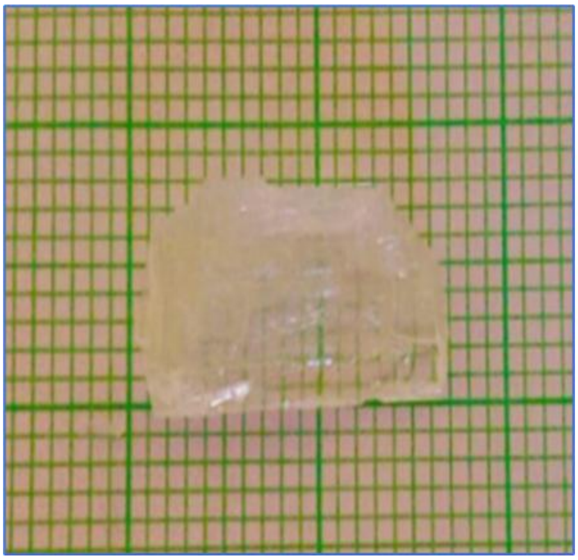
I. Introduction

Nonlinear optical materials have several applications such as frequency conversion, optical switching, light modulation, optical memory, and optical storage. Apart from their significant nonlinear optical (NLO) responsiveness, organic materials possess the benefit of providing a high level of synthetic flexibility for customizing their optical properties through structural modifications [1]. Photonics pertains to the utilization of photons for information and image processing and has been a prominent technology for the past three decades. Nonlinear optical processes within this field find diverse optical applications based on specific needs [2]. The widest advantage of working with organic material is that it allows tuning of chemical structures and properties for desired non-linear optical properties [3]. Numerous studies in the literature indicate that the optical properties of organic compounds can be enhanced through molecular engineering [4]. Also, Oxalic acid forms hydrogen bonds and stands out as the sole compound where two carboxyl groups are directly connected, making it one of the most potent organic acids. The incorporation of oxalic acid into ADP is anticipated to boost the crystal's nonlinearity [5]. Chithambaram et al. have observed the optical properties of urea and oxalic acid in the ratio 2:1 and they found the UV-cut-off wavelength at 240 nm. Oxalic acid is a carboxylic acid with two carboxyl groups. The arrangement of carboxyl groups can lead to a non-centrosymmetric crystal structure, promoting SHG. So, in this research, we have attempted to improve the optical enhancement of oxalic acid in the presence of nickel nitrate for applications in the optoelectronic field [6]. In this current study, single crystals of oxalic acid were grown in the presence of nickel nitrate and subsequently examined using techniques such as single crystal X-ray diffraction (XRD), Fourier-transform infrared (FTIR) studies, thermogravimetric analysis (TGA/DTA), UV-Vis spectral analysis, and second harmonic generation (SHG) studies.

II. Experimental Procedure

The analytical reagent grade oxalic acid salt was slowly dissolved in double distilled water within a beaker and placed on a magnetic stirrer for continuous stirring until supersaturation occurred. To investigate the impact of nickel nitrate on oxalic acid crystal formation, a measured amount of 1 mol of nickel nitrate salt was added to the filtered and homogeneous supersaturated oxalic acid solution. This mixture underwent stirring for 5 hours, followed by filtration using Whatman filter paper. The filtrate was then subjected to a consistent and gradual evaporation process at 35°C in a constant temperature bath. The crystals were collected within 20 days, presenting as colorless and transparent with dimensions reaching up to 15 x 8 x 6 mm³ in the beaker. The grown crystals of nickel nitrate added oxalic acid are depicted in Fig. 1.



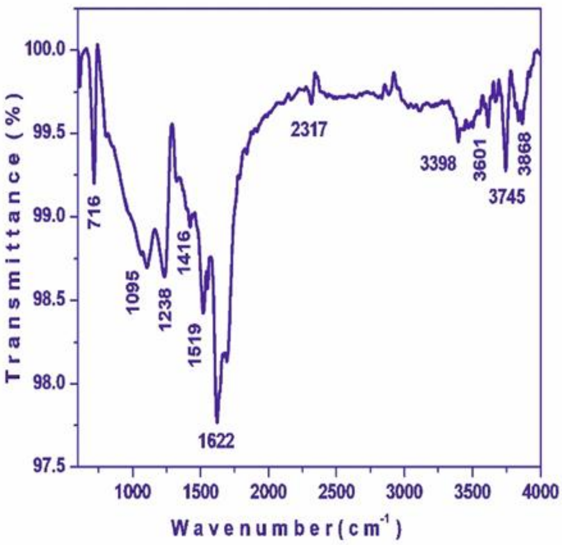


FIGURE 1. Photograph of oxalic acid-nickel nitrate crystal
FIGURE 2. FT-IR of subjected crystal

III. Results And Discussion

Single crystal X-ray diffraction analysis

The single-crystal X-ray diffraction method was employed for the characterization of the oxalic acid - nickel nitrate crystal, confirming its crystalline nature, using the Enraf Nonius CAD4-MV31 Bruker Kappa APEXII Bruker D8 Venture crystal X-ray diffractometer. The single crystal XRD analysis expresses the grown crystal belongs to the Monoclinic crystal system having cell parameters a=6.14 Å, b=3.61 Å, c=11.92 Å and $\alpha=90^0$, $\beta= 103^0$ and $\gamma=90^0$ with volume 264 $(Å)^3$.

Fourier-transform infrared spectroscopy (FTIR)

FTIR spectra were recorded to analyze the functional groups present in the oxalic acid nickel-nitrate crystal between the ranges of 500-4000 cm^{-1} with Bruker (ALPHA-T), as shown in Figure 2. The assignments of all wavenumbers corresponding to the transmittance are shown in Table 1.

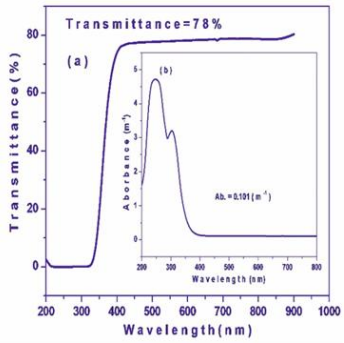
The wavenumber 716 cm^{-1} is assigned to NO_3 Bending in the transmittance spectrum. The bands 1095 cm^{-1} and 1101 cm^{-1} are assigned to C-O stretching. The peak 1230 cm^{-1} observed belongs to CH_2 wag and C-O stretching is observed at peak 1224 cm^{-1}. The assignments observed in the transmittance spectrum at 1513 cm^{-1} correspond to CH_2 deformation similarly wave number peak at 1616 cm^{-1} is assigned due to C=O stretching. The peak at 2317 cm^{-1} can be assigned to C-H stretching. The bands 3385 cm^{-1} and 3610 cm^{-1} were assigned to the O-H stretching of the grown crystal [7].

TABLE 1. Observed IR frequencies (cm^{-1}) of oxalic acid nickel-nitrate crystal

Grown Crystal	Assignment
3745	OH str.
3610	O-H stretching
3385	O-H stretching
2317	C-H stretching
1616	C=O stretching
1513 1224	CH_2 def. C-O stretching
1230 1101	CH_2 wag C-O stretching
1095	C-O stretching
716	NO_3 Bending

UV-visible studies

UV-Vis spectroscopy is an analytical method that assesses the number of distinct wavelengths of UV or visible light absorbed or transmitted through a sample. The optical transmission spectrum of oxalic acid-nickel nitrate crystal single crystals was recorded in the range of 200 nm to 900 nm using an Avaspec-ULSi2048L spectrophotometer. Figure 3(a) shows the linear optical transmission spectrum of oxalic acid-nickel nitrate crystal and observed transmittance of 78 % in the entire visible spectrum and the lower cut-off wavelength found to be 315 nm which shows the grown crystal may have applications in NLO, frequency conversion devices [8]. The absorption of light in the UV-visible region is typically associated with electronic transitions involving the movement of electrons between different energy levels. The nickel compounds often exhibit absorption in the UV and visible regions due to transitions involving the 3d orbitals of the nickel ions. The presence of the d orbitals allows transition metal ions to form coordination complexes with ligands. In the case of nickel nitrate, the nitrate NO_3 ions act as ligands coordinating with the nickel ions. The interactions between the d orbitals of the transition metal ion and the orbitals of the ligands can influence the overall electronic structure and properties of the compound.



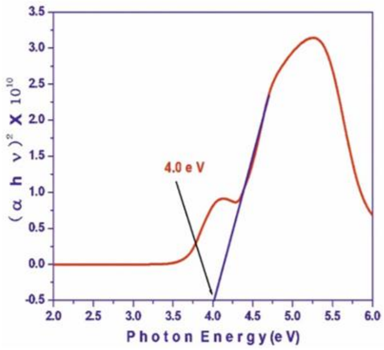
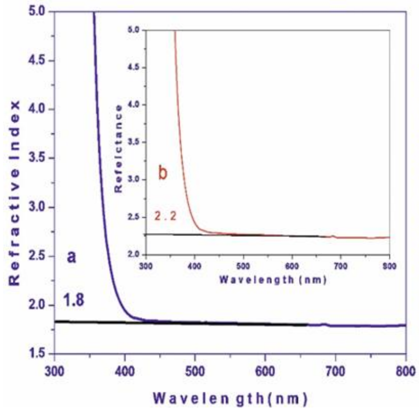


FIGURE 3. (a) Transmittance spectrum
(b) Absorbance Spectrum
FIGURE 4. (□h□□□□vs. photon energy (hν)

It is also observed in the transmittance spectrum as a sharp fall near 315 nm which is expressed due to strong n to π* transition associated with nitro chromophore of nickel nitrate [9]. Also, in Figure 3 (b) absorbance spectrum shows that the crystal has a lower absorbance value, which is a good sign for the applications of crystal in antireflection phenomenon in different areas. Figure 4 shows band gap energy of the grown crystal is 4.0 eV which has applications in optoelectronic devices [10]. It is higher than that of reported bis thiourea lithium potassium sulphate [11], benzylidene malononitrile [12], and LAAN and doped Zn, Cu, and Mg crystals [13]. The formula used to calculate the optical absorption coefficient (α) is $\alpha = [2.303 \log (1/T)]/t$, where T is the Transmittance value and t is the thickness of the grown crystal used for UV visible spectral study. The refractive index and reflectance were derived by formulas $n = [1/T + (1/T - 1)]$ and $R = (n-1)^2/ (n+1)^2$ respectively depicted in Figure 5(a) and (b) respectively. The value of the Refractive index and the reflectance of the subjected crystal is found to be 1.8 and 2.2 respectively in the entire visible spectrum. The extinction coefficient optical conductivity as a function of photon energy was calculated by equations $K= \lambda\alpha/2\pi$ and□□□p□□□□nc□□□□ where c is the velocity of light, □is depicted in figure 6(a) and (b). The value of real and imaginary susceptibilities has been calculated using the fundamental equations and plotted in graphs 7(a) and (b). From cumulative UV-visible study, it is concluded that in the entire visible region, higher value of transmittance, lower value of refractive index, and reflectance of a grown crystal are advantageous in applications of antireflection coating in solar thermal devices. The lower value of extinction coefficient and the high value of optical conductivity of grown crystal is better for frequency conversion photonic devices. The prospective optical characteristics of the developed crystal indicate its appropriateness for effective use in optical limiting, nonlinear optics (NLO), and various device applications [14].



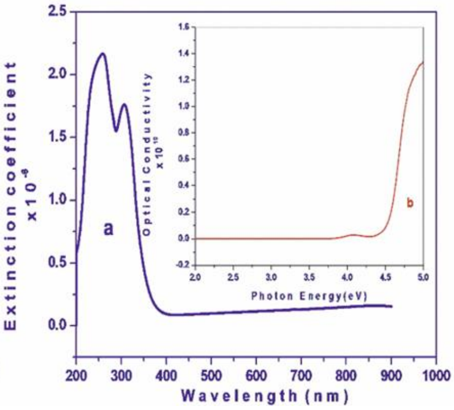
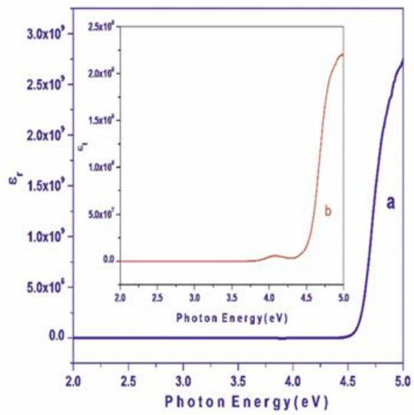


FIGURE 5. (a) Refractive index
(b) Reflectance vs. wavelength.

FIGURE 6. (a) Extinction coefficient vs. wavelength,
(b) Optical conductivity vs. E



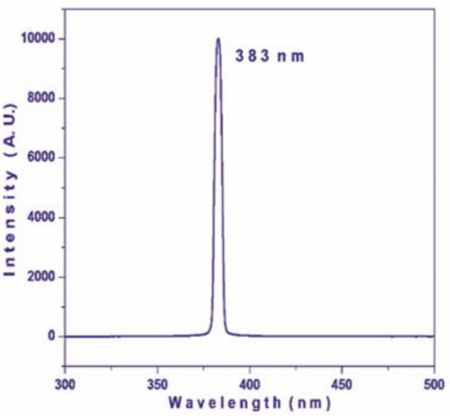
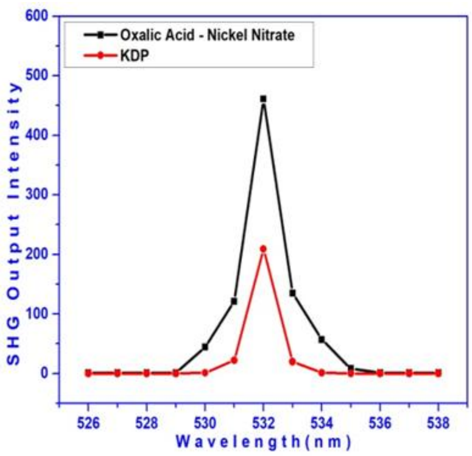


FIGURE 7. (a) Real and vs. E **(b)** Imaginary dielectric constant vs. E

FIGURE 8. PL response

Photoluminescence studies (PL)

Hitachi FL-7000 spectrophotometer was a crucial tool for capturing the photoluminescence spectrum of the subjected crystal under investigation. The photomultiplier tube played a pivotal role in detecting the output signal with precision. During the experimentation, both emission and excitation slit widths were set at 2.5 nm and the response time was maintained at 0.1 seconds. The recorded emission spectrum, presented in Figure 8 spanned the range of 300 to 500 nm. A distinctive nano-wide peak emerged notably between 378 nm and 386 nm, with the highest prominently observed at 383 nm. This conspicuous peak signifies the presence of violet emission in the oxalic acid-nickel nitrate crystal, offering valuable insights into its photo luminescent properties. These findings contribute to a deeper understanding of the crystal's behavior and pave the way for potential applications in diverse research domains [15].



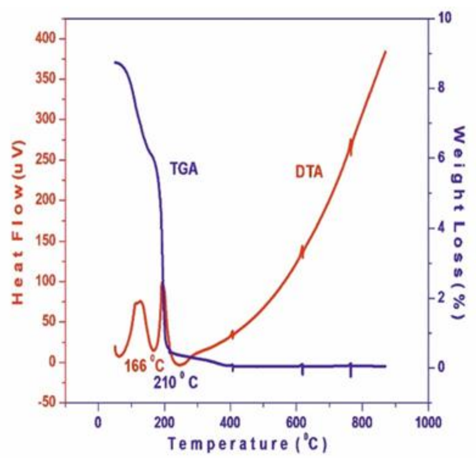


FIGURE 9. Plot of SHG output intensity

FIGURE 10. TGA/DTA Analysis

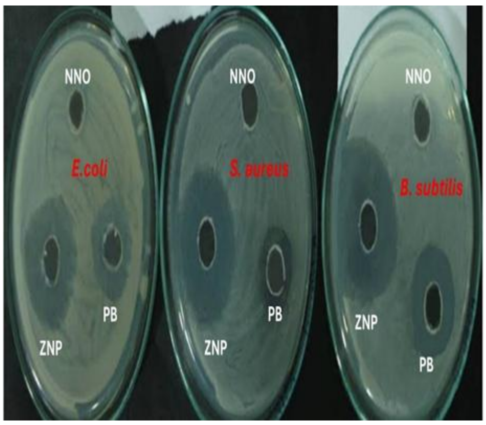


FIGURE 11. Antibacterial and antifungal activities of NNO crystal

Second harmonic generation

Second harmonic generation is a coherent optical process of radiation of dipoles in the material, dependent on the second term of the expansion of polarization. In the present analysis, the 1064 nm Nd: YAG laser has been used which operates in a Q-switched mode having a pulse width of 6 ns and repetition rate of 10 Hz. The recorded SHG output response of oxalic acid-nickel nitrate crystal material is shown in Figure 9. It is to be mentioned here that oxalic acid crystals exhibit centrosymmetry, leading to the absence of second harmonic emission. However, when oxalic acid nickel-nitrate crystal, introducing this dopant induces a deviation from centrosymmetry, resulting in the manifestation of second harmonic emission. This phenomenon is attributed to the enhanced polarizability of the molecule, underscoring the crucial role of molecular properties in dictating the nonlinear optical behavior of the crystal. Carboxyl groups contain polar C=O bonds, which contribute to the overall polarizability of the molecule. Higher polarizability enhances the response to an applied electric field, which is fundamental for SHG. Conjugation of double bonds and resonance within a molecule can affect its electronic structure. For the enhancement of second harmonic generation, the d orbitals may play a role in creating a suitable electronic environment for efficient SHG.

The transition metal ions contribute to the overall polarizability and electronic structure of the material, influencing its nonlinear optical properties. The measured SHG output intensities for 1 mol % oxalic acid-nickel nitrate crystal and KDP were 461 and 209 respectively at 532 nm wavelength. It reveals that the oxalic acid-nickel nitrate crystal is 2.2 times more efficient as compared to the KDP crystal. Thus, the grown crystal is as a potential candidate for designing laser frequency conversion and electro-optic devices [16].

Thermogravimetric analysis (TGA/DTA)

Thermogravimetric analysis or thermal gravimetric analysis is a method of thermal analysis in which the mass of a sample is measured over time as the temperature changes. The TGA and DTA of the grown crystal were carried out using the Perkin Elmer STA 6000 thermogravimetric analyzer in a nitrogen atmosphere at a heating rate of 25 (°C)/min. The TGA/DTA trace of the grown crystal is shown in Figure 10. The bulk weight loss of the sample is observed at 210 ^{0}C which indicates the decomposition of volatile components of the material. Further, the DTA curve confirms the decomposition endothermic peaks were observed at 225 ^{o}C and 120 ^{o}C. The major and sharp endothermic peak in the DTA curve at 210 ^{o}C confirms the melting point of the grown crystal. Thus, the grown crystal is suitable up to 210 ^{0}C for device applications [17].

TABLE 2. Result of antimicrobial activity

No	Sample	Zone of inhibition of growth(mm)		
1	NNO	E. coli	B. subtilis	S. aureus
2	Result	Nil	Nil	Nil

Antimicrobial activity

Some NLO crystal behaves as antimicrobactarial properties particularly specific organic molecules or some doped with certain ion, can be behave as antimicrobial properties and this crystal can be characterized for their NLO and antimicrobial activity, potentially leading to their use in biomedical applications as reflected in figure the antibacterial and antifungal activities of NNO crystal along with other two crystals is the absent of bacterial growth is indicated by clear wells as shown in figure 11.

The samples of oxalic acid insisted nickel-nitrate were subjected to antimicrobial activity assay also to test cultures of E. coli, B. subtills and S. aureus were used. The results of test were reflected in the Table 2. The test cultures and NNO was not antimicrobial in nature against the test cultures [18].

IV. Conclusions

Oxalic acid single crystals were effectively grown using the slow evaporation solution method at ambient temperature. The lattice parameters of the grown crystal were determined through a single-crystal X-ray diffraction study. The incorporation of nickel nitrate in oxalic acid crystal has been identified by FT-IR spectral analysis. The augmentation in the second-order nonlinear optical (NLO) response was validated using the Kurtz-Perry powder technique suggesting 2.2 times more efficient as compared to the KDP crystal. The test cultures and NNO was not antimicrobial in nature against the test cultures. The optical absorption response of nickel nitrate-oxalic acid was analyzed through UV-visible, Photoluminescence, and NLO studies and has applications in NLO and antireflection coating in solar thermal devices.

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