Asian Journal of Chemistry; Vol. 33, No. 5 (2021), 1085-1089

ASIAN JOURNAL OF CHEMISTRY

https://doi.org/10.14233/ajchem.2021.23130

Growth, Experimental Studies and DFT Calculations on Gallic acid 5-Nitrouracilate Single Crystals for Non-linear Optical Applications

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Received: 21 January 2021; *Accepted*: 1 March 2021; *Published online*: 16 April 2021; AJC-20328

The growth and characterization of gallic acid 5-nitrouracilate (GA5NU) single crystals were grown using slow evaporation solution growth technique at room temperature. Single crystal XRD analysis revealed that the grown crystal belongs to monoclinic crystal system. HOMO-LUMO and molecular electrostatic potential (MEP) has been visualized and analyzed. The presence of various functional groups present in the host material was examined using FTIR spectra. Mechanical stability of the grown crystal is validated using Vickers microhardness study and the grown crystal belongs to soft material category. Various hardness parameters like fracture toughness, brittleness index, elastic stiffness constant, tensile strength and other hardness parameters were also calculated. Thermal stability of the grown crystal was also determined. The second harmonic generation (SHG) efficacy of grown crystal was 2.97 times higher than potassium dihydrogen phosphate (KDP), which makes the grown crystal as suitable candidate material for non-linear optical applications.

Keywords: NLO single crystal, Gallic acid 5-Nitrouracilate, DFT calculations, Mechanical studies, Thermal analysis.

INTRODUCTION

The unforeseen advances in the area of non-linear optics have been revolutionized in the field of optical memory storage devices, production of display technologies and telecommunications. In contrast with inorganic host, organic materials exhibit massive nonlinear optics (NLO) response due to the presence of active π-bonds. The π-electron mechanism in organic host asymmetrized by electron acceptor and donor group is extensively polarizable entities for NLO applications [1,2]. 3,4,5-Trihydroxybenzoic acid is termed as gallic acid and it's an organic compound present in variety of herbs and foods [3,4]. Other than antioxidant and anticancer properties [5], it also has medicinal applications for allergic diseases like allergic rhinitis, sinusitis, asthma owing to its ability to hinder the histamine release and the production of anti-inflammatory cytokines [4,6]. Three hydroxyl group of this acid having both hydrogen bonding acceptor and donor characteristics. In addition to that, O–H part of this group has strong hydrogen bonded donor groups while C=O section of carboxylic acid category has strong hydrogen bonded acceptor properties [7,8]. The present material researchers started to focus on 5-nitrouracil due to its immense number of applications in the pharmaceutical fields [9,10]. In present work, the computational (DFT), structural, spectral, dielectric, thermal, microhardness and powder second harmonic generation (SHG) properties of gallic acid 5-nitrouracilate crystals (GA5NU) are reported.

EXPERIMENTAL

Synthesis: Commercially available gallic acid ($C_7H_6O_5$) (TCI, 99%) and 5-nitrouracil ($C_4H_3N_3O_4$) (Sigma-Aldrich, 99%) were taken in equimolar ratio (1:1) and the mixture is dissolved in double distilled water and allowed the solution for constant stirring of about 8 h. After stirring, the as-synthesized solution was filtered using Whatmann filter paper to elude the insoluble particles and the upper part of the beaker was sealed with perforated sheet with tiny holes, kept the beaker undisturbed for slow evaporation. After successive recrystallization process, white coloured good quality crystals were

harvested within a time span of 35-40 days and the photograph of as-synthesized crystal is shown in Fig. 1.

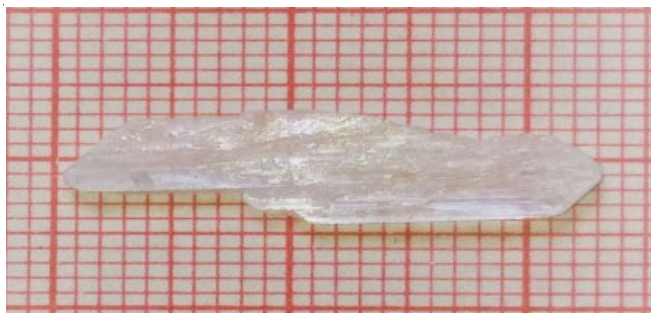

Fig. 1. Photograph of as-grown GA5NU crystal

RESULTS AND DISCUSSION

Single crystal XRD analysis: The lattice parameters and space group of the grown crystal is determined using single crystal XRD analysis. The grown crystal belongs to monoclinic crystal system with $P2_1/m$ space group and the crystal refinement data is shown in Table-1.

TABLE-1
CRYSTAL STRUCTURE AND REFINEMENT FOR GA5NU CRYSTAL

Empirical formula	$C_{11}H_9N_3O_9$
Molecular weight	159.22
Temperature	274 (2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, $P2_1/m$
Unit cell dimensions	a = 7.4581(6) Å; α = 90°
	b = 9.3526(3) Å; β = 92.251(3)°
	c = 12.8457(9) Å; γ = 90°
Volume	173.18(9) Å^3
Z, Calculated density	7, 1.457 Mg/m^3

Computational details: The theoretical calculations were completed by Gaussian 09 program on Intel Pentium dual core with the 1.80 GHz processor and demonstrated with Gauss view 6.0. The fundamental errand of computational calculations was to build an enhanced structure with least energy. The result of this run yields with minimum energy was -834.65815 a.u. The estimation was performed utilizing Beckee exchange potential (B3LYP) method under the basis set 6-311++G(d,p) because of its simplicity with minimum time consumption.

HOMO-LUMO: The ability to add an electron is mentioned as HOMO while the ability to acquire and electron is expressed by LUMO energy. The eigen value of HOMO and LUMO and their energy gap reflect the chemical activity of the molecule. The calculated energies of GA5NU molecules are E_{HOMO} = -0.23963 a.u., E_{LUMO} = -0.18469 a.u. and ΔE = 0.05524 a.u. (Fig. 2). Using Koopman's theorem, other electrical transport properties like electron affinity (A), chemical hardness (η) and other properties are listed in Table-2.

Molecular electrostatic potential (MEP) analysis: This study explains about the nature of reaction mechanism among the molecules, *i.e.* electrophilic and nucleophilic conditions.

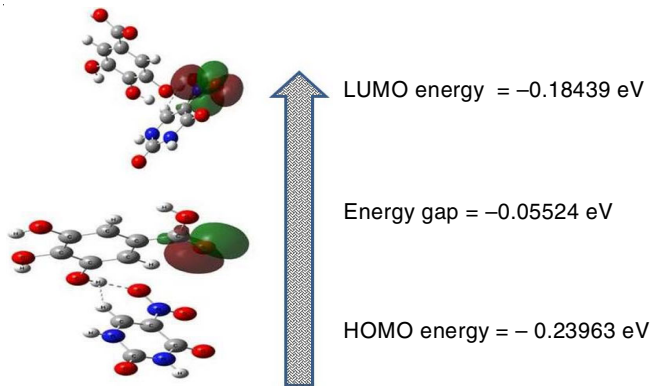

Fig. 2. HOMO-LUMO structure of GA5NU crystal

TABLE-2
LIST OF PARAMETERS CALCULATED USING HOMO-LUMO

Molecular properties B3LYP/6-311G (d,p)	
$HOMO_{energy}$	-0.23963
$LUMO_{energy}$	-0.18439
$HOMO\text{-}LUMO_{energygap}$	-0.05524
Ionization potential (I)	0.23963
Electron affinity (A)	0.18439
Chemical hardness (η)	0.02762
Reciprocal of hardness (S)	18.10282
Chemical potential (μ)	-0.21201
Electronegativity (χ)	0.21201
Electrophilicity index (ω)	0.81369
Nuclcofugality (ΔE_n)	0.6156
Electrofugality (ΔE_e)	1.0432

The MEP map of GA5NU single crystal is shown in Fig. 3. The colour code of MEP ranges from -1.213 × 10^{-2} to 1.213 × 10^{-2} by using Gaussview 6.0 program with DFT/6-311++ G(d,p). The electrostatic potential distribution of colour is increased in the order of red < orange < yellow < green < cyan < blue. The most positive area is called nucleophilic site and represented by the blue region. For GA5NU crystal, around hydrogen atom present in the molecule have more positive region which is appeared by blue colour (proton acceptor) nearest to the oxygen atom indicates the negative region of the molecule as shown by red colour (electron acceptor). The coloured region of the structure was recognized by electron and proton interactions, which shows good NLO reactivity of the compound.

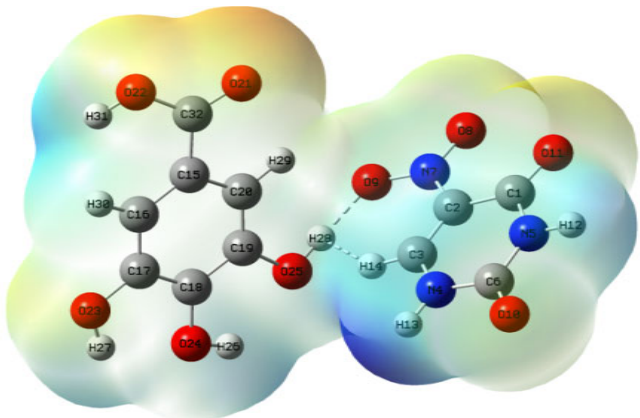

Fig. 3. MEP analysis of GA5NU molecule

FTIR spectra: FTIR spectral analysis was performed using Perkin-Elmer FTIR spectrometer in the wavelength range 4000 and 500 cm^{-1} and the obtained spectra is shown in Fig. 4. The strong, broad peak inferred at 3452 cm^{-1} is due to intermolecular bonded O–H stretching. The weak peak arises at 3052 cm^{-1} is due to intramolecular bonded O–H stretching. Small medium peak occurs at 2649, 2813 cm^{-1} occurs due to C–H stretching. A small peak at 2011 cm^{-1} is due to C–H bending. Various spectral assignments are given in Table-3.

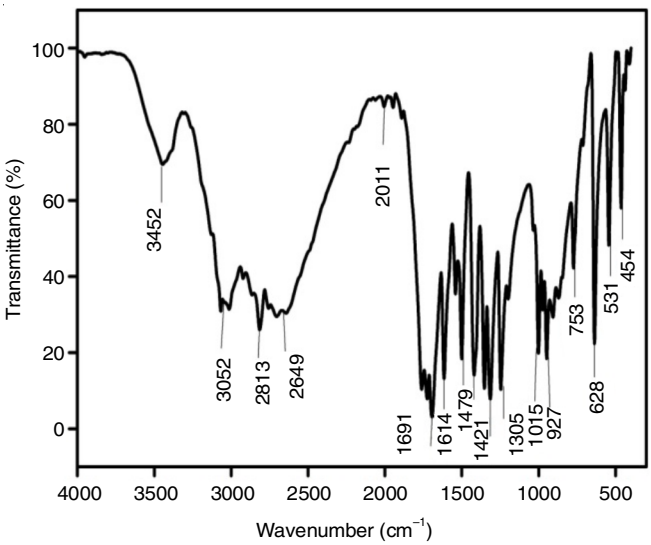

Fig. 4. FTIR spectra of GA5NU

TABLE-3
VIBRATIONAL FREQUENCIES OF GA5NU CRYSTAL

FTIR	Assignments
3452	O–H stretching
2813	C–H stretching
1691	C=O stretching
1614	C=C stretching
1305	O–H bending
1015	C–N stretching
927	C=C bending
753	1,2-disubstituted C-H bending

Mechanical study: The hardness test was carried out using Futuretech FM 800 type E series for constant indentation period of 10 s and diagonal length 'd' is measured for varying loads 'P'. Variation of H_v against load P is shown in Fig. 5 and plot of log P *vs*. log d (Fig. 6) yields straight line and the slope gives work hardening coefficient 'n' and the value of n is found out to be 2.14 and the grown crystal comes under soft material category. According to reverse indentation size effect (RISE) the hardness value increases with increasing loads and in normal indentation size effect (ISE), H_v value decrease with increasing loads [11-13].

The elastic stiffness constant (C_{11}) was calculated using eqn. 1 [14]:

$$\text{Wooster empirical relation } C_{11} = (H_v)^{7/4} \quad (1)$$

Brittleness index (B_i) is another property of mechanical behaviour is calculated using eqn. 2:

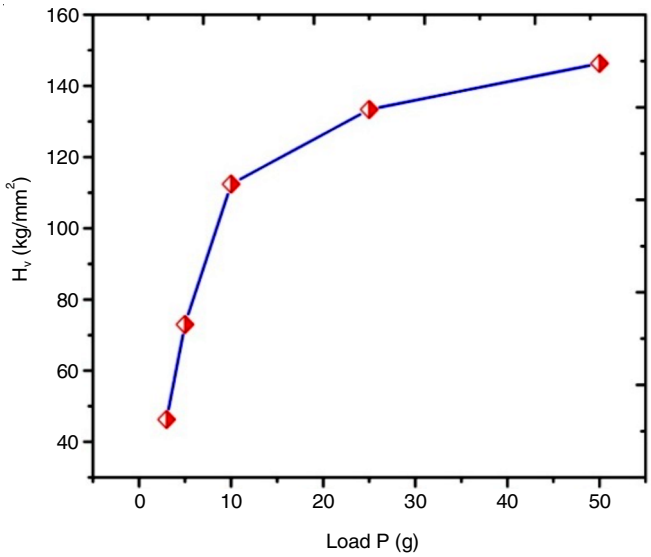

Fig. 5. Plot of H_v *vs.* load P

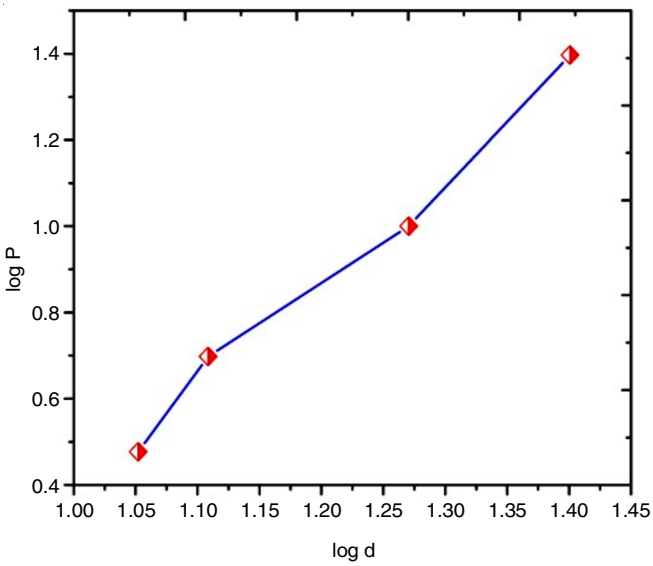

Fig. 6. Plot of log P *vs.* log d

$$B_i = \frac{H_v}{K_c} \quad (2)$$

where 'K_c' is coined as fracture toughness and it is calculated using eqn. 3 [15]:

$$K_c = \frac{P}{\beta c^{3/2}} \quad (3)$$

The value of $\beta = 7$ for Vicker's indenter, c is known as crack length and it is measured from the midpoint of the indentation mark to the tip of crack.

The tensile strength of the crystal (T) and yield point (Y) was calculated using the following relations [16]:

$$\text{Tensile strength (T)} = 0.2\ H_v + 6 \quad (4)$$

$$\text{Yield point (Y)} = 0.23\ H_v - 13.5 \quad (5)$$

The mechanical parameters such as K_1, K_2, H_v, K_c, B_i, σ_v and C_{11} obtained for grown crystal are given in Table-4.

TABLE-4
CALCULATED HARDNESS
PARAMETERS OF GA5NU CRYSTAL

Parameters	Values
n	2.14
K_1 (kg mm^{-1})	0.0535
K_2 (kg mm^{-1})	1.146
H_v (kg m m^{-2})	102.278
K_c (MN m$^{-3/2}$)	0.3134
B_i (m$^{-1/2}$)	31.104
$C_{11} \times 10^{14}$ Pa	61.796
σ_v (M Pa)	72.458
Tensile strength T (M Pa)	116.24
Yield point Y (M Pa)	18.72

Thermal analysis: TG-DTA thermogram was carried out in nitrogen atmosphere and recorded at a heating rate of 20 ºC/min. There was a sharp weight loss at 240 ºC, which is attributed to the decomposition of grown crystal (Fig. 7). Below the onset of decomposition, no significant weight loss was observed hence the crystal is completely free from physically adsorbed water. DTA trace indicates an intense sharp endothermic, covering the temperature range 240 to 260 ºC and it is interesting to note the absence of any exotherm/endotherm process occured below > 240 ºC. From thermal analysis, it was also observed that decomposition occurs in successive steps but the process of disintegration is very slow process [17,18]. Hence, the grown material is capable for NLO applications upto 240 ºC.

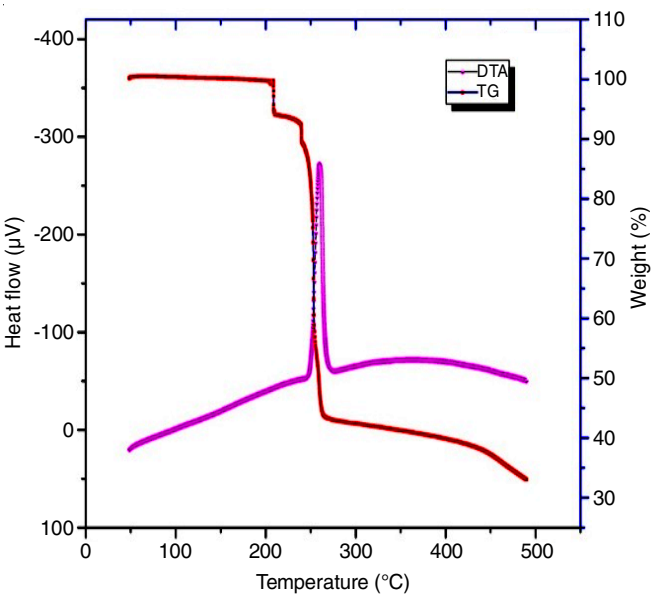

Fig. 7. TG/DTA curve of the GA5NU crystal

SHG analysis: GA5NU frequency doubling efficacy was determined using Kurtz and Perry powder technique. The sample was irradiated to Q-switched Nd:YAG laser of wavelength 1064 nm, 10 ns pulse width. SHG signal emitted at 532 nm was separated from the fundamental frequency by using IR separator. From the detectors coupled to read output energy, the peak intensity was observed to be 2.97 times higher than that of urea. The SHG efficacy of grown crystal is in comparison with other reported crystals (Table-5).

Conclusion

The gallic acid 5-nitrouracilate crystals (GA5NU) single crystal was synthesized using slow evaporation solution growth method. The SXRD analysis substantiates the grown crystal belongs to monoclinic crystal system with space group $P2_1/m$. The presence of various functional groups present in the host material was affirmed by FTIR analysis. From Vicker's microhardness study, the mechanical strength of the grown crystal was determined and exhibits a reverse indentation size effect. From thermal analysis, it was evident that the grown material is capable for NLO applications upto 240 ºC. The SHG efficacy is 2.97 times higher than standard KDP.

ACKNOWLEDGEMENTS

One of the authors, (S. Arulmani) thanks the University Grants Commission), India for the award of Senior Research Fellowship (SRF) (201516-RGNF-2015-17-SC-TAM-23685).

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

1. S.M. Sharipova and A.A. Kalinin, *Chem. Heterocycl. Comp.*, **53**, 36 (2017); https://doi.org/10.1007/s10593-017-2017-9
2. A. Driessen, Nonlinear Optics for the Information Society, Springer (2007).
3. S. Kiokias, C. Proestos and V. Oreopoulou, *Foods*, **9**, 534 (2020); https://doi.org/10.3390/foods9040534
4. B. Badhani, N. Sharma and R. Kakkar, *RSC Adv.*, **5**, 27540 (2015); https://doi.org/10.1039/C5RA01911G
5. M. Daglia, A. Di Lorenzo, S.F. Nabavi, Z.S. Talas and S.M. Nabavi, *Curr. Pharm. Biotechnol.*, **15**, 362 (2014); https://doi.org/10.2174/1389201015041408251207 37
6. S. Choubey, S. Goyal, L.R. Varughese, V. Kumar, A.K. Sharma and V. Beniwal, *Mini-Rev. Med. Chem.*, **18**, 1283 (2018); https://doi.org/10.2174/1389557518666180330114010
7. R. Kaur, S. Cherukuvada, P.B. Managutti and T.N.G. Row, *CrystEngComm*, **18**, 3191 (2016); https://doi.org/10.1039/C5CE01965F
8. K.L. Jyothi, R. Gautam, D. Swain, T.N. Guru Row and N.K. Lokanath, *Cryst. Res. Technol.*, **54**, 1900016 (2019); https://doi.org/10.1002/crat.201900016

TABLE-5
COMPARISON OF SHG EFFICIENCY WITH OTHER REPORTED CRYSTALS

Crystal	SHG efficiency	Ref.
Gallic acid 5-nitrouracilate (GA5NU)	2.97	Present work
4-*N*,*N*-Dimethylamino-4'-*N*'-methyl-stilbazolium 2,4,6-trimethylbenzenesulfonate (DSTMS)	2.20	[19]
N-Benzyl-2-methyl-4-nitroaniline (BNA)	2.25	[20]
6-Methyl nicotinic acid (6MNA)	2.00	[21]
4-Hydroxy tetramethylpiperazinium picrate (TMPP)	1.50	[22]

9. R.M. Shaker, M.A. Elrady and K.U. Sadek, *Mol. Divers*., **20**, 153 (2016); https://doi.org/10.1007/s11030-015-9595-1
10. E. Colacino, G. Sindona, G. Gosselin and C. Mathé, *Nucleos., Nucleot. Nucleic Acids*, **22**, 2013 (2003); https://doi.org/10.1081/NCN-120026403
11. P.S.L. Mageshwari, R. Priya, S. Krishnan, V. Joseph and S.J. Das, *Opt. Laser Technol.*, **85**, 66 (2016); https://doi.org/10.1016/j.optlastec.2016.06.002
12. S. Krishnan, C.J. Raj, R. Robert, A. Ramanand and S.J. Das, *Cryst. Res. Technol.*, **42**, 1087 (2007); https://doi.org/10.1002/crat.200710981
13. D.A. Kumar, R.S. Babu and S. Kalainatha, *Opt. Mater.*, **109**, 110286 (2020); https://doi.org/10.1016/j.optmat.2020.110286
14. W.A. Wooster, *Rep. Prog. Phys.*, **16**, 62 (1953); https://doi.org/10.1088/0034-4885/16/1/302
15. M.P. Nancy, J.R. Priya and J.M. Linet, *J. Mater. Sci. Mater. Electron.*, **31**, 8144 (2020); https://doi.org/10.1007/s10854-020-03265-2
16. D. Sivavishnu, R. Srineevasan and J. Johnson, *Mater. Sci. Energy Technol*., **1**, 205 (2018); https://doi.org/10.1016/j.mset.2018.08.004
17. J. Arumugam, M. Selvapandiyan, S. Chandran, M. Srinivasan and P. Ramasamy, *Appl. Phys., A Mater. Sci. Process.*, **126**, 888 (2020); https://doi.org/10.1007/s00339-020-04077-1
18. K. Senthil, K. Elangovan, A. Senthil and G. Vinitha, *Spectrochim. Acta A Mol. Biomol. Spectrosc.*, 247, 119063 (2021); https://doi.org/10.1016/j.saa.2020.119063
19. T.H. Wang, L. Cao, D. Zhong, J. Liu, F. Teng, S. Ji, S. Sun, J. Tang and B. Teng, *CrystEngComm*, **21**, 2754 (2019); https://doi.org/10.1039/C9CE00150F
20. R. Kalaivanan and K. Srinivasan, *Opt. Laser Technol.*, **90**, 27 (2017); https://doi.org/10.1016/j.optlastec.2016.11.001
21. S. Delphine, A.R.S.J. Rani Juliet, S. Janarthanan and R.S. Samuel, *Opt. Laser Technol.*, **90**, 133 (2017); https://doi.org/10.1016/j.optlastec.2016.11.013
22. T. Dhanabal, G. Amirthaganesan, M. Dhandapani and S.K. Das, *J. Chem. Sci.*, **124**, 951 (2012); https://doi.org/10.1007/s12039-012-0289-2