

Synthesis, growth, spectral and thermal studies of Acenaphthene Oxalic Acid (ANO) Organic NLO Crystals

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Abstract

Single crystals of nonlinear optical material Acenaphthene Oxalic acid (ANO) have been grown successfully by the slow evaporation solution growth technique. To begin with, solubility tests were carried out for two solvents such as acetone and chloroform-water. Among the two solvents, the solubility of ANO was found to be the highest in chloroform-water, so crystallization of ANO was done from its aqueous solution. The elemental percentage of the material was carried out CHN analysis. The crystalline nature of ANO crystal was confirmed by the powder X-ray diffraction study and diffraction peaks were indexed. Vibration modes of the functional groups were recognized and studied by recording a FTIR spectrum. The optical transparency range and absorption has been studied throughout UV-Vis-NIR spectroscopy. The second harmonic generation efficiency of the grown ANO crystal has been obtained by the Kurtz-Perry powder technique. The grown crystals were subjected to TG/DTA analysis. The dielectric activities of the title compound crystal was investigated and measuring the dielectric loss and dielectric constant properties. The photoluminescence spectrum was also studied.

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1. Introduction

Organic nonlinear optical materials are amongst the most technologically important materials in existence today due to their intriguing physical and optical properties such as large electro-optic coefficient, small dielectric constant, etc. and their wide range of applications in various attractive and emerging technologies including non-linear optics (NLO), electro-optic modulation (EOM), optical communication, Terahertz (THz) wave generation as well as detection [1-4]. Many investigations are being carried out to synthesize such materials. Organic materials are much promising candidate for all such nonlinear behaviors. One of the advantages in working with organic materials is that they permit one to fine tune the chemical structure of the material to get the desired nonlinear effect [5]. Acenaphthene oxalic acid (ANO) has been chosen to study as a potential material for non-linear optics because of its non-centrosymmetry structure. Some new nonlinear optical crystals of noncentrosymmetric structures based on

hydrogen bond interactions were recently discovered [6-9]. In this present work, we report the growth, crystalline nature by powder X-ray diffractometry (PXRD), optical, thermal, electrical and non linear optical studies on ANO single crystals and the results are discussed in detail. All the relevant characteristic studies were performed for grown crystals and compared with pure acenaphthene (ANP).

2. Experimental Method

2.1. Solubility Studies

The prismatic growth of the organic crystals is attributed to the selection of the suitable solvents. Solvents offering moderate solubility temperature gradient will be chosen for growing good quality optical crystals. The different solvents were used to identify the appropriated solvent for the growth of ANO crystals. The solvents Chloroform-Water 1:1 mixture and Acetone were used to study the solubility of the selected compounds. It is found that the solubility of ANO in chloroform-water 1:1 is higher than that of Acetone. Solubility curves for these solvents are shown in Fig 1. From the result of the graph the Chloroform- water 1:1 mixture was selected for the growth of the ANO crystals.

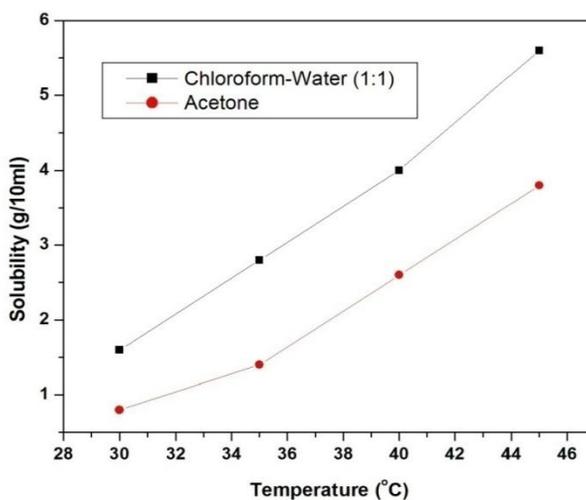
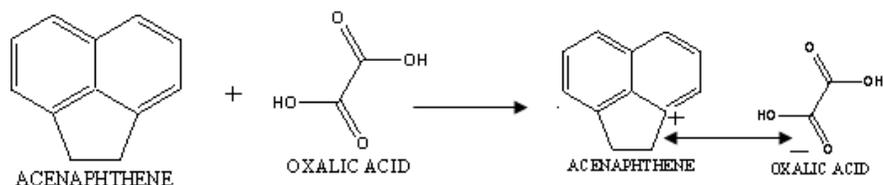


Fig. 1 Solubility curves of ANO crystals

2.2. Synthesis

ANO was synthesized from acenaphthene and oxalic acid which taken in the ratio of (1:1). The scheme.1 shows the reaction involved in material synthesis. The two reactants were prepared separately in chloroform and water and then mixed together. The resulting solution was stirred well for about one hour using a magnetic stirrer to ensure homogeneous solution. The stirred solution was filtered off using whatmann filter paper. The filtered solution was transferred to crystal growth vessels followed by slow evaporation at room temperature. Good transparent crystals were obtained in a period of 10 days. The photograph of as grown crystals of ANO is shown in Fig.2.



Scheme 1. The reaction involved in material synthesis

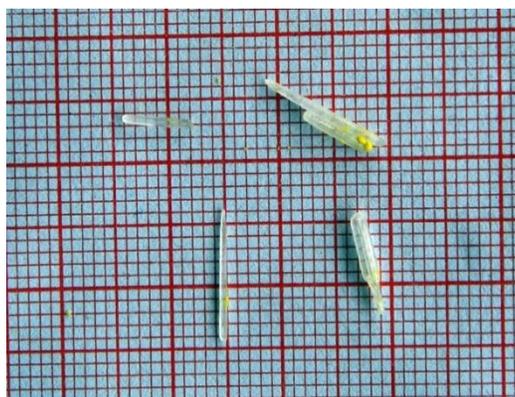


Fig. 2 Photograph of grown ANO single crystals

2.3 Characterization

X-ray powder diffraction data for the ANO (acenaphthene oxalic acid) was taken by Bruker AXS D8 Advance Powder diffracting system of X-ray Radiation of wavelength 1.54059 \AA in the range 2θ which is scanned from 5° - 80° at room temperature. Fourier transform infrared spectrum (FTIR) of ANO crystal was recorded in the range of 4000 - 400 cm^{-1} employing a Perkin- Elmer spectrometer using KBr pellet technique. The UV-visible absorption and transmittance spectrum of ANO crystal was recorded using SYSTRONICS DOUBLE BEAM UV-Vis spectrophotometer in the wavelength range 200 - 1200 nm . The dielectric study of grown ANO single crystal was carried out using 3532 - 50 HIOKI LCR meter. The dimensions of the used samples were $9 \times 9 \times 2 \text{ mm}^3$. To find out the melting point and phase transition of ANO, TG/DTA studies were performed with SDT Q600 V8.2 analyzer. Direct band gap energy was calculated from photoluminescence studies. Elemental composition percentage presents in ANO were done using Elementer vario EL III. The powder second harmonic generation output of the sample was measured by Nd-YAG laser.

3. Results and Discussion

3.1 Elemental Analysis

The chemical composition of the constituent elements presents in ANO was verified through elemental analysis. The results of the theoretical and experimental elemental percentages are depicted in the table 1. The measured data are having good agreement with the theoretical values which indicate the presence of ANO crystal.

Table 1 Elemental analysis for ANO chemical composition

Element	Experimental value (%)	Theoretical value (%)
C	67.12	68.85
H	6.47	4.95

3.2 X-Ray Diffraction Studies

The recorded powder X-ray diffraction spectrum of ANO is shown in Fig (3a) and the reported XRD spectrum of acenaphthene (ANP) [10] is shown in Fig (3b). The experimental values of 2θ and d of ANO were obtained from powder XRD spectrum and are compared with previous literature of acenaphthene and are tabulated in table 2. The values of 2θ and d of ANO are having good agreement with that of acenaphthene and with some additional peaks.

Table 2. Powder XRD spectrum of ANO and ANP

2θ	ANO (h k l)	ANP (h k l)
13	1 2 1	1 2 1
18	0 2 1	0 2 1
22	1 1 2	-----
25	0 4 2	0 4 2
29	3 2 1	3 2 1

The additional peak at 2θ (22°) confirms that the grown crystals are ANO. The sharp peaks and full-width at half maximum (FWHM) values confirms the crystallinity of the grown crystal is good.

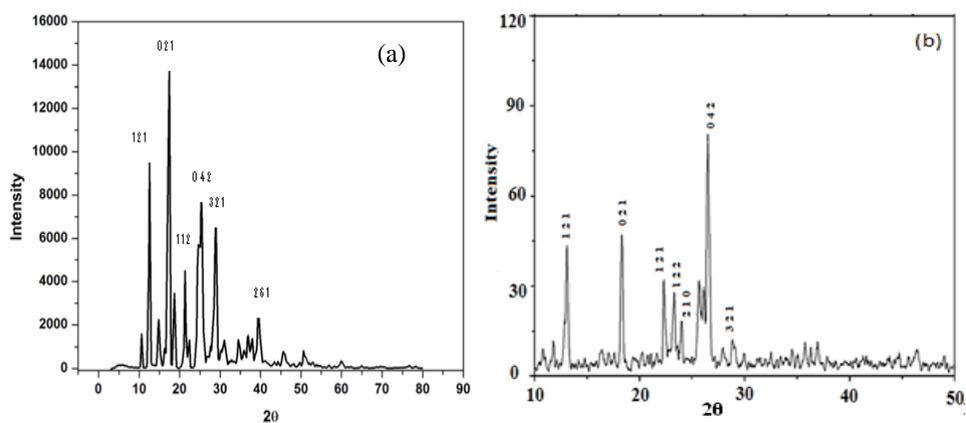


Fig. 3 X-Ray powder diffracton of (a) ANO and (b) ANP crystal

From XRD spectral data, the microscopic structural parameters grain size (D), dislocation density (δ) and strain (ϵ) values were calculated. For the prominent peak ($2\theta = 17.372$), the grain size (D), dislocation density (δ) and strain (ϵ) are calculated and are tabulated in table.3.

Table 3. Shows Structure of parameters value

Structural parameters	Value
Grain size (D)	22.74 nm
Dislocation density (δ)	19.40×10^{13} lines/m ²
Strain (ϵ)	1.59×10^{-3}

3.3 Fourier Transform Infrared Spectral Analysis

FTIR spectra of ANO and that of pure ANP [11] are depicted in Fig (4a) and Fig (4b) respectively. In the case of ANP having aromatic ring show band in this region of the FTIR spectrum. But ANO spectrum shows the broad absorption band this may be due to CH stretching vibration. The CH₂ stretching vibration is observed at 2300 cm⁻¹. C-C stretching modes are observed from 1700 to 1680 cm⁻¹ for both molecules ANO and ANP are in good agreement with the general appearance of C-C stretching modes. The Naphthalene ring wagging starts below 1250 cm⁻¹ in case of ANP and 1129 cm⁻¹ in case of ANO.

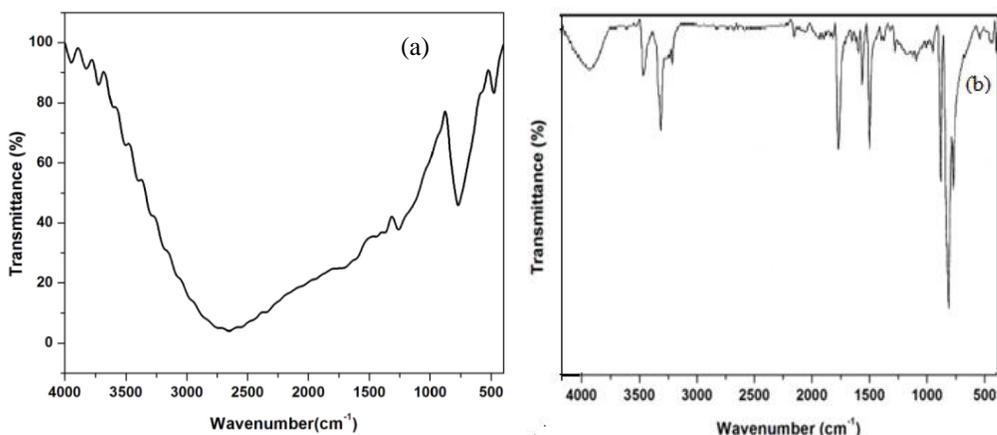


Fig.4 FTIR spectrum of (a) ANO crystal and (b) ANP crystal

The modes appearing 750 cm⁻¹ are scribed to skeletal out of plane deformations or the torsional modes. Although this spectrum also carries similar features of that of ANP, there is distinct evidence for presence of Oxalic in the single crystals of ANO. The frequency assignments for ANO and ANP with various functional groups are presented in table 4.

Table 4 FT-IR spectral data of ANO and ANP

<i>ANP (Reported) in cm⁻¹</i>	<i>Experimental ANO in cm⁻¹</i>	<i>Assignments of dominant modes</i>
2920	2700	C-H stretching vibration
—	2300	CH ₂ stretching vibration
1601	1700	C-C stretching vibration
1601	1680	
938	1250	CH out plane N _p ring Wagging

745	750	Skeletal out of plane or torsional modes deformation
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3.4 UV-visible Spectrum

3.4.1 Absorption Spectrum

The electronic absorption spectrum of the ANO crystal is depicted in Fig 5. The absorption band appear at 270 nm is due to the charge transfer transition in the compound. There is no significant absorption in the range 320-1100 nm, which provides the wide transparency window for the grown crystals. UV-visible spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves the promotion of the electron from the ground state to higher energy states. The spectrum reveals that the absorption bands attributed to the charge transfer transition and appears around 250 nm. This is attributed to the promotion of an electron from the highest occupied orbital of oxalic acid to the lowest unoccupied molecular orbital of acenaphthene. This confirms the formation of charge transfer molecular complex.

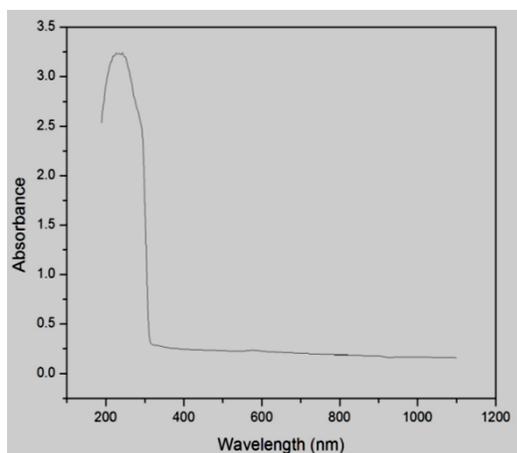


Fig. 5 UV- visible absorption spectrum of the ANO crystal

3.4.2 Transmission Spectrum

The spectrum of ANO and that of pure ANP are shown in Fig 6a and 6b respectively. The ANP crystal was transparent from 320 nm, in the case of grown ANO crystal the transparency starts at 300 nm with above 50% and beyond 400 nm it reaches above 70% transparency. The blue-shift occurs compared to the transmission spectrum of ANP reveal that the strong interaction between $H_2C_2O_4$ and acenaphthene in the sample. The dip at 540 nm is due to the absorption of energy in the green region. This reveals that the grown ANO crystals are promising candidate for NLO activity. There is no distortion was observed in the transmittance spectrum, which indicates the good optical quality and the suitability of the crystal for second harmonic generation and various optical applications [12].

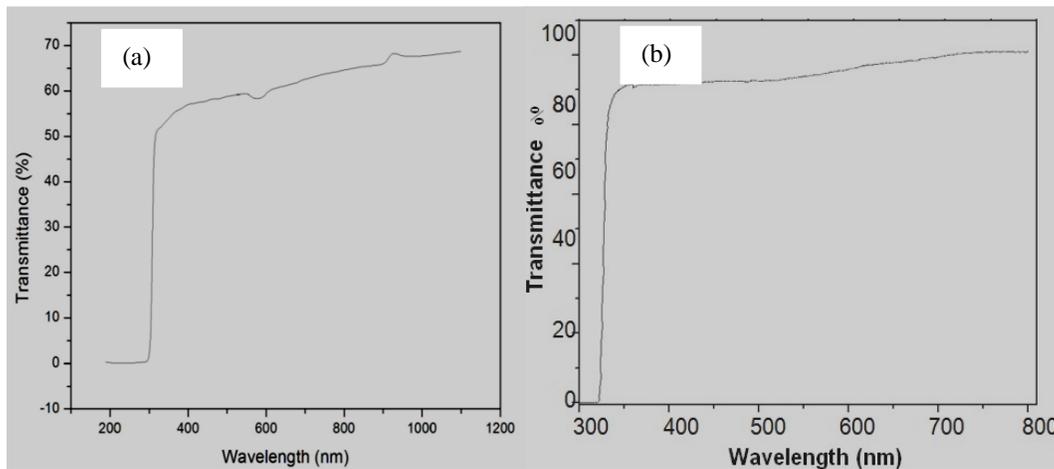


Fig. 6 UV-visible transmission spectrum of (a) ANO and (b) ANP crystal

3.5 Second Harmonic Generation

The SHG property of as grown ANO crystals was determined using the powder technique developed Kurtz and Perry [13]. In this method, powdered sample of randomly oriented crystallite particles were tightly packed in a micro-capillary tube. The sample was then subjected to the output of Q-switched Nd:YAG laser emitting a wavelength of 1064 nm with power 2.1 mJ/P. The laser beam was well focused on the sample and the output signal of wavelength 532 nm was generated. This reduction in wavelength of input radiation by half confirms the second harmonic generation property. The green light intensity was registered by a photomultiplier tube and converted into an electrical signal. The signal was then displayed on the oscilloscope screen. The SHG conversion efficiency was computed by the ratio of signal amplitude of the ANO sample to that of KDP signal amplitude recorded for the same input power. The SHG efficiency for pure Acenaphthene was only about 19 mV which is almost equal to that of KDP 18mV. The SHG efficiency of grown ANO crystal (80 mV), which is four and half times more than that of KDP (18 mV), for the input power 2.1 mJ/P. The enhancement of SHG efficiency in ANO is may be due to the addition of oxalic acid with acenaphthene. Hence, it is promising candidate for NLO application.

Table 5. Comparison of SHG Signal Energy Output

Input power mJ/ pulse	KDP (mV)	ANP (mV)	ANO (mV)
2.1	18	19	80

3.6 Dielectric Studies

Cut and polished samples of dimensions 9x9x2 mm³ were used for dielectric measurement. Two opposite surfaces across the breadth of the sample were treated with good quality silver paste in order to obtain good ohmic contact. Using LCR meter, the capacitance of the crystal was measured for the frequency range 52-200 KHz at various temperatures. Fig.7 shows the plot of dielectric constant (ϵ_r) versus frequencies for temperature 303K, 323K, 343K, 363K. The dielectric constant of the crystal was calculated using the relation

$$\epsilon_r = C_{\text{crys}}d/\epsilon_0A$$

where, C_{crys} is the capacitance of the crystal, d is the thickness, ϵ_0 is free space permittivity and A is the area of the crystalline sample used. The dielectric constant has higher values in the lower frequency region and then it decreases with increasing frequency. The very high values of dielectric constant at low frequencies may be due to the presence of space charge, orientation, electronic, and ionic polarizations. The low value of dielectric constant at higher frequencies may be due to the loss of significance of these polarizations gradually. At high frequency, the defects no longer have enough time to rearrange in response to the applied voltage; hence the capacitance decreases [14]. In accordance with Miller rule, the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient [15]. The variation of dielectric loss with frequency is shown in Fig 8. The dielectric loss of the crystal was measured for the frequency range 100Hz-200MHz. The characteristic of low dielectric loss at high frequencies for a given sample suggested that the sample possesses enhanced optical quality with lesser defects and this parameter plays a vital role for the fabrication of nonlinear optical devices [16].

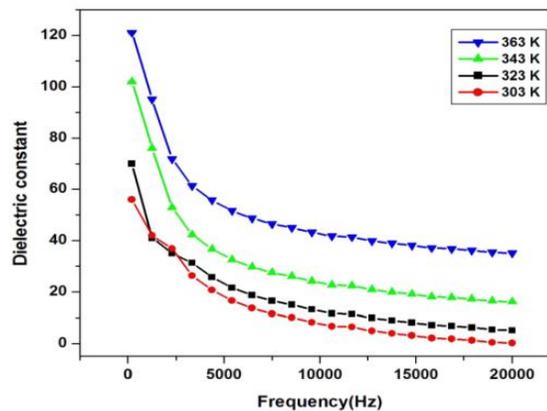


Fig. 7 The plot of dielectric constant vs. frequency of ANO crystal

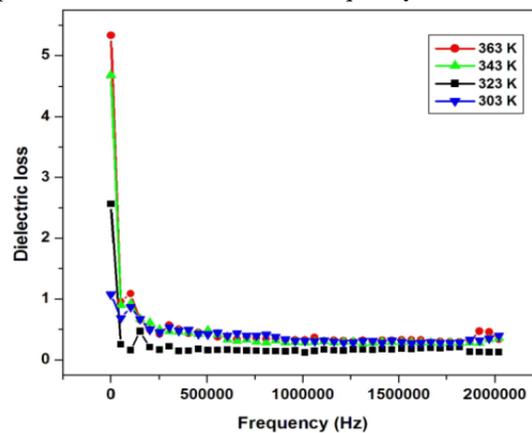


Fig. 8 The plot of dielectric loss vs. frequency of ANO crystal

3.7 Thermal Analysis

The thermo gravimetric spectrum of ANO crystal was recorded between 30⁰C and 1000⁰C at heating rate of 10⁰C/min in nitrogen gas atmosphere. Fig 9a and 9b illustrate the TGA and DTA curves for the grown crystals of

ANO and pure ANP. ANO crystals are thermally stable up to 76.15^oC and decomposition starts only at 76^oC. ANO spectrum indicates that there are two stage weight losses, one is at 76^oC and another is at 168^oC, where as ANP shows only one stage weight loss. A major loss (99%) occurs between 76^oC and 200^oC and 0.01% is obtained as residue. The DTA curve shows endothermic peak at 126^oC corresponds to melting point. The sharpness of endothermic peak shows good degree of crystallinity and purity of the sample. Above the melting point only gradual weight loss is observed as the temperature is increased.

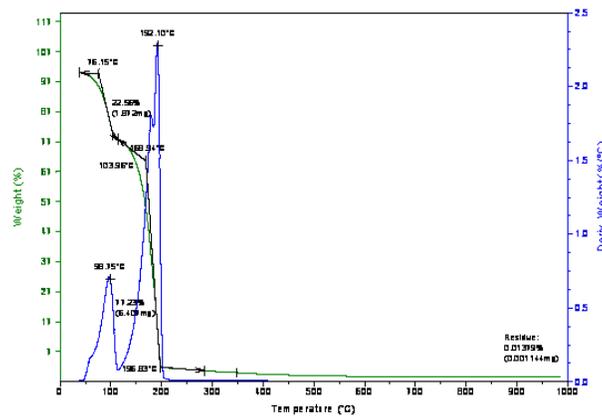
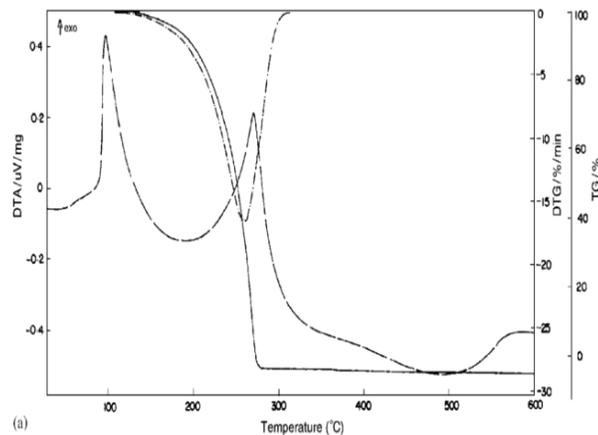


Fig.9a TGA and DTA curves of grown ANO crystal

Fig. 9b TGA and DTA curves of ANP crystal



3.8 Photoluminescence

The intensity and spectral content of photoluminescence (PL) is a direct measure of various important material properties like band gap determination, impurity levels and defect detection, recombination mechanisms and material quality. Emission spectrum gives the luminescence intensity as a function of wavelength while the wavelength of the exciting radiation is kept constant. Emission spectra yields information about the position of activator levels. Fig 10 shows the emission spectrum of ANO crystal. Photoluminescence spectrum has been recorded at room temperature with an excitation wavelength of 440nm for the sample. A strong and broad band is

occur at 440nm and this indicate that the material exhibit blue fluorescence. A small peak is observed at 575nm and this indicates that green fluorescence is present. Emission is associated with defects emerging during the growth of crystallites and one related to deformation of crystallinity due to dislocations and vacancies. The band gap energy (E_g) is calculated from the formula

$$E_g = h\nu$$

where, $\nu = c/\lambda$, λ is the wavelength, C is the velocity of light (3×10^8 m/s) and h is the planks constant 6.634×10^{-34} Js. The calculated band gap energy value is $E_g = 2.82$ Ev

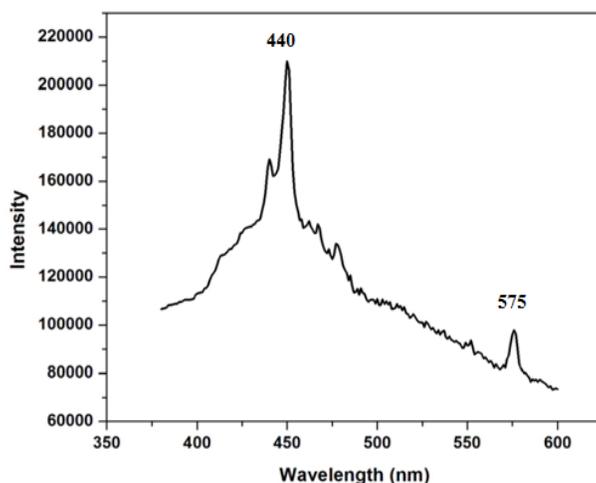


Fig. 10 Photoluminescence spectra of ANO crystal

4. Conclusion

The nonlinear optical ANO single crystals were synthesized and grown by slow evaporation technique at room temperature and compared with reported ANP crystal studies. In X-ray diffraction pattern, the well defined Bragg's peak at specific 2θ values confirms the crystallinity of the grown crystals, the additional peak around 22° confirms the addition of oxalic acid with ANP. The microscopic structural parameters were calculated for prominent peak values. The FTIR spectra illustrated that the presence of characteristic absorption bands are due to the presence of various functional groups in grown NLO crystal. The additional modes of vibrations in FTIR spectrum reveals that the introduction of oxalic acid in the acenaphthene molecular structure. UV-Vis absorption analysis reveals the electron transition around wavelength 270 nm which confirms the formation of charge transfer in grown crystal. The extended transparency beyond 300 nm says that ANO having better transparency than acenaphthene, which is the desired property for various NLO applications. SHG efficiency of grown ANO crystal (80 mV) was found to be 4.5 times greater than that of KDP (18 mV) and ANP (19 mV). The enhancement of SHG efficiency in ANO is due to the addition of oxalic acid with acenaphthene. Low value of dielectric loss at high frequencies for grown crystals suggests that the grown crystals possess good optical quality. TG/DTA curves of ANO indicated that melting point of ANO is 76.15°C . Photoluminescence spectra revealed both blue and green fluorescence emission. The chemical

composition in ANO was verified through elemental analysis.

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