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Highlights

- ASOX crystallizes in triclinic structure with non-centro symmetric space group P_1 .
- Frequency conversion efficiency was found to be 68% that of inorganic KDP.
- Absorption spectrum reveals wide transparency of ASOX in UV-Vis-NIR region.
- The LDT energy density value was found to be greater than inorganic KDP.
- Thermal and mechanical study confirms the adequate stability of ASOX.

Studies on a novel organic NLO single crystal:

L-asparaginium Oxalate

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ABSTRACT

A new organic nonlinear optical (NLO) material, L-asparaginium Oxalate (ASOX) was synthesized and single crystals of ASOX with dimension (10*5*5) mm³ was grown from aqueous solution by slow evaporation solution growth technique. Single crystal XRD data reveals that ASOX belongs to triclinic crystallographic system with non-centrosymmetric space group P1. The grown organic NLO crystal was subjected to various characterizations like PXRD, FT-IR analysis, thermal studies, micro hardness test and optical studies for identifying the transparency range and the emission spectrum. The laser damage threshold value was found to be 2.04GW/cm². The second harmonic efficiency of the grown crystal was examined using Kurtz Perry powder technique and it was found to be 68% that of KDP. Hence it can be effectively employed for various optoelectronic and photonic applications.

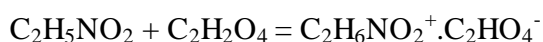
1. INTRODUCTION

Non-linear optical materials have gained wide exposure in recent years due to their potential applications in the era of optoelectronics and photonic technologies. Currently, the most thoroughly studied third order non-linear optical (NLO) materials are inorganic oxides, semiconductors, conjugated organic polymers, octopolar metal complexes, organic and organo-metallic materials, semi-organic materials etc. Among those materials, organic molecular crystals have acquired vast potential applications due to its high values for the nonlinear coefficients, large birefringence values, high damage thresholds in laser beams and large transparency range [1]. A significant optical nonlinearity of organic molecules originates mainly from a strong donor-acceptor intermolecular interaction and de-localized π electron conjugated system. Under the perturbation of an external electric field, a strong electron donor and an electron acceptor groups are generated on the either side of the conjugated π -electron. The donor and acceptor groups proffer the ground state charge asymmetry of the molecule, which is obligatory for the second-order nonlinearity[2]. Amino acids crystals with delocalized π electrons are important organic materials for the design and formation of the different laser operated optoelectronic devices such as modulators, optical triggers, high optical disk data

storage and optically operated fibers because of its high nonlinear susceptibilities. The importance of amino groups holds the fact that the multitude of protein structures arises simply from the structural variety of amino acids and the wide usage is mainly due to the existence of a proton donating carboxyl group and a proton accepting amino group holding chiral symmetry. These materials have acquired a wide exposure since they can easily be crystallized in enormous symmetries and forms which can rather well pave the way for rapid change in the physical and chemical properties of the compounds and have therefore become a topic very actively researched [3]. The positively charged amino group of the asparagine molecule (cation) and the negatively charged carboxylic acid group of the oxalic acid (anion) are interconnected via a hydrogen bond created through proton transfer in a head to tail arrangement. Such a protonation between π electron conjugated molecules results in an asymmetric polarization responsible for various electro optic and nonlinear applications[4].

2. EXPERIMENTAL PROCEDURE

The title compound, ASOX was synthesized by taking L-asparagine monohydrate and Oxalic acid dihydrate (Sigma Aldrich, 99.9% purity) in the stoichiometric ratio 1:1 in double distilled water[5]. The required amounts of the raw materials were calculated using the reaction mechanism depicted as follows:



The reactants were completely dissolved in double distilled water and stirred well together for obtaining the required homogenous mixture of solution, using a temperature controlled magnetic stirrer for 6 hours. The obtained solution was filtered using grade 1 Whatmann filter paper in order to eliminate the undissolved impurities. The solution was then transferred to a beaker and covered with a polythene cover and kept for slow evaporation at room temperature. Optically transparent colorless single crystals of ASOX were formed after a few days, whose quality was then improved through successive recrystallization. Bulk growth of the sample was carried out by determining the solubility of ASOX in water by the gravimetric method.

The solubility of ASOX was determined in the temperature range from 35°C to 65°C using water and ethanol as solvents. The solubility as a function of temperature is shown in Fig.1. Analyzing the solubility curve, it is evident that the optimized saturated growth condition agrees well with double distilled water as solvent. The observed amount of ASOX salt was saturated in 100 ml of distilled water at 50°C and the good quality crystals of dimension (5*2*1)mm³ grown by self-nucleation at 50°C were used as the seed crystals to initiate the growth. Under the optimized growth condition, the mother solution temperature (50 °C) was kept as constant for the further growth process. After 20 days good quality transparent single crystals of dimension (10*5*5) mm³ were harvested under the controlled temperature. The as grown crystal of ASOX is shown in Fig.2.

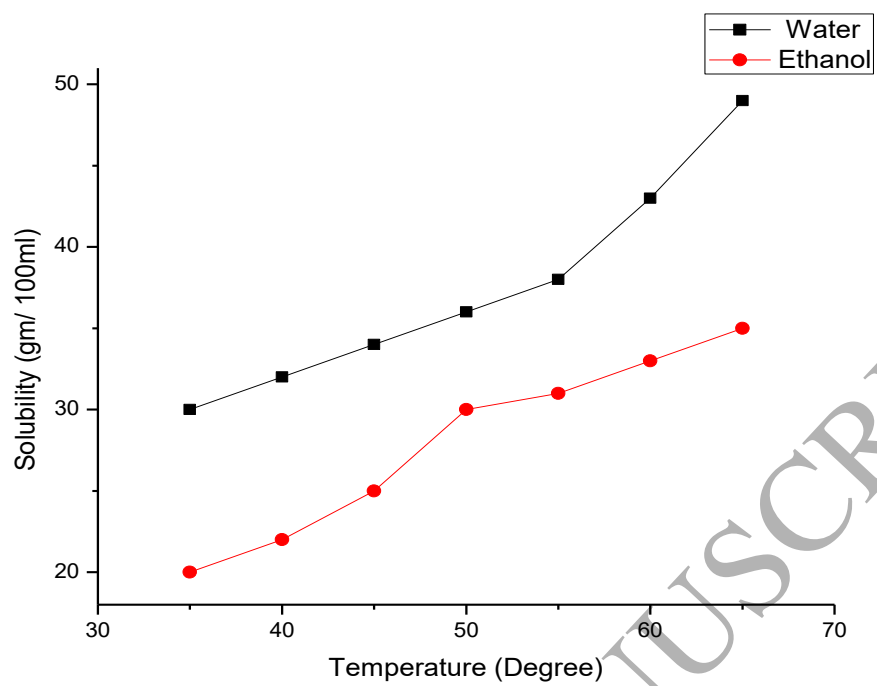


Fig.1.Solubility curve of L-asparaginium oxalate in water and ethanol

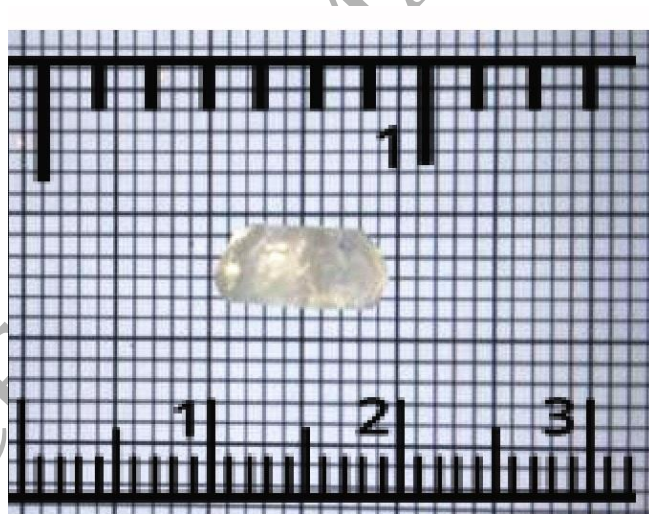
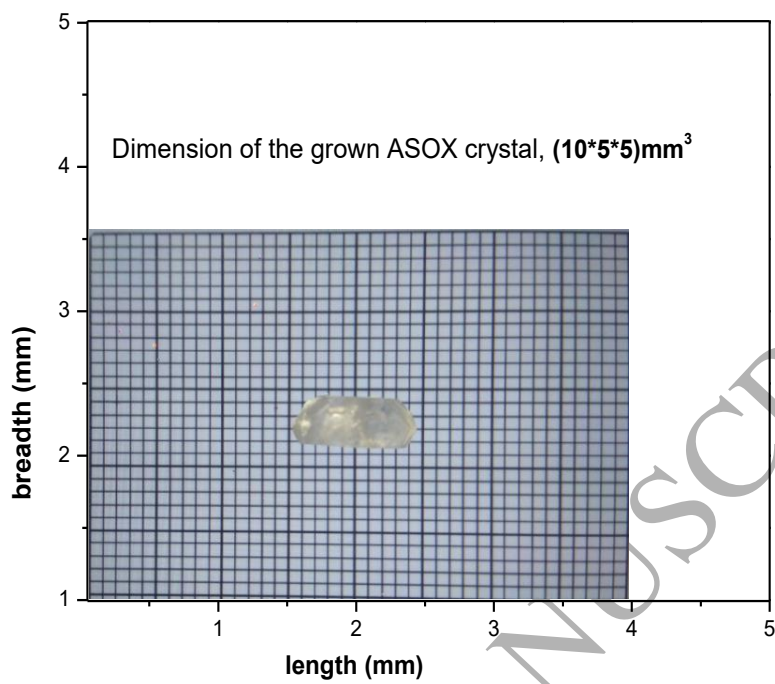


Fig.2.Grown crystal of L-asparaginium oxalate in water

3. CHARACTERIZATION TECHNIQUES

Single crystal XRD analysis was performed using ENRAF NONIUS CAD-4 software for determining the crystallinity and the cell parameters of the grown ASOX crystal. Fourier Transform InfraRed spectrum analysis was carried out using Thermo Nicolet Avatar 370 for identifying the various functional groups resides within the obtained compound. TG/DSC studies through NETZSCH STA 449F5 STA449FSA-0231-M thermal analysis system helps us to understand the thermal stability of the material. UV-Vis-NIR spectrum was recorded by Varian Carry 5000 spectrophotometer and Photoluminescence spectrum by Shimadzu Spectrofluorophotometer to detect the transparency and fluorescence of the material. The mechanical stability of ASOX crystal was confirmed using LEITZ WETZLER Vickers micro hardness tester with diamond indenter and the LDT values was found using a high-power Q-switched Nd:YAG laser of wavelength 1064 nm with 10 ns pulse width. The second order non-linearity of the material was evaluated using Kurtz Perry powder technique.

4. RESULTS AND DISCUSSION

4.1. X-RAY DIFFRACTION STUDIES

The single crystal X-ray diffraction pattern of asparaginium oxalate crystals were examined by using ENRAF NONIUS CAD-4 software. The registered spots in the present pattern (Fig.3) indicates the intensities corresponding to reflection of X-rays incident on the lattice sites in the grown crystal [5]. The present study reveals that the crystallized ASOX crystal belongs to triclinic system with non-centrosymmetric space group P1 with unit cell parameters as $a = 6.34$ (Å), $b = 7.27$ (Å), $c = 10.56$ (Å), $\alpha = 93.89$, $\beta = 100.19$, $\gamma = 98.14$ and the volume of the unit cells is found to be $V = 472$ (Å³).

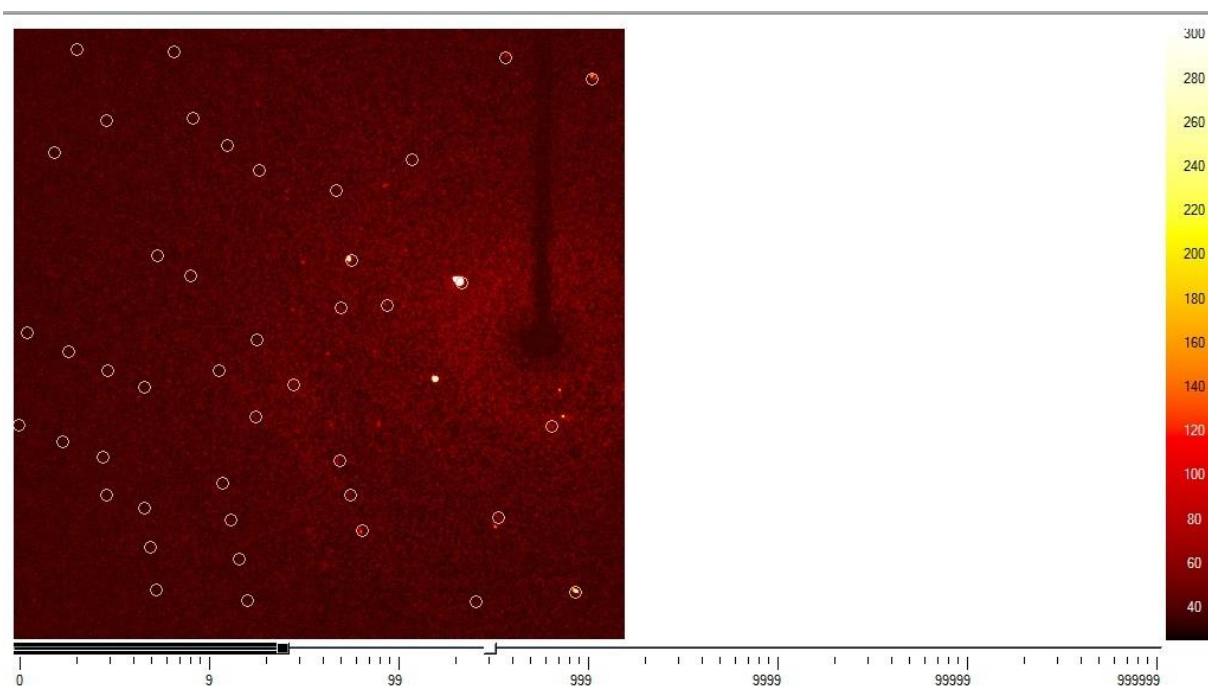


Fig.3.Single crystal XRD pattern of Asparaginium oxalate crystal grown in distilled water

In the powder X-ray diffraction analysis, the powdered sample was subjected to $\text{CuK}\alpha$ ($\lambda=1.5148\text{nm}$) radiation and the various Bragg's peaks corresponding to different 2θ angles will be plotted. Here the sample was scanned for the angular range 5° - 70° of 2θ with a step increment of 0.02° . The presence of well-defined diffraction peaks obtained in the spectra (Fig.4) reflects the good crystalline nature and the purity of the obtained crystal.

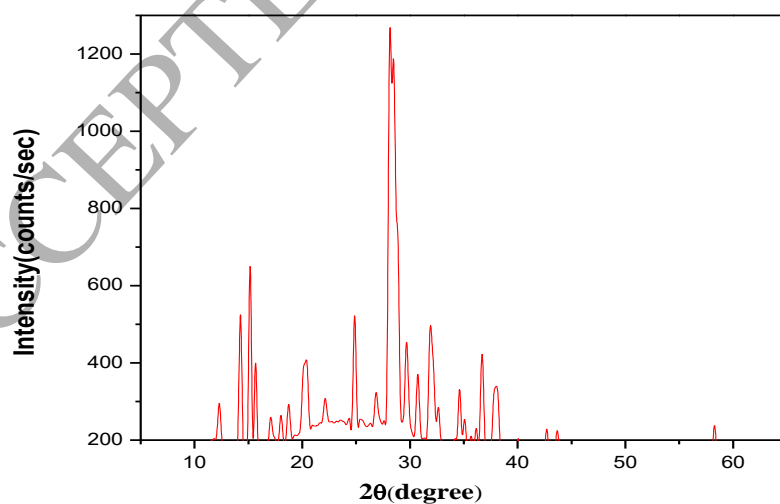


Fig.4. Powder XRD pattern of L-asparaginium oxalate

4.2. FTIR ANALYSIS

The FTIR studies were performed using Thermo Nicolet Avatar 370 Spectrometer having KBr pellet technique in the range $400\text{-}4000\text{cm}^{-1}$. IR spectra help us to determine the various functional groups present in a molecule with the absorption band exhibited in the given spectra. The recorded spectrum is shown in (Fig.5). The sharp absorption band at 2030.70cm^{-1} assigns the combination band and overtone of NH_2 group and the deformation mode of NH_2 group occur at 1683.60cm^{-1} shows the presence of amide group within the material. The medium strong infrared band at 2965.17cm^{-1} is attributed to symmetric stretching mode of CH_2 group. The intense bands at 1426.92cm^{-1} and 1252.84cm^{-1} confirms the bending deformation and rocking vibration of CH_2 group and the peak at 715.57cm^{-1} is due to the formation of COO^- in plane bending mode, with the effect of amino groups and carboxylic acid groups resides in the obtained crystal. The remaining vibrational assignments are compiled in Table.1;

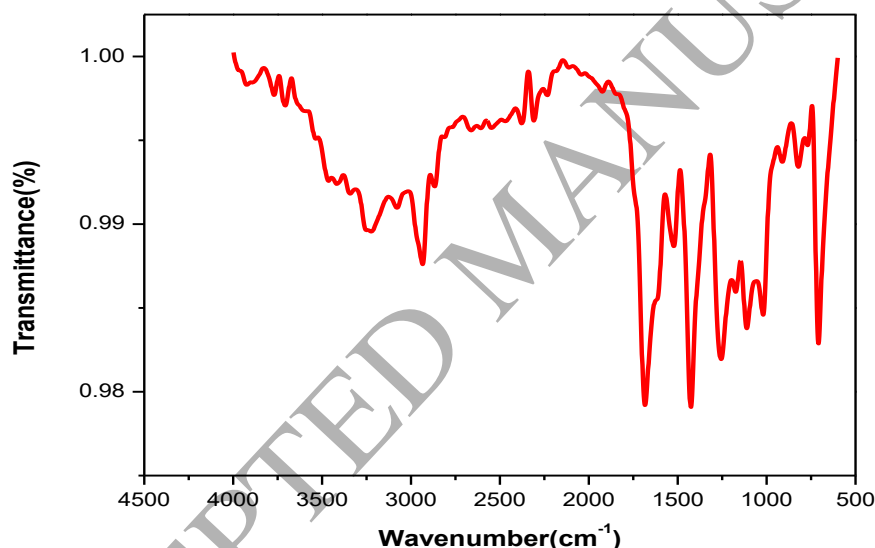


Fig.5. Recorded FT-IR spectra of L-asparaginium oxalate crystal

Wavenumber(cm^{-1})	Tentative assignments
3462.30,3255.13	Characteristics of OH stretching vibration
3233.60,3217.23	NH_3^+ asymmetric stretching mode
2965.17	CH_2 symmetric stretching mode
2030.70	The combination band and overtone of NH_2 group
2861.42	O-H stretching
1683.60	Deformation mode of NH_2 group
1606.99,1547.37	NH_3^+ asymmetric deformation mode

1514.82	NH ₃ ⁺ symmetric stretching mode
1426.92	CH ₂ bending deformation
1252.84	Characteristics of CH ₂ rocking vibration
1171.47,1113.43	C-H in plane bending vibration
1045.35	CH ₂ rocking out vibration
1015.78	O-H stretching mode
911.59	Wagging mode of NH ₂ group
822.1,789.64	C-C stretching mode
715.57	COO ⁻ in plane bending mode
699.45	COO ⁻ out of plane bending mode

Table.1.Molecular vibrational assignments of ASOX crystal

4.3. THERMAL ANALYSIS

The thermo gravimetric studies of the grown crystal was carried out using NETZSCH STA 449F5 STA449FSA-0231-M Thermal Analysis system between 35°C and 500°C with a heating rate of 10°C/min in the nitrogen atmosphere using Al₂O₃ crucible. Most commonly the thermal analysis gives information regarding dehydration, mass change, melting, decomposition, phase analysis etc. There is a weight loss which may be due to decomposition of constituent molecules present in the crystal. From the Thermo Gravimetric (TG) curve (Fig.6), the absence of absorbed water in the crystal lattice was confirmed by the constant mass of the sample below 190°C. Initially a feeble weight loss is observed between 111°C and 175°C, and it may be due to the dissociation of constituent molecules of the crystal. Beyond 175°C, there is a gradual weight loss due to decomposition of the crystal and thus can be inferred that the grown crystal is stable up to 175°C. The decomposition process starts at 175°C and ends at 250.5°C with the liberation of 95% of the material into gaseous products like CO₂, OH, NO₂, NH₃ etc. In the Differential Scanning Calorimetric (DSC) trace, a sharp endothermic peak was observed at 111°C which coincides with the TG curve and thus confirming the decomposition of the starting material before melting. The sharpness of this peak exhibits the purity and crystallinity of the sample. The second broad endothermic peak illustrates the elimination of the hydroxyl and amino groups expelled from the compound [6,7]. Based on the above results, the ASOX crystals can be nominated as a potential candidate for any application below 175°C and the melting point (175°C) was determined and verified by the melting point capillary method also [8].

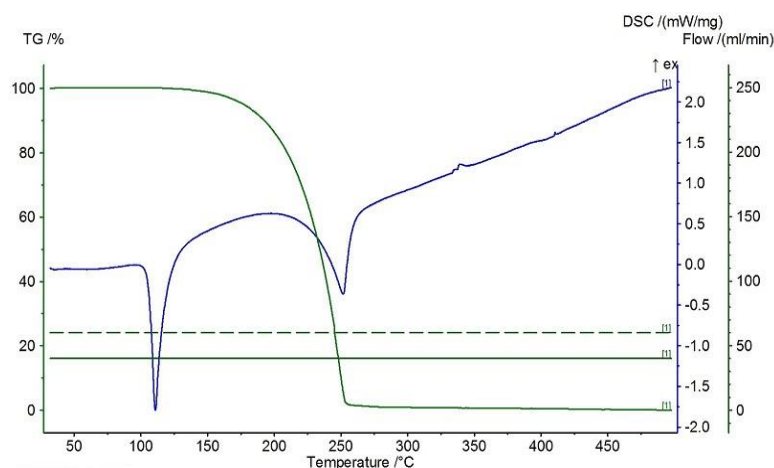


Fig.6. TG/DSC curve of ASOX Crystal

4.4. UV-VIS-NIR SPECTRUM ANALYSIS

The importance of UV-Vis-NIR spectrometry lies within the fact that, the optical parameters like optical transmission range, transparency cut-off and absorbance band plays a vital role in laser frequency conversion applications like second harmonic generation, parametric oscillations, frequency generations etc. The UV-Vis-NIR spectrum can only provide some limited information about the nature of the components present within the material because the entire process involves promotion of the electron in the ' σ ' and ' π ' orbital from ground state to higher energy with the energy absorbed [9]. The optical absorption spectrum of the grown ASOX crystal was assessed in the wavelength range 200-800nm (Fig.7) by dissolving the crushed crystal in the specified solvent. Here, The UV spectrum shows less absorption between 400 and 800nm which reflects the presence of a wide transparency window in the entire visible and the IR region. The high transmittance property is attributed to the good optical quality and the defect free volume of the grown crystal. This promising translucence property can enhance the grown crystal for excellent second order NLO applications[10]. The good optical transmission and the enhanced non-linearity between these wavelengths is mainly due to the π - π^* transition or the electron cloud delocalization arises in the carboxyl group i.e.; the carboxyl group is protonated between the asparaginium cation and the oxalate anion comprising in the asymmetric unit of L-asparaginium oxalate[11]. The grown crystal has a characteristic absorption band in ultraviolet region(UV) around 300nm and this may arise due to electronic transitions from the valence to the conduction band of the materials associated with charge transfer between carboxylate anions(COO^-) in the oxalic acid and the amine(NH_3^+) bonds in the amino acid. For optical device applications, the transparency in the visible and near IR region is more significant because wavelength range is exploited in modern optical telecommunication systems [12].

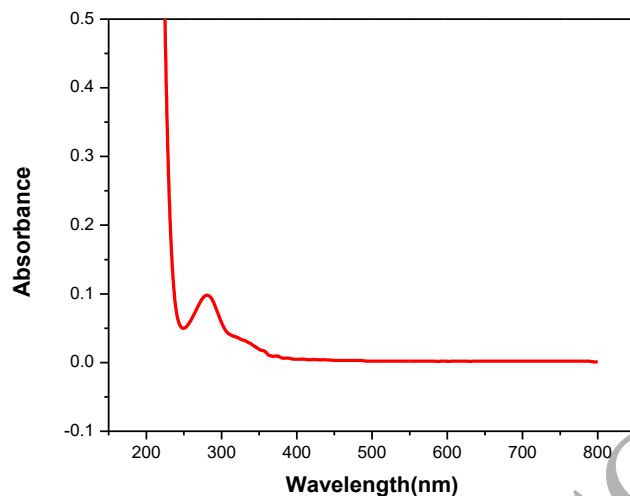


Fig.7. UV-Vis-NIR spectrum of ASOX crystal

4.4.1. DETERMINATION OF OPTICAL BAND GAP ENERGY

The optical absorption is the most imperative tool to determine the band gap of optical materials which gives us an idea of the HOMO-LUMO combination of the material and this absorption is due to the direct transition of an electron from a non-bonding 'n' orbital to an anti-bonding ' π^* ' orbital designated as $\pi^*(n \rightarrow \pi^*)$. To evaluate the optical band gap, the optical absorption Co-efficient (α) was evaluated from the absorption spectra using the relation,

$$\alpha = (2.3036 \cdot A) / t \quad (1)$$

Where A is the absorbance and t is the thickness of the crystal. The study of optical absorption coefficient with the photon energy helps to understand the type of transition of the electron and the band structure

In the high photon energy region, Tauc et al suggested that the occurrence of direct band gap in crystals deals with the energy dependence of absorption coefficient (α) related by the following expression[13];

$$\alpha h\nu = A(h\nu - E_g)^{1/n} \quad (2)$$

Where 'h' is the Planck's constant, ' ν '-frequency of vibration, ' E_g '- optical band gap and 'A'-a proportionality constant. The value of the exponent 'n', denotes the nature of the sample transition[14]. Here $n = 2$ because only the direct allowed sample transition is considered in ASOX crystal. The optical band gap of ASOX single crystal is evaluated by the linear extrapolation of the Tauc's graphplot[15] between $(\alpha h\nu)^2$ and $(h\nu)$ to the energy axis as shown in Fig.8.

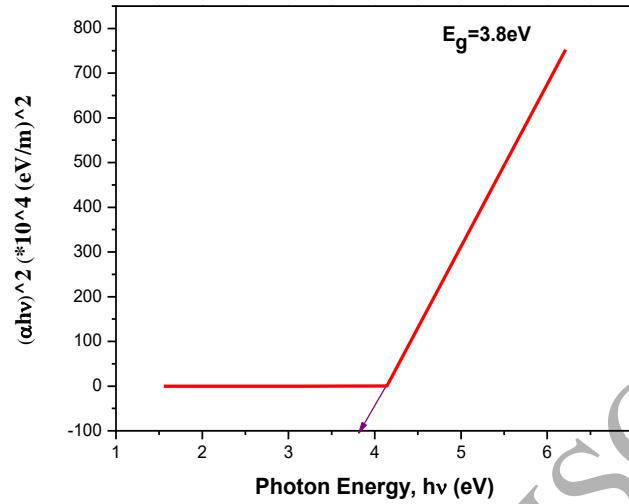


Fig.8. Band Gap energy of the grown ASOX crystal

Within the fundamental absorption region, the band gap energy for the crystal was computed as 3.8 eV. The relation between refractive index (n) and forbidden energy gap (E_g) is given by Reddy et al [16] as;

$$E_g e^n = 36.3 \quad (3)$$

The refractive index(n) was found to be 2.25 and the optical reflectance (R) of the material was calculated by the relation;

$$R = \frac{(n-1)^2}{(n+1)^2} \quad (4)$$

The reflectance of the material was observed as 0.1479 for the grown crystal in the transmission range. The electrical susceptibility (χ_c) was evaluated using the formula;

$$\chi_c = n^2 - 1 \quad (5)$$

It was determined that ' χ_c ' is 4.0625 and since it is greater than 1, the grown crystal can easily be polarized with the highly intensified incident light.

The extinction coefficient (K) as a function of wavelength(λ) can be represented by the equation;

$$K = \lambda \alpha / 4\pi \quad (6)$$

From the above relations, it can be noticed that the absorption coefficient of the material plays as backbone in determining the optical constants like refractive index, optical reflectance, electrical susceptibility and extinction coefficient. Thus, by obtaining accurate band gap energy via suitable approximation of absorption coefficient, one can improve the internal efficiency of the optical materials which was greatly demanded by electro- optical devices[17].

4.5. FLUORESCENCE STUDIES

Photoluminescence studies were carried out by Shimadzu Spectrofluorophotometer with Xenon arc lamp as the excitation source. This analysis is a non-destructive tool to carry out the luminescence manners and emission properties of the grown optical material which have broad applications in biochemical, medical and chemical research fields for interpreting organic compounds [18,19]. Here the PL emission spectrum of ASOX was recorded in the range 400-700nm with an excitation wavelength of 280 nm chosen from UV-Vis-NIR spectrum and the obtained emission pattern is illustrated in (Fig.9). The detector shows a flat response up to 400nm and a broad spectrum with maximum intensity was obtained at 414nm, which corresponds to violet emission. It was concluded that the violet luminescence may be due to the protonation between the electron contributing (amino group) and the electron withdrawing (carboxyl group) groups, which can enhance the mobility of ' π ' electrons [20]. The broadening of emission band is due to intermolecular interactions generating within the crystal lattice of the material.

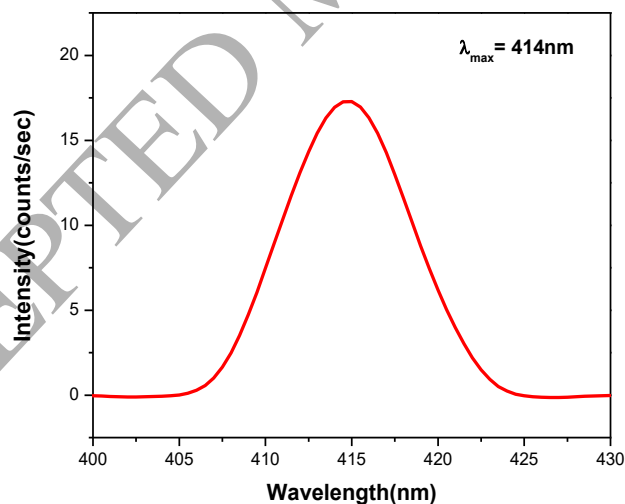


Fig.9. PL emission spectrum of ASOX crystal

4.6. MICROHARDNESS ANALYSIS

In order to determine the mechanical stability of the obtained crystal, Vickers micro hardness test were carried out on ASOX single crystals and that Mechanical behavior of the grown crystal were studied using LEITZ WETZLER Vickers micro hardness tester. The mechanical strength of the crystals directly depends upon the structure and composition of the crystalline solids. The calculation of hardness is simplest and effective method for understanding the mechanical behavior of the material like molecular binding, yield strength, elastic constants, cracking temperature and brittle value of the material [21]. For carrying out this hardness test, a well-polished crystal is subjected to different magnitude of loads ranging from 10g to 100g over a fixed indentation time of 10 seconds for all loads.

The hardness of the material was calculated using the relation [22];

$$H_v = 1.855P/d^2 \text{ in kg/mm}^2 \quad (7)$$

Where 'H_v' is the Vickers hardness number, 'P' is the applied load in kg and 'd' is the diagonal length of the indentation in mm.

As the load increases, the hardness number also increases up to 50g, which can be attributed to the work hardening of the surface layers and after that, as load increases beyond 50g, the hardness number decreases which shows that multiple cracks were occurred on the smooth crystal surface due to the release of internal stresses generated locally by indentation because the micro hardness shows a tendency to saturate at the maximum indenter load[23]. And the hardness number of the compound was found to be 88.42 Kg/mm².

The variation of Vickers micro hardness value with load is shown in (Fig.10).

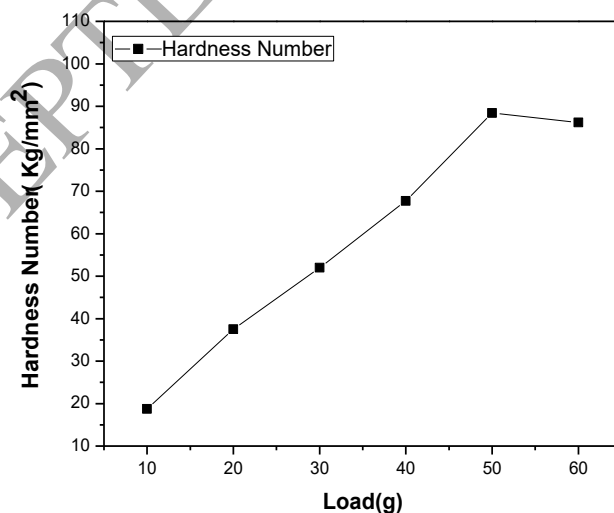


Fig.10. Variation of micro hardness with load of ASOX crystal

The relation connecting the applied load and diagonal length 'd' of the indenter is given by Meyer's law;

$$P = ad^n \quad (8)$$

where 'n' is the Meyer's index (work hardening coefficient). This is calculated from the slope of the straight line connecting logP Vs. logd. From the keen observations on various materials Onitsch[24] and Hanneman[25] confirmed that when 'n' lies between 1 and 1.6, the material seems to be moderately hard and if it is more than 1.6, material comes under soft category. Here the value of 'n' obtained for ASOX is 1.07. Hence ASOX belongs to a harder material category.

The elastic stiffness constant (C) for different loads were evaluated, to get an idea about the bond strength of the material between neighboring atoms, using Wooster's empirical formula and it is tabulated in Table.2;

$$C = (Hv)^{7/4} \quad (9)$$

Sl no.	Load(P)	Hardness No.(Hv)	Stiffness constant(C)
-	g	Kg/mm ²	*10 ² N/m
1	10	18.73	1.686
2	20	37.50	5.683
3	30	52.00	10.069
4	40	67.70	15.978
5	50	88.40	25.485
6	60	86.20	24.386

Table.2. Stiffness constant of ASOX crystal for various loads

4.7. SURFACE LASER DAMAGE THRESHOLD STUDIES

Like other photonic materials used in Laser technology, NLO crystals are susceptible to optically induced catastrophic damage. Optical damage in materials may adversely affect the performance and efficiency of high power laser systems and therefore it seems to be an extensive subject to be researched to find out single crystals having large tolerance to the incoming laser power intensity [26, 27], i.e.; the laser damage threshold value reflects the efficiency of the material without being damaged or it determines the maximum permissible power of the laser energy up to which an optical material can be exposed. And it was found that the damage occurs in crystals, when the irradiation of beam causes a thermal conduction in the atomic lattice leading to photo-ionization of crystal surface in the form of melting or decomposition or crack or fusion of material [28, 29].

The laser damage threshold studies have been carried out for Asparaginium oxalate single crystal using a Q-switched Nd:YAG laser of wavelength 1064nm with a pulse width of 20ns. The laser exposure time on the sample was kept as 30 s for all energies and the output intensity of the laser was controlled with a variable attenuator and focused to the test sample on the goniometer located at the near focus of the converging lens for setting the spot size to the desired value.

During laser radiation, and the energy density of the input laser beam was recorded by coherent power meter before the crystal gets damaged.

The power density was calculated using the formula [30];

$$\text{Power density, } P_{(d)} = E/\tau A \quad (10)$$

Where E is the input energy of the laser in millijoules, τ is the pulse width in ns and A is the area of the circular spot size (πr^2 , r is radius of the spot in mm) of the crystal.

The laser damage threshold values of some organic materials are stacked in the table (Table.2) for the ease of comparison.

LDT value of the L-Asparaginium Oxalate with KDP and Urea is as shown [31];

Compound	LDT (GW/cm ²)
L-Asparaginium Oxalate	2.04
KDP	0.20
Urea	1.50

In this present study the LDT energy density was found to be 2.04 GW/cm². This value is greater than the threshold value of KDP and other known organic single crystals [32, 33]. All the above studies reveal that ASOX crystal is a promising optical material with adequate LDT which can be effectively employed for enhancing high-tech laser assisted NLO applications such as mode-locking, photonics, optical limiting, SHG, data processing, holographic data storage devices vital for high-tech technological systems.

4.8. SECOND HARMONIC GENERATION STUDIES

Kurtz- Perry method [34] performed to find out the Second harmonic generation of the crystal L-asparaginium Oxalate. The crystal of L-Asparaginium Oxalate grained to form a homogenous powder and is packed tightly in a micro-capillary tube. Q Switch ND-YAG laser of wavelength 1064 nm of beam energy 0.801J (10Hz, 10ns) was passed through an IR reflector and then directed to the sample of asparaginium oxalate. From the emission of radiation with green wavelength from the compound, the second harmonic signal is confirmed. In this case, Potassium

dihydrogen Phosphate (KDP) was used as the reference material and the output voltage of ASOX was observed to be 10mV and that of KDP was 16mV therefore the relative second harmonic generation efficiency of L-Asparaginium oxalate was found to be 0.68 times that of KDP. Due to the enhanced nonlinear value when compared to other amino acid compounds (Table.3), it confirms that the L-asparaginium oxalate is the potential material for NLO device fabrication.

SHG efficiency of some organic amino acid compounds are given in the table below for the ease of comparison.

Organic Amino Compounds	SHG Values
L-alaninium Fumarate	0.06 [35]
L-Proline lithium Chloride Monohydrate	0.20 [36]
L-Phenylalaninium Maleate	0.27 [37]
L-Asparagine-l-tartaric acid	0.31 [38]
Urea L-Asparagine	0.50 [39]
L-Asparaginium Oxalate	0.68 [present work]

Table.3. Comparison of the SHG value of ASOX crystal with some reported values

5. CONCLUSION

The NLO material ASOX was synthesized and good quality single crystals were grown by slow evaporation solution growth technique. The cell parameters and crystalline nature of L-Asparaginium Oxalate is confirmed by single crystal XRD. The functional groups of the crystal have been identified by FTIR analysis. The grown crystal of ASOX is translucent to all the UV-visible-NIR radiation. Hence it can be used for photonic applications where transparency near IR seems to be a challenging factor. The laser damage threshold value was found to be 2.04GW/cm². The mechanical strength of the sample is confirmed by Vickers micro hardness method. The Kurtz-Perry powder technique reveals the SHG efficiency of the material as 68% that of standard KDP used as the reference sample. Hence the grown single crystals of ASOX can be effectively employed for various optoelectronic and photonic applications.

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