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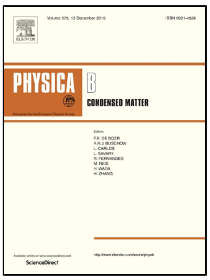

Synthesis and characterization analysis of unique organic crystal – Urea Glutaric Acid, an optimistic candidate for optical device applications

C. Rathika Thaya Kumari, S. Sudha, G. Vinitha, M. Nageshwari, M. Lydia Caroline, G. Mathubala, A. Manikandan

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Synthesis and characterization analysis of unique organic crystal – Urea Glutaric Acid, an optimistic candidate for optical device applications

C. Rathika Thaya Kumari [a], S. Sudha [b], G. Vinitha [c], M. Nageshwari [d], M. Lydia Caroline [e,*], G. Mathubala [f], A. Manikandan [f]

[a] Department of Physics, Bharath Institute of Higher Education and Research, Chennai, Tamil Nadu, India

[b] Department of Physics, Arignar Anna Govt. Arts College, Cheyyar, Tamil Nadu, India

[c] Department of Physics, School of Advanced Sciences, VIT, Chennai, Tamil Nadu, India

[d] Department of Physics, Peri Institute of Technology, Chennai, Tamil Nadu, India

[e] Department of Physics, Dr. Ambedkar Govt. Arts College, Vyasarpadi, Tamil Nadu, India

[f] Department of Chemistry, Bharath Institute of Higher Education and Research, Chennai, Tamil Nadu, India

Corresponding author Email ID and contact no:

lydiacaroline2006@yahoo.co.in (M.Lydia Caroline);

Tel: 044-25520151: Fax: 044 - 2552 1852:+91 9841720216

Co-authors Email id: rathikak06@gmail.com (C. Rathika Thaya Kumari); sudhavaidhy@gmail.com (S. Sudha); vinitha.g@vit.ac.in (G. Vinitha); nageshwari.sb@gmail.com (M. Nageshwari); lydiacaroline2006@gmail.com (M.Lydia Caroline); madhu2705@gmail.com (G. Mathubala); mkavath15@gmail.com (A. Manikandan)

Abstract

Urea Glutaric acid (UGA), an organic compound was grown and its diverse characterizations were studied. XRD results confirmed the structure as monoclinic with the space group of C2/c. FTIR results confirmed the basic functional groups present in crystal **was** noticed. The optical properties have been studied by absorbance measurements in the wave length region from 200nm to 800nm. NLO (third order) properties were studied by Z- Scan method declares UGA, a successful material in nonlinear optics. The fluorescence spectrum indicates an electronic excitation at 481nm and its thermal studies was done to determine the stability of the grown material under decomposition. Laser damage threshold was calculated to predict its resistance for high power laser radiation. The hardness and dielectric properties of UGA was explained from Vicker's micro hardness and dielectric analysis. Hence, the results from various characterizations **confirmed that** UGA is an enticing aspirant over device fabrication in nonlinear optics.

Key words: Organic compound; **Urea Glutaric acid**; Crystal growth; Hardness studies; Dielectric studies; Nonlinear Optics.

1. Introduction

Recent implementation of many new materials with good optical parameter creates noteworthy interest on young researchers nowadays. The major task for the present researchers is to produce superior crystals with better mechanical strength to enhance its nonlinear optical properties **[1, 2]. Single crystals are** the strength to support various engineering and technological revolutions [3]. In general, most of the opto electronic instruments are in need of good nonlinear crystals to enhance its applications. In search of above needs an organic material

was chosen because of its higher efficiency and larger nonlinear susceptibilities than inorganic materials [4]. The focus on the growth of organic NLO material is **due to its application** of fast data transfer over long distances, optical frequency conversion, dynamic holography and optical guiding of laser beams [5].

Urea, a well-known organic material used significantly on crystal engineering, reveals high nonlinear optical coefficients with strong laser damage threshold and elevated degree of birefrigerence. The study of urea crystal **is fascinated, due** to their nonlinear optical piezo electric properties [6]. In past literature, Urea p nitrophenol crystals [6], Urea L-valine [7], Urea succinic acid [8], Glycine glutaric acid [9] were synthesized and their NLO properties were discussed. The description of different combinations of the present compound in the ratio 1: 1, 1:2 and 2:1 was studied already and the structure with connectivity patterns of the 1:1 complex was discussed [10]. Further the trend on organic compound highlights that urea is an efficient material which often holds extreme degree of delocalization [6] and signifies its importance over nonlinear optical applications [11]. Moreover, **urea (N_2H_4CO)** is a bi-functional material with N-H, H_2 bond donors and H_2 bond acceptors. The carboxylic acids are the ideal elements for co-molecular formations [12]. In the current work, slow evaporation solution growth technique was implemented to take Urea Glutaric acid (UGA) crystal in the ratio of 2:1 whose crystal structure has been reported by Veneta Videnova Adrabinska [12]. The growth and extensive characterizations were analyzed for the first time and is reported.

2. Synthesis of UGA

A material UGA was taken from urea and glutaric acid of 2/1 ratio. The weighed amount of the material was stirred separately with double distilled water to attain homogeneous solution

using magnetic stirrer. It continues for 6 hours. Further, the mixture is transferred into clean beaker. Cover the beaker with transparent paper having small holes and kept for evaporation to take place slowly. Under clear observation, an optically impressive crystal was seen after 30 days. After successive recrystallization to attain purity it was well photographed and is shown in Fig. 2. The synthesis method of UGA is given below [Fig. 1]:

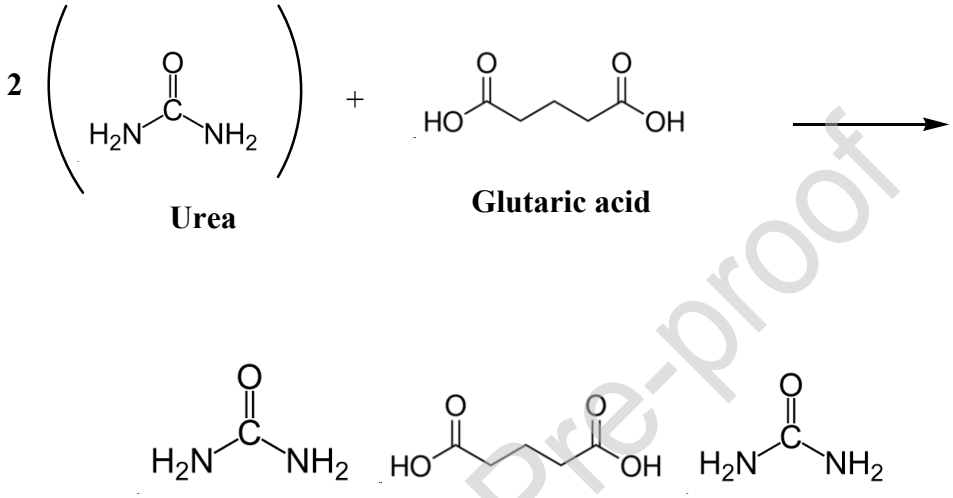

Fig. 1. Reaction Outline for UGA

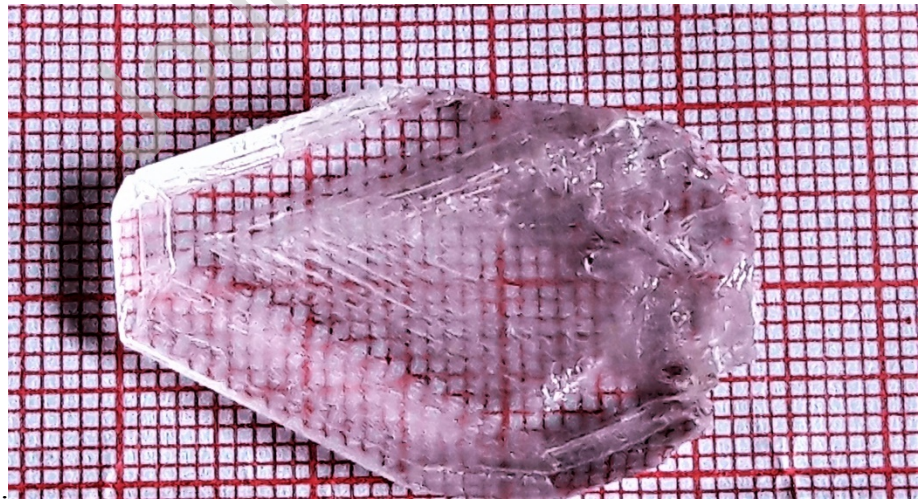

Fig. 2. Image of UGA single crystal

3. Results & Discussion

3.1. Single XRD analysis

The XRD was accomplished from NONIUS - CAD4-F diffractometer with MoKα (Å) ray to verify the UGA crystal. XRD study declares that this crystal discloses in monoclinic structure with C2/c space group. The measured values of a, b and c **values** are 12.07 Å, 11.05 Å and 9.17 Å respectively, having volume 1210 $Å^3$, which was in accordance with the already **published by Veneta Videnova Adrabinska et al.** [12].

3.2 Investigation of FT- IR & Raman Spectrum

The FT-IR and RAMAN spectrum for UGA was investigated with PERKIN ELMER spectrometer and BRUKER RFS 2.7 spectrometer from 4000 cm^{-1} by KBr pellet technique. The documented spectrum is delineated in Fig. 3 and various vibrations observed were discussed. The OH stretching wave number was pointed around 3550 cm^{-1} – 3200 cm^{-1} [13]. The vibrations observed near 3579 cm^{-1}, 3319 cm^{-1} in IR as well as Raman were attributed to OH symmetric stretching vibration [8]. The plane deformation vibration of OH and bending out of plane vibrations of OH were allotted at 752 cm^{-1}, 933 cm^{-1} and 903 cm^{-1}. The bands at 3198 cm^{-1} and 770 cm^{-1} arises because of symmetric stretching and rocking of NH_2 respectively [9]. The peak 1414 cm^{-1}, 1421 cm^{-1} clearly represents N-C-N vibrations corresponding to asymmetric stretching of urea [8]. The C=O vibrations corresponding to stretching is present in both at 1697 cm^{-1}, 1701 cm^{-1} respectively. C-H band's wagging vibrations are positioned at 1163 cm^{-1} in IR and 1169 cm^{-1} in Raman counterpart. The CH stretching vibrations overlap upon O-H band near 2905 $cm^{-1,}$ 2907 cm^{-1} in both spectra respectively [9]. The stretching of C-O is visible at 1188 cm^{-1} and the pointed band at 1697 cm^{-1} is ascribed to C=O stretching. The peaks at 1291

cm^{-1} in IR as well as Raman show the existence of carboxylic acid in glutaric acid. The presence of NH_3^+ was identified at 2573 cm^{-1} and is mainly ascribed to the protonation of NH_2 by COOH group of glutaric acid [14]. The asymmetric stretching of COO^- is seen at 1594 cm^{-1} and 1564 cm^{-1} and COO^- bending mode is seen in 612 cm^{-1}, 613 cm^{-1} in both spectra respectively [6]. The vibrational band allotments were summarized in Table 1.

Table 1. Different Vibrations of IR and RAMAN spectra - UGA (2/1)

IR Wave number in cm^{-1}	RAMAN Wave number in cm^{-1}	Assignments
3579	3319	OH sym.stretching
3198		sym. stretching NH2
2905	2907	CH stretching
2573		NH_3^+ stretching
1697	1701	C=O stretching
1594	1564	COO^- asym stretching
1414	1421	N-C-N asym stretching
1291	1291	COO^- rocking
1188		C-O stretching
1163	1169	CH Wagging
933	903	O-H out of plane
770		NH_2 rocking
612	613	COO^- bending

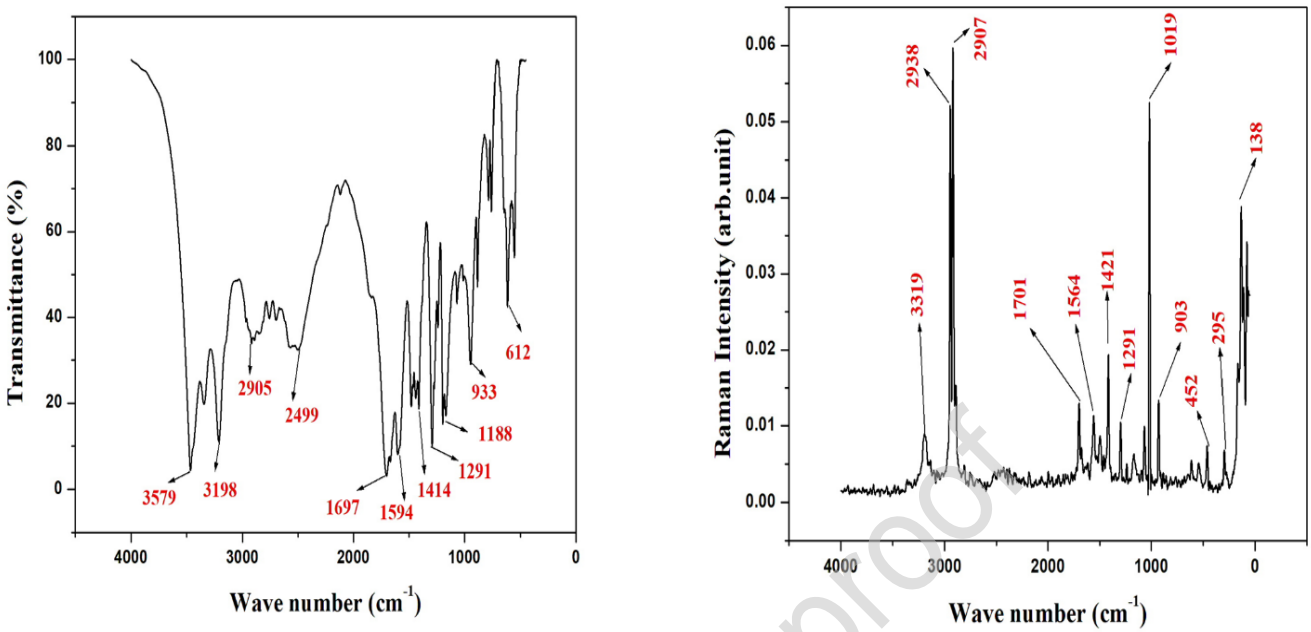

Fig. 3. FT-IR and FT – RAMAN spectrum of UGA

3.3 Optical studies

The UV-Vis spectrum was actualized from 200 - 800 nm employing PERKIN - ELMER LAMADA 35 spectrophotometer. The important enticing characteristics of the material to analyze its usage for device applications are transmission width and cutoff wavelength [15]. Desired lower cutoff wavelength must lie within the range 200 nm – 400 nm for an efficacious NLO material [16]. Fig. 4 portrayed the absorption spectra for UGA crystal. The prominent lower cut off wavelength for UGA is observed as 240 nm. From 240 nm to 800 nm no further absorption occurs which extremely supports clear transmittance in the whole visible band suggests its excellency over application of opto electronics.

The extension of the linear part [17] that is depicted in Fig. 5, the energy gap was assessed. The optical bandgap value for UGA was computed as 5.46 eV. The more transmittance

and broad energy gap confirms low defect concentration in the UGA crystal which shows outstanding possibilities for nonlinear device applications [18].

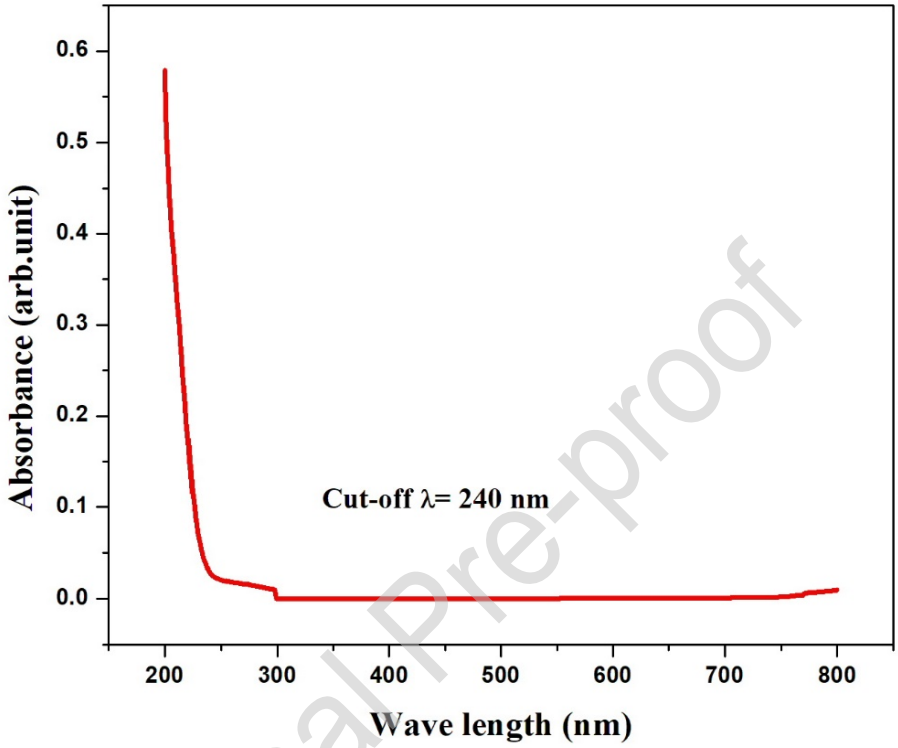

Fig 4. UV- Visible Spectra of UGA

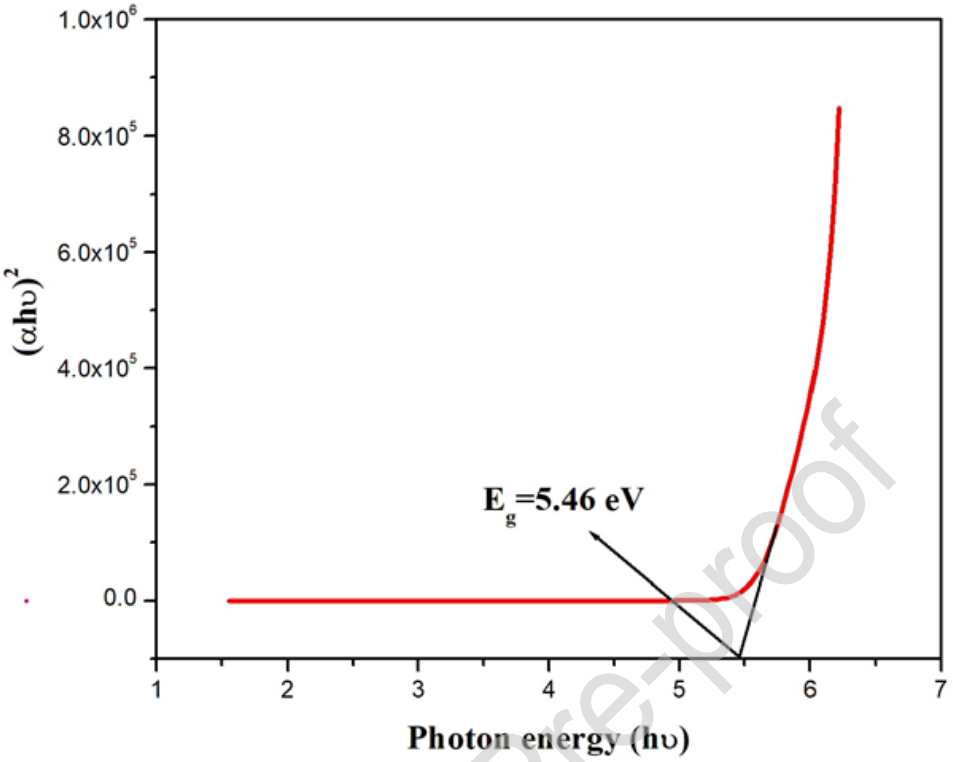

Fig 5. Band gap (Tauc's plot) of UGA crystal

3.3.1 Urbach Energy

The absorption coefficient (α) was estimated from Urbach formula [19],

$\alpha (h\upsilon) = \alpha_0 \exp (h\upsilon/E_u)$ -------- (1)

The graph hν with ln (α) is predicted in Fig. 6. The crystalline feature of the as grown material is identified from the increase in value of α along photon energy (hυ).The observed slope of straight line got by plotting logarithm and photon energy (hυ), interprets excellent crystallinity in the grown crystal. The inverse of the slope was detected to be 0.3933 eV, **which is Urbach**

energy for UGA. Moreover, low (0.3933 eV) estimated Urbach energy signifies minimum defect in the grown crystal [20].

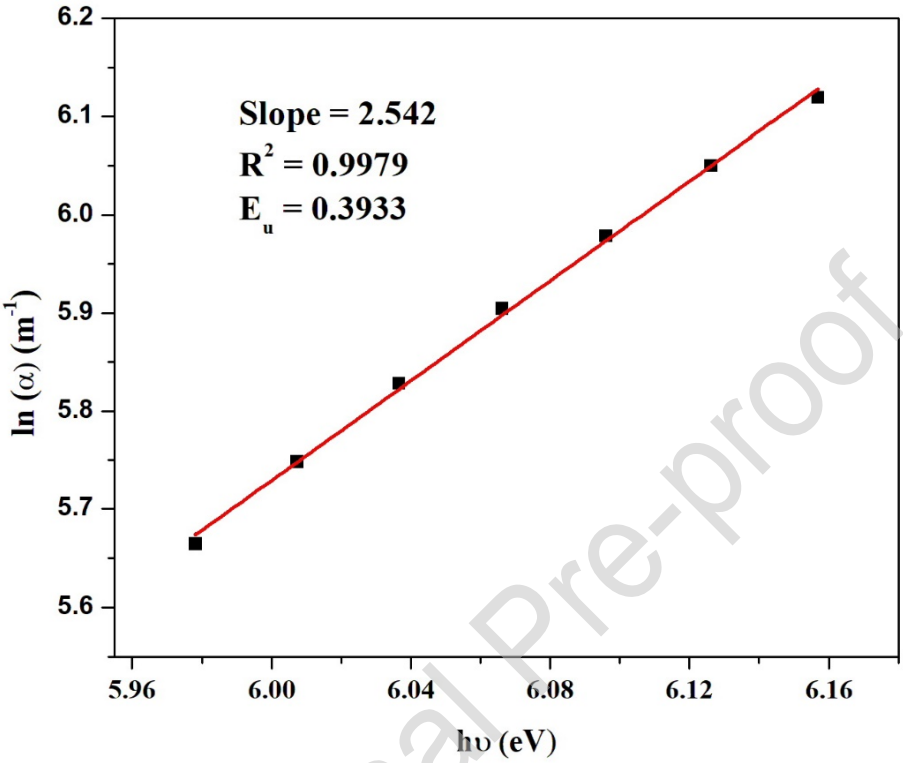

Fig 6. Variation of photon energy hν verses ln (α)

3.4 THG – Z-Scan Studies

The Z-scan method for UGA has been employed using Nd-YAG laser (Coherent compass TM215M-50) with 532 nm to show third order nonlinearities. This was a regular method to identify the nonlinear property of the material in centrosymmetric media. It is a delicate technique to predict the nonlinear parameters for centrosymmetric materials. Generally for optical switching, optical limiting sensors and sensor protection applications, the materials should have vast nonlinearities [18]. Z Scan technique measures absorption and refraction of NLO based on the scanning of spatial beam modifications based on the laser beam focused and

defocussed in time through a nonlinear material and yields the nonlinear parameters from the open and closed aperture pattern.

The closed aperture configuration is gentler to yield nonlinear absorption and refraction. From the observed peak followed by valley configuration in Fig. 7, illustrates the negative nonlinearity which is attributed to self-defocussing nature [18]. In the open aperture configuration the transmittance curve shown in Fig. 8, is symmetric with respect to focus and shows two **photon absorption processes** [21]. This open aperture curve is used to calculate the nonlinear absorption coefficient and was found to be 0.02 x 10^{-4} cm/W.

The assessable quantity (ΔT_{P-V}), shows the variation from the maximum and minimum values of transmittance is represented using the formula,

$$\Delta T = 0.406\ (1 - S)^{0.25} |\phi| \qquad \text{-------} \quad (2)$$

$$S = 1 - \exp\ (\ -2r_a^2/\omega_a^2\ ) \qquad \text{--------} \quad (3)$$

The on-axis phase shift |ϕ| [22] is specified by,

$$|\phi| = k\, n_2\, L_{eff}\, I_0 \qquad \text{-------} \quad (4)$$

L denotes the length, α and k signifies linear absorption coefficient and wave number.

From the configuration of open aperture Z-scan,

$$\beta = \frac{2\sqrt{2}.\ \Delta T}{I_0\ .\ L_{eff}} \qquad \text{--------} \quad (5)$$

The above computed data was utilized to study the real and imaginary components of nonlinear optical susceptibility χ3.

$$Re\ \chi^{(3)}(esu) = 10^{-4} \frac{\varepsilon_0 C^2 n_0^2}{\pi} n_2\ (\frac{cm^2}{W}) \qquad \text{--------} \quad (6)$$

$$Im\ \chi^{(3)}(\ esu) = 10^{-2} \frac{\varepsilon_0 C^2 n_0^2\ \lambda}{4\pi^2} \beta\ (\frac{cm^2}{W}) \qquad \text{--------} \quad (7)$$

Also,

$$|\chi^{(3)}| = [\, Re\,(\chi^{(3)})^2 \; + (Im\,(\chi^{(3)})^2\,]^{1/2} \qquad \text{-------- (8)}$$

Table 2 elucidates the experimental particulars namely Nonlinear refractive index (n_2), Nonlinear absorption coefficient (β), Real susceptibility ($\chi_R^{(3)}$) , Imaginary susceptibility ($\chi_I^{(3)}$) and Absolute susceptibility $|\chi^{(3)}|$ are the outcome for UGA crystal. The third-order nonlinear optical susceptibility χ3 of UGA shows a larger value compared to the other crystals and is presented in Table 3.

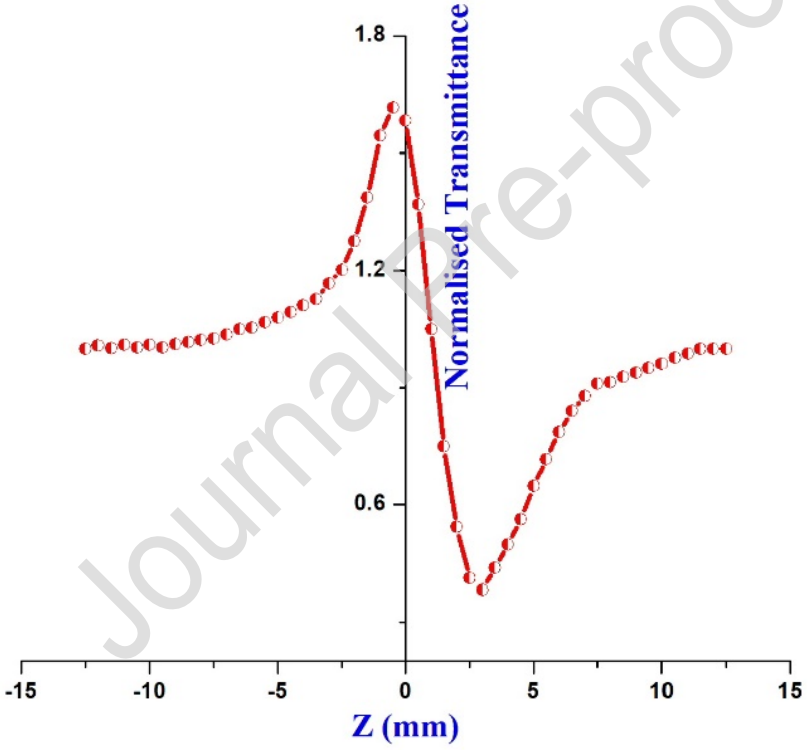

Fig 7. Z-Scan Transmittance curve for closed aperture

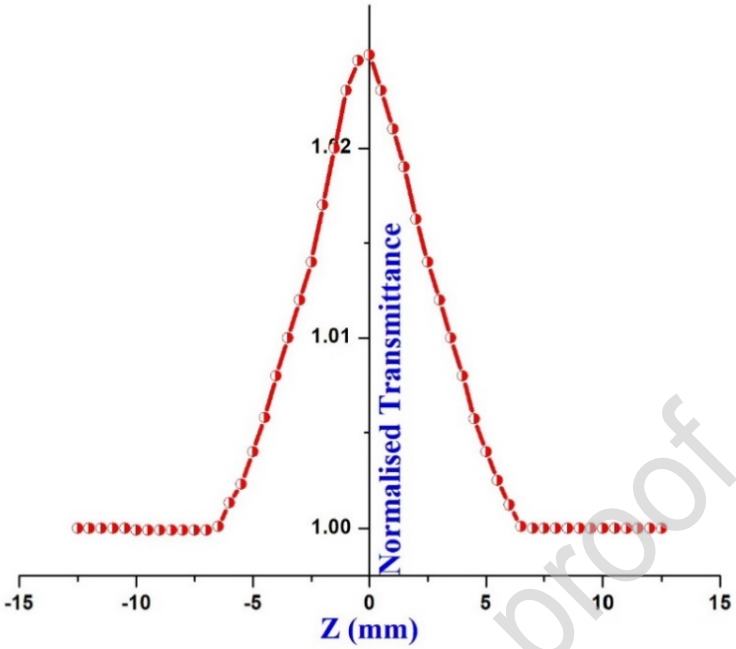

Fig 8. Z-Scan Transmittance curve for Open aperture.

Table 2. Nonlinear optical (Third order) parameter of UGA

	n_2 cm^2/W	β cm^2/W	$\chi_R^{(3)}$ esu	$\chi_I^{(3)}$ esu	$\lvert \chi^{(3)} \rvert$ esu
UGA	7.80×10^{-8}	0.02×10^{-4}	8.54×10^{-6}	0.14×10^{-6}	8.54×10^{-6}

Table 3. The $\chi^{(3)}$ values of some Organic nonlinear optical crystals

Crystal	Third order susceptibility	References
UGA	8.54 x 10^{-6} esu	**Present work**
UAA	6.44 x 10^{-8} esu	[23]
LMSA	6.346 x 10^{-6} esu	[24]
DLMA	4.18 x 10^{-6} esu	[25]

3.5 Photoluminescence Spectrum

The fluorescence and lifetime of UGA were recorded with the help of FLUOROCUBE Spectrofluorophotometer between 200–800nm. The fluorescence spectral investigation was predicted to gain information about higher order energy levels during radiative recombination [26]. The emitted spectra from the excited state and its decay components are studied clearly for UGA crystal. This was pictured for the excitation wavelength of 240 nm [Fig. 9 (a)]. A pointed peak at 481 nm (2.58 eV) discloses the blue light of electromagnetic spectrum near the visible region. Time Resolved Fluorescence Spectroscopy is used to extract the life time. **The measurements of decay time with thrice of its exponential decay function are evaluated and were** illustrated in Fig. 9 (b). The decay time measurement was analyzed with a three exponential decay function [26] of the form,

$$F(t) = A_1 e^{-t/\tau_1} + A_2 e^{-t/\tau_2} + A_3 e^{-t/\tau_3} \qquad \text{-------(9)}$$

where different orders of A, τ indicates the amplitudes and lifetimes of prompt and delayed emissions respectively. The actual decay curve was accessed in Fig. 9 (c). Thus based on the residuals, worthy curve fit was measured and the value χ^2 ratio was estimated. The shortest decay component of the present work was depicted in Table 4.

Table 4. Fluorescent life time data for UGA single crystal.

Three Exponential Analysis of UGA Crystal						
Life Time			Amplitude			χ^2
τ_1	τ_2	τ_3	A_1	A_2	A_3	
3	9	1	53.34	16.72	29.94	1.098

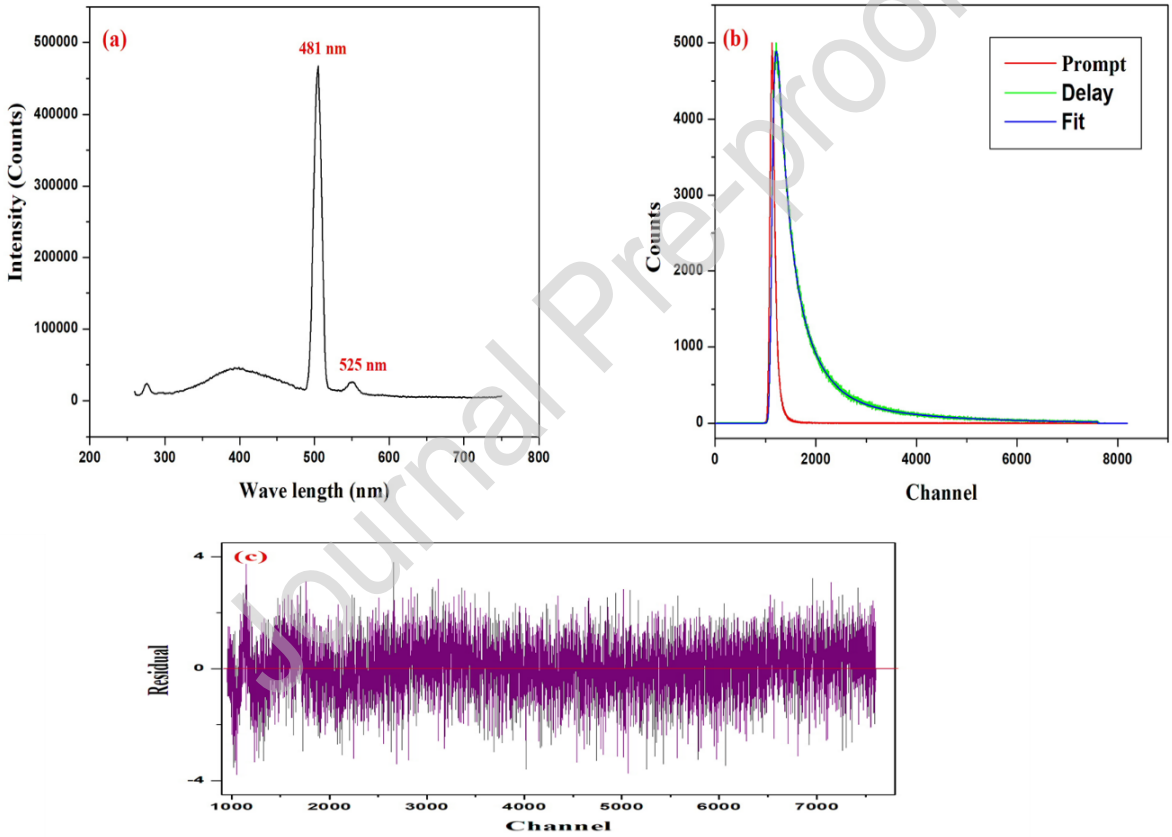

Fig. 9(a) Emission spectrum **(b)** Life time measurement **(c)** Residual fit of UGA

3.6 LDT Studies

The LDT of an optical crystal is the noticeable parameter to strengthen its ability and capability towards linear and nonlinear characteristics and must be endure with greater power intensities [27]. The multi shot surface laser damage threshold experiment was also done for UGA using Nd-YAG laser system (1064 nm). The LDT of UGA was determined utilizing the relation,

$$\text{Power density } (P_d) = E / \tau A \quad (GW/cm^2) \qquad \text{-------} \ (10)$$

The computed LDT value of UGA is 3.617 GW/cm^{2}and it possesses higher value in comparison with KDP and urea (0.20 GW/cm^2 and 1.50GW/cm^2) [28]. This larger LDT value of UGA authenticates its aptness in the field of laser applications [29]. Table 5 shows some LDT values of other organic crystals.

Table 5. Comparison chart of UGA with Urea and related crystals

Material	Laser Damage Threshold values (GW/cm^2)	References
Urea	1.5	[28]
L -Valinium L -Valine chloride	2.59	[30]
Benzimidazole	2.9	[31]
Urea Glutaric acid	3.617	**Present Work**

3.7 TG/DTA Analysis

Thermal analysis is one of the substantial criteria for examining thermal stability, decomposition, mass change and melting point of the material. The thermal behavior of the

grown crystal was studied using TG/DTA analyses at the temperature ranges from 30-500˚C using NANO TECHNOLOGY-MODEL 6200 thermal analyzer in N_2 atmosphere at a thermal rate of 20˚C/min to study its thermal stability. The noted TG and DSC graph is shown in Fig. 10. From the TG profile, the major weight loss (98.82 %) was observed at 137.69 ^{0}C. The sharp peak observed at 137.69 ^{0}C in DSC curve shows the decomposition of the material. The weight loss starts at 137.69 ^{0}C (5.969 mW/mg) and second stage at 181.2 ^{0}C (2.009 mW/mg) further it down to zero weight. The loss in weight is mainly due to the ejection of water present in the material [32]. This shows the stability of UGA is up to 137.69 ^{0}C and beyond this limit it undergoes decomposition.

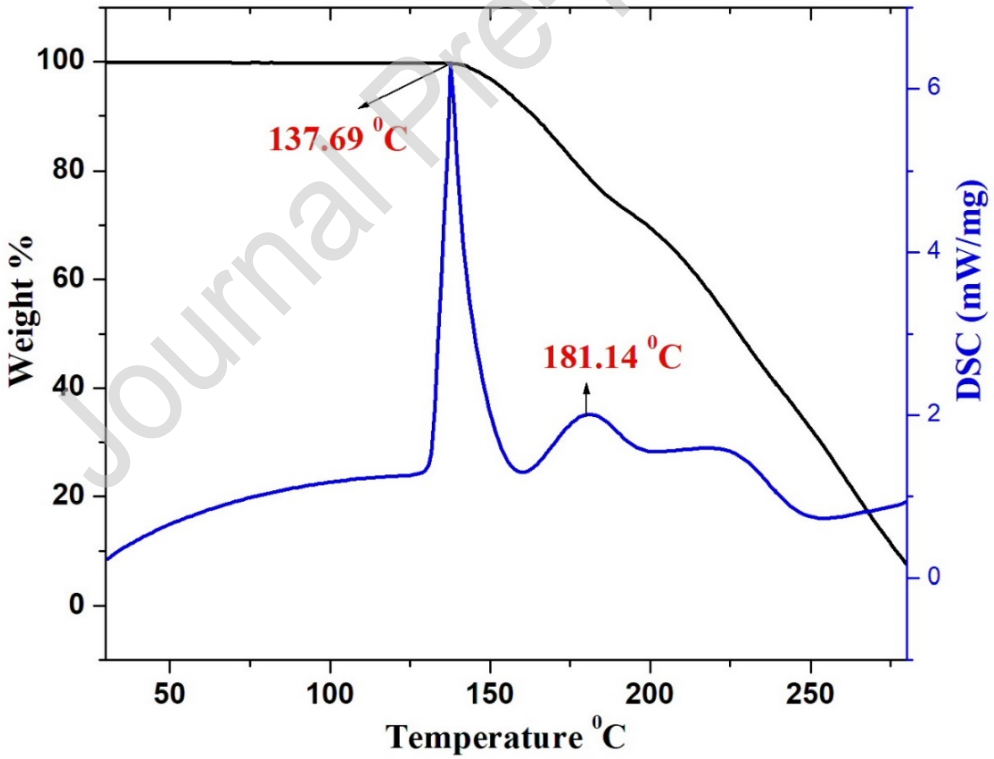

Fig 10. TG/DSC curve for UGA crystal

3.8 Micro hardness Analysis

The strength and hardness of the organic compounds are most decisive to regulate the potentiality of the material in the electronic and optical device fabrication. The mechanical strength was determined by the Vickers microhardness test for cutting and polishing the crystal. In support to study the mechanical stability of the present material Vickers microhardness analysis was done. Highly transparent pure crystals were subjected to indentations with different loads with the duration of 10 s. The microhardness value (H_v) was evaluated using,

$$H_v = 1.8544 \frac{P}{d^2} \left(kg / mm^2 \right) \qquad \text{--------(11)}$$

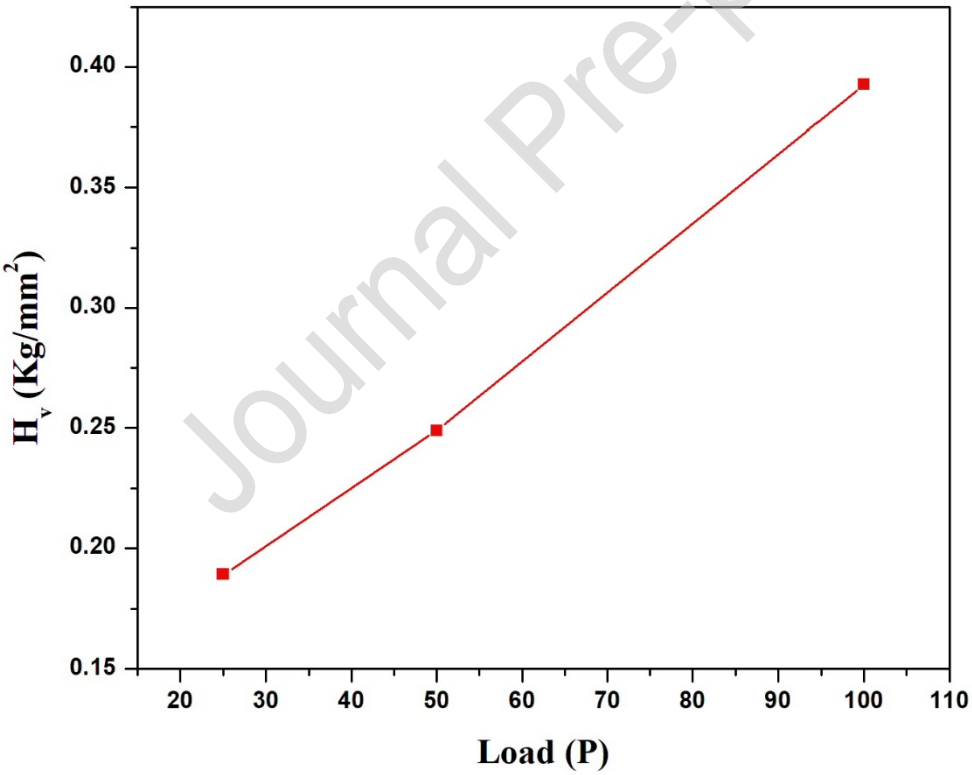

Fig 11. Variation of load P verses H_v for UGA crystal

It is noticed from the Fig.11, that H_v value raises on applying the load substantiates high mechanical strength of UGA crystal. Fig. 12 declares the work hardening coefficient (n = 4.12) highlights that UGA material is soft [33].

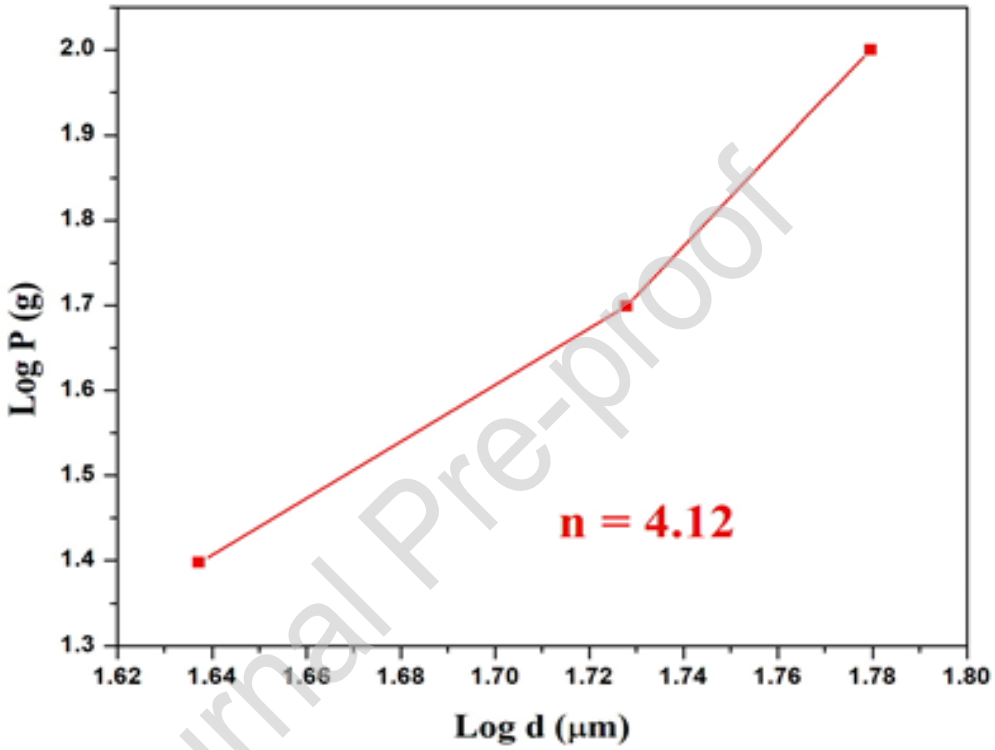

Fig 12. Variation of log d verses log P for UGA crystal

3.9 Dielectric studies

The various parameters from dielectric analysis correlates the electro and optic properties of the materials [25]. The dielectric constant and loss based on frequency and temperature was studied to gain more evidence about the structural variations, flaw behavior and the phenomena of transport.

The dielectric permittivity of the material has been formulated using the relation,

$$\varepsilon = Cd/A\varepsilon_0 \qquad \text{-------} \qquad (12)$$

where C indicates capacitance, d denotes thickness and A be the area of the sample and ε_0 indicates the permittivity of free space. Fig 13(a,b) shows the variation of dielectric constant and loss verses frequency at several temperatures. From the graph it is pointed that the dielectric permittivity lowers as the frequency raises and almost remains same over a wide range of frequencies. The overlapping of the curve for different range of temperatures indicates the occurrence of similar mechanism throughout. The low dielectric loss at greater frequency shows good optical property with few defects present in UGA crystal and is more suited for nonlinear optics.

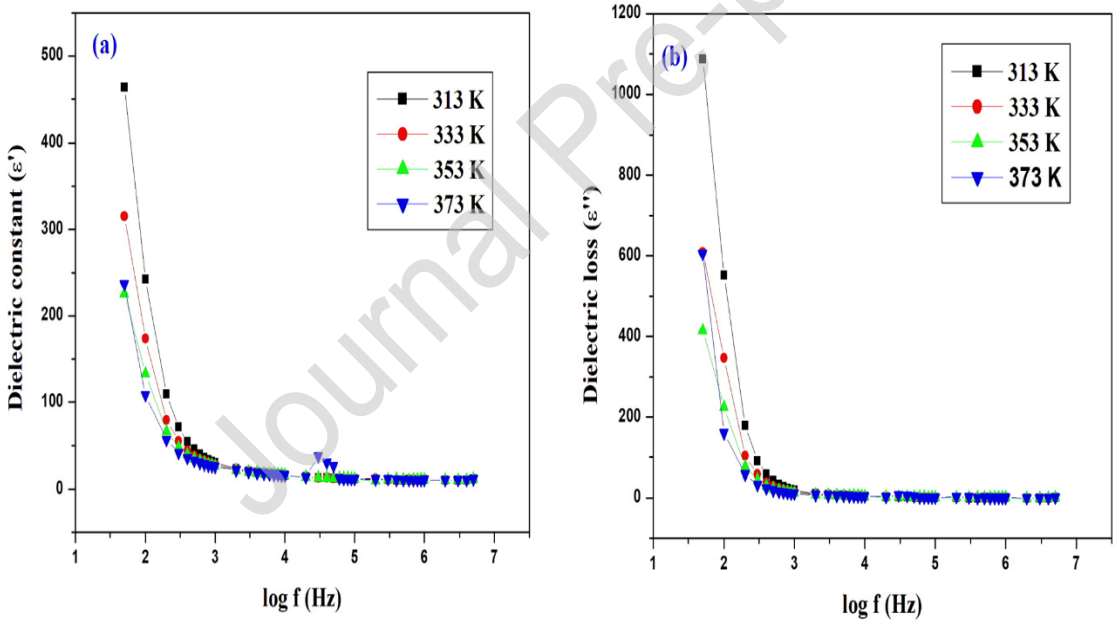

Fig 13. Variation of log F verses (a) Dielectric constant (b) Dielectric loss

4. Conclusion

In this present analysis, an optically transparent third order organic crystal Urea- Glutaric acid (UGA), was harvested successfully. The grown material undergoes various characterizations and the results were reported. The single crystal XRD elucidates the monoclinic structural symmetry with the space group of C2/c and the corresponding lattice parameters were also determined. The various vibrational modes were predicted from IR and RAMAN spectrum. The absorbance spectrum shows good transparency with the broad gap of 5.46 eV with the wavelength down to 240 nm. The NLO behavior has been confirmed from the Z-scan analysis which notifies the strong defocussing nature and negative nonlinearity. The crystal has maximum absorption peak at 481 nm in the electronic absorption spectrum and its life time was appraised. The TG/DSC curve confirms that the crystal is stable upto 137.69 ^{0}C favors in the fabrication of photonic device. The various characteristics estimated from hardness analysis supports the good mechanical stability. The dielectric constant and loss for different range of frequencies suggests that UGA is more favorable in the field nonlinear applications. From the results discussed, it is settled that UGA is a suitable applicant for future photonics and opto electronic device fabrications.

References

[1]. M. Shakir, B. Riscob, K.K. Maurya, V. Ganesh, M.A. Wahab, G. Bhagavannarayana, Unidirectional growth of L-asparagine monohydrate single crystal: first time observation of NLO nature and other studies of crystalline perfection, optical, mechanical and dielectric properties, J. Cryst. Growth 312 (2010) 3171 – 3177.

[2]. C. Zhang, Z. Li, H. Cong, J. Wang, H. Zhang, R.I. Boughton,Crystal growth and thermal properties of Single Crystal Monoclinic NdCOB ($NdCa_4O(BO_3)_3$), J. Alloys compd. 507 (2010) 335 – 340.

[3]. R. Sankar, C. M. Raghavan, R. Mohan kumar, R. Jayavel, Growth and Characterization of a new semiorganic nonlinear optical Thiosemicarbazide Cadmium Chloride Monohydrate ($Cd(NH_2NHCSNH2)Cl_2.H_2O$) single crystals, J. Cryst. Growth 305 (2007) 156 – 161.

[4]. K. Russel Raj, P. Murugakoothan, Effect of CO^{2+} on the growth and physical properties of potential nonlinear optical l-Asparaginium picrate crystal, optik 124 (2013) 2696 – 2700.

[5]. T.M. Kolev, D.Y. Yancheva, S.I. Stoyanov, Synthesis and Spectral Elucidation of Some Pyridinium Be- taines of Squaric Acid Potential Materials for Nonlinear Optical Applications, Advanced Functional Materials, 14(2004) 799 – 805.

[6]. A. Rathika, R. Ganapathi Raman, Growth and characterization of an efficient nonlinear optical single crystal: Urea p-nitrophenol, Optik - International Journal for Light and Electron Optics, 125 (2014) 2978-2982.

[7]. R.N. Jayaprakash, P. Kumaradass**,**Growth and characterization of Urea L-valine, an organic nonlinear optical single crystal, Oriental journal of chemistry, an international research journal of pure and applied chemistry, Vol. 29, ISSN: 0970-020 X,ONLINE ISSN: 2231-5039.

[8]. B.K. Singh, N.Sinha, N.Singh, K.Kumar, M.K.Gupta , Binaykumar, Structural, dielectric, optical and ferroelectric property of urea succinic acid crystals grown in aqueous solution containing maleic acid, Oriental Journal of Chemistry Journal of Physics and Chemistry of Solids 71 (2010) 1774–1779.

[9]. B. Riscob,M. Shakir, J.K. Sundar, S. Natarajan, M. A. Wahab, G. Bhagavannarayana Synthesis, growth, crystal structure and characterization of a new organic material: glycine glutaric acid, Spectrochim. Acta. A, Mol. Biomol. Spectrosc., 78 (2010) 543-548.

[10]. Veneta Videnova-Adrabinska,Pre-designed Structural Building Blocks of a (1:1) Urea-Glutaric. Acid Co-crystal, J. Mater. Chem., 5 (1995) 2309-2311.

[11]. S. Boomadevi, R. Dhanasekaran, P. Ramasamy, Investigations on nucleation and growth kinetics of urea crystals from methanol, Cryst. Res. Technol. 37 (2002) 159–168.

[12]. Veneta Videnova Adrabinska, Margaret C. Etter, Urea-glutaric acid (2∶1) structural aggregates as building blocks for crystal engineering, Journal of chemical crystallography, 25 (1995)12.

[13]. G. Socrates, Infrared characteristic group of frequencies, John Wiley and sons, New York, (1980).

[14]. K. Nakamoto, IR spectra of Inorganic and coordination compounds, 2nd ed., Wiley Interscience , New York, 1978.

[15] S. Gunasekaran, G. Anand, R. Arun Balaji, J. Dhanalakshmi, S. Kumaresan, Crystal growth and comparison of vibrational and thermal properties of semi-organic nonlinear optical materials,Indian Academy of science, PRAMANA Journal of Physics, 75 (2010)683-690.

[16] M. Peer Mohamed, P. Jayaprakash, M. Nageshwari, C. Rathika Thaya Kumari, P. Sangeetha, S. Sudha, G. Mani, M. Lydia Caroline, Crystal growth, structural, spectral, thermal, linear and nonlinear optical characterization of a new organic nonlinear chiral compound: L-tryptophan-fumaric acid-water (1/1/1) suitable for laser frequency conversion, J. Mol. Struct. 1141 (2017) 551–562.

[17] J. Tauc, Amorphous and liquid semiconductors, J. Tauc Edition, Plenum, New York (1974).

[18] M. Peer Mohamed, S. Sudha, M. Nageshwari, P. Jayaprakash, P. Sangeetha, M. Prakash, M. Lydia Caroline, Growth and Characterization of Chloro Bis Thiourea Mercury (II) Chloride (CBTMC) Grown by Slow Evaporation Technique for Nonlinear Optical Applications, Recent trends in material science and applications, Springer Proc. Phys. 189, doi: 10.1007/978-3-319-44890-948.

[19] F. Urbach, The long-wavelength edge of photographic sensitivity and of the electronic absorption of solids, Phys. Rev. 92 (1953) 1324.

[20] P. Jayaprakash, M. Peer Mohammed, M. Lydia Caroline, Growth, spectral and optical characterization of a novel nonlinear optical organic material: D-Alanine DL-Mandelic acid single crystal, J. Mol. Struct., 1134 (2017) 67-77.

[21] C. Rathika Thaya Kumari, M. Nageshwari, P. Jayaprakash, P. Sangeetha, S. Sudha, M. Lydia Caroline, Investigation on growth, optical, thermal, mechanical, dielectric, LDT studies of sulphanilic acid monohydrate: A promising third order nonlinear optical material, J. Nonlinear Optic. Phys. Mat., 26 (2017)1750020.

[22] C. Rathika Thaya Kumari, P. Jayaprakash, M. Nageshwari, M. Peer Mohamed, P. Sangeetha and M. Lydia Caroline, Growth, optical, photoluminescence, dielectric, second and third order nonlinear optical studies of benzoyl valine acentric crystal, Molecular Crystals and Liquid Crystals, 658(2017) 186 – 197.

[23] A. Shanthi , C. Krishnan, P. Selvarajan, Growth and characterization of a single crystal of Urea Adipic acid (UAA)-a third order nonlinear optical material, Spectrochim. Acta A Mol Biomol Spectrosc.,122 (2014) 521-528.

[24]. M. Nageshwari, C. Rathika Thaya Kumari, G. Vinitha, M. Peer Mohamed, S. Sudha, M. Lydia Caroline, Crystal growth, structural, spectral, thermal, dielectric,linear and nonlinear

optical characteristics of a new organic acentric material: L-Methionine Succinic acid (2/1), J. Mol. Struct., 1155 (2018) 101–109.

[25]. P. Jayaprakash, P. Sangeetha, M. Peer Mohamed, G. Vinitha, S. Muthu, M. Prakash , M. Lydia Caroline, Growth and characterization of DL-Mandelic acid ($C_6H_5CH(OH)CO_2H$) single crystal for third-order nonlinear optical applications, J. Mol. Stru., 1148 (2017) 314 -321.

[26]. P. Sangeetha, P. Jayaprakash, M. Nageshwari, C. Rathika Thaya Kumari, S. Sudha, M. Prakash, G. Vinitha, M. Lydia Caroline, Growth and characterization of an efficient new NLO single crystal L-phenylalanine D-methionine for frequency conversion and optoelectronic applications, Phys. B, 525 (2017) 164-174.

[27] G. C. Bhar, A. K. Chaudhary, P. Kumbhakar. Study of laser induced damage threshold and effect of inclusions in some nonlinear crystals,Applied Surface Science, 161(2000) 155–162.

[28] S.A. Martin Britto Das, S. Natarajan,Growth and characterization of L-prolinium tartrate – A new organic NLO material.Cryst. Res. Technol. 42 (2007) 471 – 476.

[29].V. Sangeetha, K. Gayathri, P. Krishnan, N. Siva Kumar, N. Kanagathara, C. Anbalagan, Growth, optical, thermal, dielectric and microhardness characterization of melaminium bis (tri fluoro acetate) tri hydrate single crystal, J. Cryst.Growth, 389 (2014) 30–38.

[30]. M. Nageshwari, P. Jayaprakash, C. Rathika Thaya Kumari, G. Vinitha, M. Lydia Caroline, Growth, spectral, linear and nonlinear optical characteristics of an efficient semiorganic acentric crystal: L-valinium L-valine chloride, Phys. B, 511 (2017) 1-9.

[31]. N. Vijayan, G. Bhagavannarayana, K. R. Ramesh, R. Gopalakrishnan, K. K. Maurya, P. Ramaswamy,A Comparative Study on Solution- and Bridgman-Grown Single Crystals of Benzimidazole by High-Resolution X-ray Diffractometry, Fourier Transform Infrared,

Microhardness, Laser Damage Threshold, and Second-Harmonic Generation Measurements, Cryst. Growth. Des.,6 (2006) 1542–1546.

[32]. R. Shantha kumari, K. Ramamurthi, Structural, thermal and optical characterization of an organic NLO material—Benzaldehyde thiosemicarbazone monohydrate single crystals, Spectrochim. Acta A, 78 (2011) 653-659.

[33]. E.M. Onitsch,The present status of testing the hardness of materials,Mikroskopie95 (1956) 12-14.

Conflict of Interest Form

- All authors have participated in (a) conception and design, or analysis and interpretation of the data; (b) drafting the article or revising it critically for important intellectual content; and (c) approval of the final version.

- This manuscript has not been submitted to, nor is under review at, another journal or other publishing venue.

- The authors have no affiliation with any organization with a direct or indirect financial interest in the subject matter discussed in the manuscript