



Review Article – Physics

Spectroscopic, thermal, second order and third order NLO studies of N, N' -dimethyl urea crystal

U. Rajesh Kannan^{1*}, G.Narayanasamy¹, S. Subramanian², P. Selvarajan³

¹Department of Physics, Kamaraj College, Tuticorin-628003, Tamilnadu, India.

²Department of Physics, MDT Hindu College, Tirunelveli- 627010, Tamilnadu, India.

³Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628216, Tamilnadu, India.

(Received: 21-12-2017; Accepted 19-01-2018; Published Online 23-01-2018)

*Corresponding author

Abstract

Nonlinear optical (NLO) crystals are classified into organic, inorganic and semi organic crystals and these crystals are used in the fields of optical communication, optical computing, frequency doubling, optical data processing and opto electronics. In this work an organic NLO crystal namely DMU crystal was prepared. Slow evaporation technique was adopted to grow the single crystals of DMU after the growth period of 35 days. The harvested crystals have been subjected to various characterization techniques like XRD, FTIR, FT-Raman, TG/DTA, SHG, EDAX, impedance, optical and Z-scan studies. From the studies, is observed that DMU crystal has orthorhombic structure and it has the melting point at 105 °C and has the decomposition point at 275 °C. The relative SHG efficiency of DMU crystal was found to be more than one and third order NLO parameters were evaluated. The optical band gap of DMU crystal was found to be 5.008 eV. The results from various studies were analyzed.

Keywords: Solution method, XRD, NLO, FTIR, FT-Raman, SHG, EDAX, TG/DTA, Impedance, Z-Scan, Spectroscopy

Introduction

The crystals are grown to understand their scientific and technological usefulness. Many new organic crystals have been found based on the predictive molecular engineering approach and have been shown to have potential applications in nonlinear optics and these materials find wide application in telecommunication, frequency mixing, optical parametric oscillation, optical bi-stability, optical image processing and under water communication etc [1-4]. The advantage of the organic materials is that they offer high degree of synthetic flexibility to tailor their optical properties through structural modification and exhibit very high laser damage threshold. The inability of organic materials to grow to large crystal sizes impedes device fabrication. Organic materials exhibit excellent nonlinear optical (NLO) properties because of their electronic structure with π conjugated systems between donors and acceptors. This is due to non-centrosymmetry leading to huge NLO efficiency, exhibited by organic materials on the order of 10 to 100 times larger than that of inorganic NLO materials through macroscopic second order NLO response. The strong charge transfer between such groups operating across the entire extended system markedly adds to the optical nonlinearity of the structure [5-8].

Urea derivatives are notable organic compounds and some of the urea derivatives are mono methyl urea, phenylurea, urea L-malic acid and urea L-tartaric acid have been investigated for NLO applications [9-11]. 1, 3-Dimethyl urea is also a urea derivative organic compound obtained from urea by replacing two hydrogen atoms of two NH_2 groups by CH_3 groups. It has one H-donor site and two acceptor sites and it is capable of forming multiple hydrogen

bonds. It is also called as N-N'dimethyl urea (DMU) used for synthesis of caffeine, theophylline, pharmaceuticals, textile aids, herbicides and others. In the textile processing industry, it is used as intermediate for the production of formaldehyde-free easy-care finishing agents for textiles and it has NLO properties [12, 13]. Study on the effect of 1, 3 dimethyl urea doping on the properties of L-arginine phosphate monohydrate and KDP crystals have been reported [14, 15]. From the literature survey, it is observed that the various studies like XRD studies, thermal studies, impedance studies, second order and third order NLO studies, FTIR and FT-Raman studies, optical studies, EDAX studies of 1,3- dimethyl urea (N, N' dimethyl urea) crystals have not been detailed and hence this paper aims to report the various studies of title crystal here.

Materials and methods

Crystal growth

The title compound was grown in single crystal form by taking the GR grade N-N' dimethyl urea dissolved in double distilled water in an air tight container kept on the hot-plate magnetic stirrer. The solution was kept on a hot plate magnetic stirrer and stirred well for about 2 hours and by adding the salt into the solution, the saturated solution was prepared. The solubility of the solution was reduced by adding ethyl alcohol and supersaturated solution was obtained.

The solution was filtered using Whatmann filter papers twice in order to remove the unwanted suspended particles. After filtering, the solution was taken in growth vessel covered with a perforated paper for slow evaporation. Here it is to be mentioned that re-crystallization was carried out

Table 2: Powder XRD data for DMU sample

Peak No.	2θ (degrees)	Relative intensity (%)	hkl	d (Å)
1	17.7920	100	021	4.982
2	21.5704	42.49	111	4.118
3.	23.7095	46.39	020	3.751
4.	24.9680	27.70	112	3.564
5	31.2461	42.06	040	2.861
6	32.6855	7.420	041	2.739
7	36.2639	4.250	042	2.476
8	38.0631	8.010	133	2.363
9	42.7211	2.620	221	2.120
10	44.7001	4.950	151	2.026
11	46.6593	3.280	152	1.946
12	48.2785	2.610	044	1.884
13	51.4971	11.30	062	1.774
14	55.0955	2.250	153	1.666

Table 3: Observed absorption frequencies and their assignments for dimethyl urea crystal

S. No.	FTIR(cm ⁻¹)	FT-Raman (cm ⁻¹)	Band assignments
1	3352.28	-	v _{as} N-H
2	3058.81	-	NH ₂ symmetric stretching
3	2958.06	-	v _{as} CH ₃
4	2886.09	-	v _s CH ₃
5	2807.73	-	v _s CH ₃
6	2728.56	-	CH ₂ stretching
9	1638.64	1600.08	v(CO)
10	-	1524.92	δ _s (NH)
11	1423.54	1433.36	δ _s CH ₃
13	1280.40	-	v _{as} (CN) amide
14	1172.45	1141.09	ρ _{as} CH ₃
15	1043.71	1001.55	v _{as} N-H
16	935.76	-	v _s (CN)amide
17	-	897.60	v _s C-N
18	785.42	-	NO deformation
19	677.47	-	C-H out of plane deformation
20	-	313.06	δ _{as} N-H
21	-	209.10	δ _s N-H

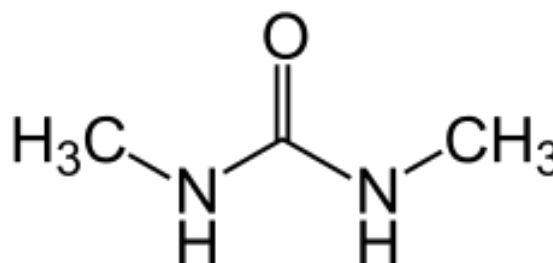
two times and after a growth period of 35 days, a very few crystals of N-N' dimethyl urea were harvested. The harvested crystal of the title compound is shown in the figure. 1 and the structural formula of DMU crystal is shown in the Figure 2.

**Fig. 1:** Photograph of the grown DMU crystal

Characterization methods

Powder XRD analysis was also carried out using a Rich Seifert diffractometer with Cu K_α (λ=1.54059 Å) radiation. A Fourier transform infrared (FTIR) spectrometer was used

to record the infrared spectrum in the wave number range 400-4000 cm⁻¹ and the model of the instrument used was Perkin Elemer RXI spectrometer.

**Fig.2:** Structural formula of DMU crystal

The FT-Raman spectrometer was used to record the FT-Raman spectrum of the sample. The absorbance spectrum was recorded using a Perkin Elemer lambda 35 UV-vis spectrophotometer in the wavelength range of 190-1100 nm. Second harmonic generation efficiency was measured using Kurtz and Perry powder technique using Nd: YAG laser [16]. Thermal analysis was carried out using SDT Q 600V 8.3 built 101 simultaneous TG/DTA analyzer in the nitrogen atmosphere. The third order NLO property of the sample crystal was investigated using Z-scan technique and in this measurement, a He-Ne laser (λ = 632.8 nm) was used as the light source and focused by a lens of 22.5 cm focal length. In order to confirm the presence of elements like carbon and

oxygen in the grown sample, the crystal was characterized by EDAX technique. In the present work an energy dispersive spectrometer (OXFORD ISIS-300 system) was used to identify the presence of the elements. The impedance properties of the sample were determined using an impedance analyzer (PSM Impedance Analyzer 1734) from 100 Hz to 1 MHz.

Results and Discussions

X-ray diffraction studies

The grown crystal of DMU was analyzed by single crystal XRD method and the relevant data were collected using a Bruker Kappa Apex II X-ray diffractometer with Mo K α radiation ($\lambda = 0.71069 \text{ \AA}$). The obtained single crystal XRD data are given in the table 1 and from the data it is observed that the DMU crystal crystallizes in orthorhombic structure. To confirm the lattice parameters and diffraction planes of the crystal, powder XRD pattern for the sample was recorded using the powder X-ray diffractometer employing CuK α radiation and is presented in the figure 3. Appearance of sharp and strong peaks confirms the good crystallinity of the grown sample and the XRD pattern was indexed [17] using the INDEXING software package. To confirm the unit cell parameters, the UNITCELL software package was used. The obtained powder XRD data for DMU crystal are provided in the table .2 Using the crystallographic data, the density of DMU crystal was determined using the relation $\rho = M Z / N V$ where M is the molecular weight, Z is the number of molecules per unit cell, N is the Avogadro's number and V is the volume of unit cell. The calculated density was found to be 1.201 g/cc.

Table 1: Single crystal XRD data for DMU crystal

Chemical formula	C ₃ H ₈ N ₂ O
Molecular weight	88.11 g/mol
a, α	10.861(4) \AA , 90 $^\circ$
b, β	4.898 (3) \AA , 90 $^\circ$
c, γ	4.582(5) \AA
V	243.74 \AA^3
Z	2
Space group	P2 ₁ 2 ₁ 2 ₁
Density	1.201 g/cc

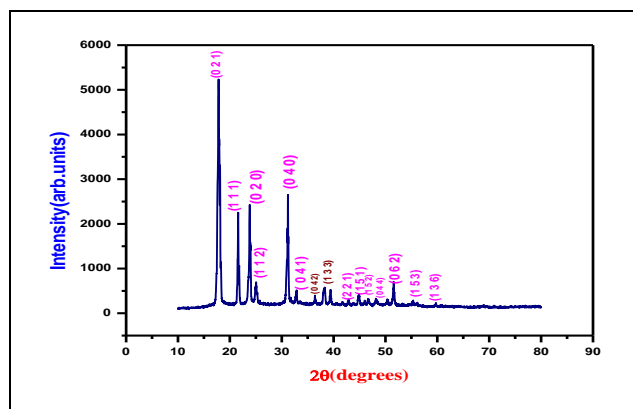


Fig.3: XRD pattern of DMU crystal

FTIR and FT-Raman spectroscopic analyses

Spectroscopic methods such as FTIR method and FT-Raman method were used to find the molecular groups of the sample. The molecular formula of the sample can be obtained after finding the functional groups of the molecules

of the sample. The presence of water of crystallization in the grown crystal can be checked by these spectroscopic methods [18, 19]. The FTIR spectrum was recorded using an FTIR spectrometer and FT-Raman spectrum was recorded using an FT-Raman spectrometer. The recorded FTIR spectrum and FT-Raman spectrum of DMU crystal are shown in the figures 4 and 5. The band at 3352.28 cm⁻¹ is corresponding to stretching vibration of vs N-H group and the band at 3050.81 cm⁻¹ is due to NH₃⁺symmetric stretching. The band at 2958.06 cm⁻¹ is due to v_{as} CH₃ group and the band at 2886.09 cm⁻¹ is due to v_s CH₃. The band at 2807.73 cm⁻¹ is corresponding to CH₂ group. The bands at 2728.56 and 2599.82 cm⁻¹ are corresponding to symmetric and asymmetric stretching of CH bondings. The band around 1638.64 to 1600.08 cm⁻¹ has high contribution from v(CO), Contributions from v(CN) and δ (NH) are found to be appreciable in the bands around 1524.9, 1433.3 cm⁻¹. The bands around 775 and 550 cm⁻¹ are tentatively assigned to the out of plane δ (CO) and δ (NCO) vibrations. The various peaks/bands of FTIR and FT-Raman spectra have been given the frequency assignments and the complete assignments are given in the Table 3.

UV-visible-NIR spectral studies

UV-Visible spectroscopy is an important tool to find the linear optical constants and optical band gap of the sample. The optical absorption spectrum of the sample was recorded using a UV-visible spectrophotometer in the wavelength range 200-800 nm. The recorded UV-visible-NIR absorbance spectrum of DMU sample is shown in the figure 6. The result shows that DMU crystal has good transmission in the visible-NIR regions and has high absorbance at 248 nm which indicates the lower cut-off wavelength of the material. The optical band gap for the grown DMU crystal was determined using the relation $E_g = 1242 / \lambda$. Here λ is the cut-off wavelength in nm. The calculated value of optical band gap is 5.008 eV. In the visible region of the spectrum, the sample has low absorption and it can be used for generating harmonic frequencies [20]. The values of transmittance (T) were determined using the relation $A = \log(1/T)$ where A is the absorbance. The absorption coefficient (α) of the sample was calculated using the following relation.

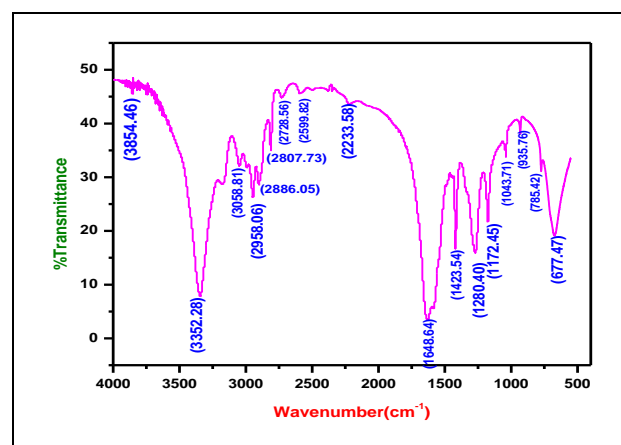


Fig.4: FTIR spectrum of DMU single crystal

$$\alpha = (2.303 \times \log(1/T)) / d$$

Where T is the transmittance and d is the thickness of the crystal in mm. The optical band gap energy (E_g) can be

evaluated from the Tauc's equation as given below.

$$\alpha h\nu = A \sqrt{(h\nu - E_g)}$$

The Tauc's graph was plotted between variation of $(\alpha h\nu)^2$ versus $(h\nu)$ and it is shown in Fig.7 and the band gap energy was calculated by extrapolation of linear part to the X-axis. The band gap energy is found to be 5.01 eV. Extinction coefficient (K) is the fraction of light lost due to scattering and absorption per unit distance in a participating medium. The extinction coefficient is calculated using following the relation [21].

$$K = \frac{\alpha \lambda}{4\pi}$$

The extinction coefficient as a function of wavelength is depicted in Fig.8 and the plot shows that the extinction coefficient increases with increase of wavelength beyond the cut-off wavelength at 248 nm. The extinction coefficient is low for the sample and hence the title sample could be used in opto-electronic devices.

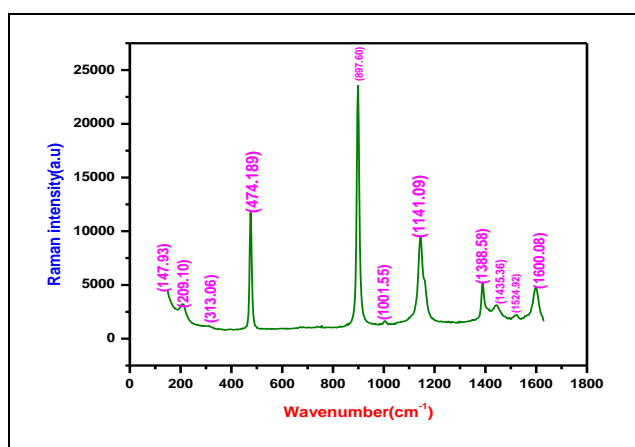


Fig.5: FT-Raman spectrum of DMU single crystal

The extinction coefficient as a function of wavelength is depicted in Fig.8 and the plot shows that the extinction coefficient increases with increase of wavelength beyond the cut-off wavelength at 248 nm. The extinction coefficient is low for the sample and hence the title sample could be used in opto-electronic devices.

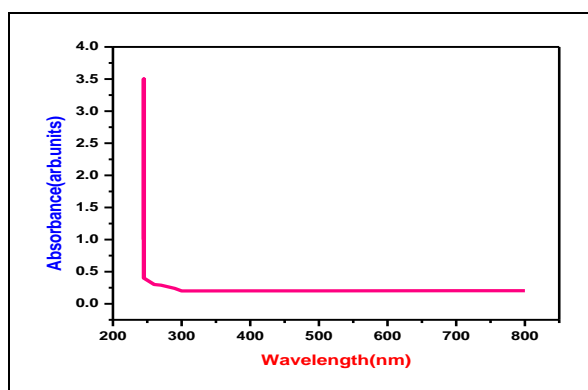


Fig. 6: UV-visible-NIR spectrum of DMU crystal

Second order NLO studies

The Kurtz and Perry powder SHG method is used to measure the SHG efficiency of the grown DMU crystal and SHG is a second order NLO property [16]. In this method, powdered sample is densely packed in a capillary tube and

irradiated with high intense infrared beam produced by a Q-switched Nd-YAG laser of wavelength 1064 nm with a pulse width of 8 ns and a repetition rate of 10 Hz.

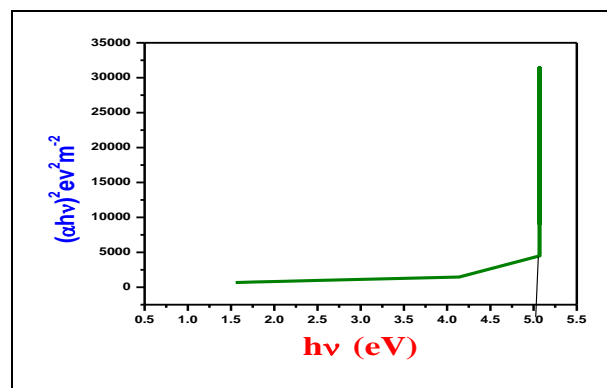


Fig.7: Plot of $(\alpha h\nu)^2$ versus optical energy for the DMU crystal

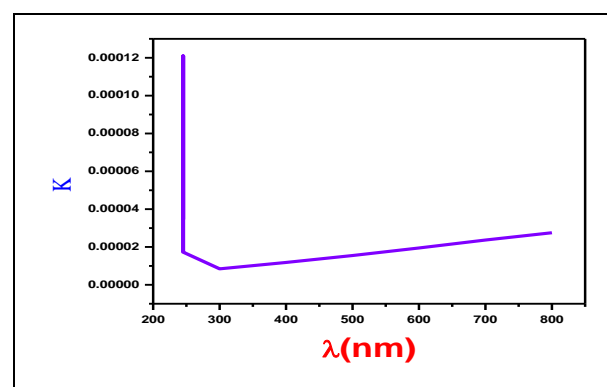


Fig.8: Plot of variation of extinction coefficient with wavelength for DMU crystal

Potassium dihydrogen orthophosphate (KDP) crushed into sample of identical size is used as reference material. The output of laser beam having the bright green emission of wavelength 532 nm confirms the second harmonic generation output. The obtained relative SHG efficiency of DMU crystal is 1.15. The output from SHG test confirms that DMU crystal is a second order NLO material. The relevant data obtained from the SHG experiment are provided in the table 4.

Table 4: The obtained SHG data for DMU crystal

Sl. No.	Name of the sample	Output energy (milli joule)	Input energy (joule)
1	DMU	10.24	0.70
	KDP		0.70
2	(Reference)	8.91	

Elemental analysis

Energy Dispersive X-Ray Analysis (EDX), referred to as EDS or EDAX, is an x-ray technique used to identify the elemental composition of materials. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed. This method is a non-destructive method and gives immediately record of all elements having $Z \geq 11$. When the sample is bombarded by an electron beam, electrons are ejected from the atoms comprising the sample's surface. The resulting electron vacancies are filled by electrons from the higher states, and an X-ray is emitted to balance the energy difference between the two electron's

states. In this method, the X-rays produced as a result of the electron beam interactions with the sample are detected to analyze it. The X-ray data is processed to obtain the percentage of each measured element present in the sample [22]. In the present work an energy dispersive spectrometer (OXFORD ISIS-300 system) was used to identify the presence of the elements. Fig.9 shows the EDAX spectrum of DMU crystal. The elements like oxygen, nitrogen and carbon were detected in DMU crystal. The experiment shows that no other impurities have entered into DMU crystal during the solution growth.

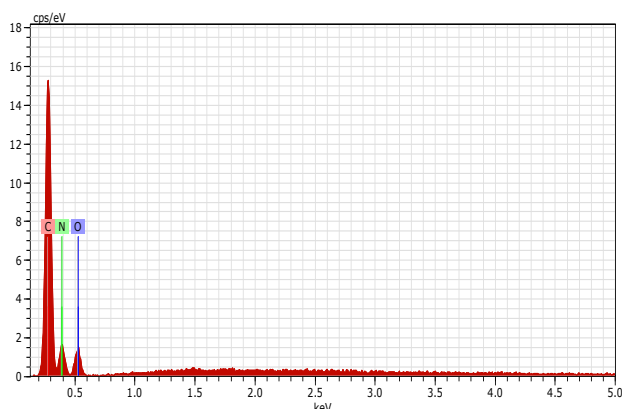


Fig.9: EDAX spectrum of DMU crystal

Thermal stability of the sample

Thermogravimetric and Differential Thermal analyses (TG/DTA) give information regarding as the phase transition temperature, melting point and the weight loss of the grown crystal, water of crystallization and different stages of decomposition of the sample [23].

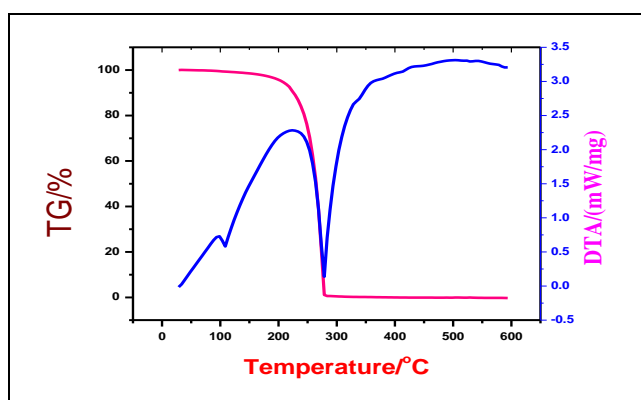


Fig.10: TG/DTA curves of DMU crystal

The recorded TG/DTA thermal curves for DMU crystal are presented in the figure 10. From the thermal curves, it is the clear indication of melting point of DMU crystal at 105 °C, at which there is no weight loss of the sample. The endothermic peak at 278 °C is corresponding to the decomposition of the sample because there is a huge weight loss at this temperature. The emission of gaseous particles is noticed in the temperature range 300-600 °C. Hence, there are three thermal processes are taking place in the sample and they are melting, decomposition and emission of gaseous particles from the sample. The sharpness of the endothermic peaks shows good degree of crystallinity of the grown DMU crystal.

Electric impedance spectroscopy

The impedance is the electrical opposition to the current when an AC voltage applied to a sample and it is the resistance and reactance of the electrical components.

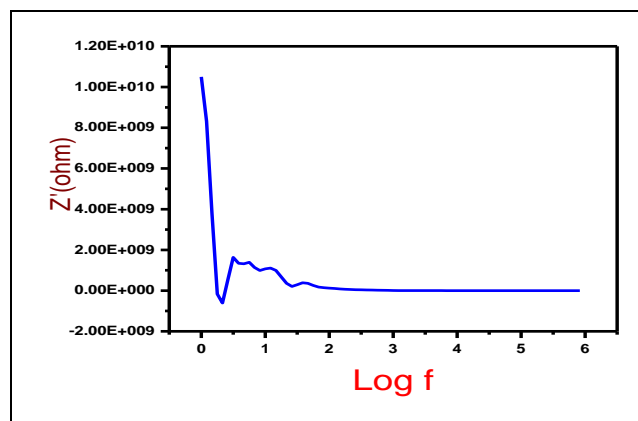


Fig.11: Variation of real part of impedance as a function of log frequency for DMU crystal at 30 °C

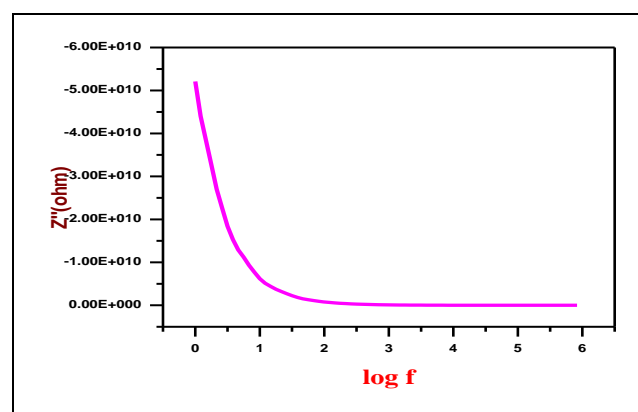


Fig.12: Variation of imaginary part of impedance as a function of log frequency for DMU crystal at 30 °C

The frequency dependent properties of a material are represented as complex impedance Z^* and which is related as $Z^*(\omega) = Z' - jZ''$ where Z' and Z'' are the real and imaginary components of impedance [24]. The variation of real part of impedance (Z') and imaginary part of impedance (Z'') with frequencies at temperature 30°C are shown in the Figures 11 and 12.

From the result it is observed that the real and imaginary part of impedance decreases with the increase in frequency. The high value of impedance at low frequency indicates low ionic mobility in the grown DMU crystal. The peaks in the plots of impedance versus frequency are corresponding to relaxation process and the peak frequency is equal to relaxation frequency. It is observed that the values of impedance of the sample are very low in the high frequency region and this is due to decrease of different types of polarization taking place in the sample.

Third order NLO studies

The Z-scan is a simple and popular experimental technique to measure the intensity dependent third order nonlinear susceptibility of the materials. It allows the simultaneous measurement of both the nonlinear refractive index and the nonlinear absorption coefficient. In this method the sample is translated in the Z-direction along the axis of a focused Gaussian beam from the He-Ne laser at 632.8 nm and the far field intensity is measured as a function

of the sample position. When both open aperture and closed aperture methods are used for the measurements, the ratio of the signals determines the nonlinear refraction of the sample. The theory part of Z-scan technique is given elsewhere [25, 26]. The Z-scan curves for the sample are shown in the Figures 13 and 14.

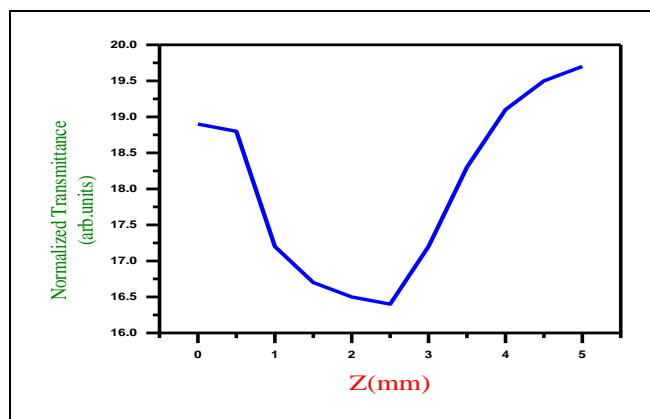


Fig.13: Open aperture Z-scan curve for DMU crystal

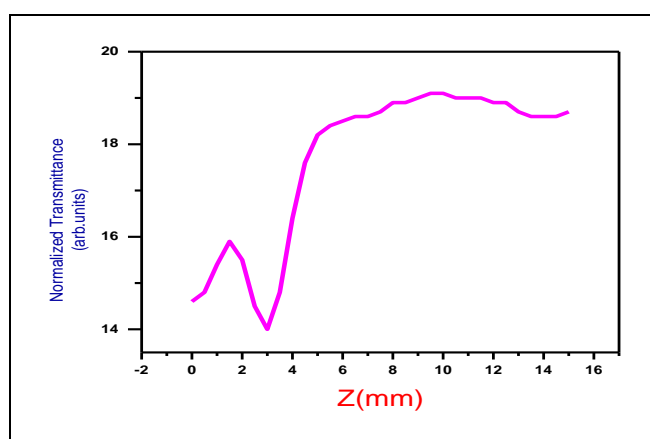


Fig.14: Closed aperture Z-scan curve for DMU crystal

In the closed Z-scan curve, there is a peak followed by a valley and it corresponds to the signature of negative nonlinearity. The calculated value of the nonlinear refractive index (n_2) is $-5.382 \times 10^{-11} \text{ m}^2/\text{W}$. As sample has positive refractive index, it results in focusing nature of the material. From open aperture Z-scan curve, it can be observed that the valley lies beyond the focus and the nonlinear absorption is coefficient is found to be $4.158 \times 10^{-4} \text{ m/W}$. Third order susceptibility of DMU crystal is $7.262 \times 10^{-7} \text{ esu}$. The value of ($\chi^{(3)}$) is found to be larger and it is due to the π electron cloud movement from the donor to acceptor which makes the molecule highly polarized.

Conclusions

Single crystals of dimethyl urea were grown from aqueous solution by slow evaporation technique. The X-ray diffraction studies confirm the orthorhombic structure of the grown DMU crystal. The FTIR and FT-Raman analyses confirm the presence of various functional groups present in DMU crystal. UV-Vis NIR spectrum confirms its suitability for SHG application. TG/DTA reveals that this compound is thermally stable up to 105°C . SHG studies reveal that DMU crystal is the promising material for NLO applications. Energy Dispersive X-ray analysis is used to identify the elemental composition of material. Third order NLO parameters for the sample were determined by Z-scan

method. The impedance spectrum results have been used to estimate the electrical properties of the sample. All these studies confirm that the grown crystal is the potential candidate for the fabrication of nonlinear optical devices.

Acknowledgement

The authors like to thank the staff members of Sophisticated Test Instrumentation Centre (STIC), Cochin University, Cochin for providing the single crystal and powder X-ray diffraction analyses and extend our thanks to Dr. Basheer Ahamed, Professor of Physics, B.S. Abdur Rahman University, Vandalur, Chennai for providing the SHG analysis of the title compound. The authors like to thank staff members of PSN College of Engineering, Tirunelveli for the impedance analysis of the sample. Also the authors are thankful for the research support provided to carry out other studies in VOC College, Tuticorin, Karunya University, Coimbatore, NIT, Trichy.

References

- [1] D.S. Chemla, J. Zyss (Eds.), *Nonlinear Optical Properties of Organic Molecules and Crystals I*, Academic Press, Orlando, 1987.
- [2] D.J. Williams (Ed.), *Nonlinear Optical Properties of Organic and Polymeric Materials*, American Chemical Society, Washington, DC, 1983.
- [3] B. Kirtman, B. Champagne, *Int. Rev. Phys. Chem.* 16 (1997) 389.
- [4] R.A. Hann, D. Bloor (Eds.), *Organic Materials for Nonlinear Optics*, Royal Society of Chemistry, London, 1989.
- [5] G.J. Ashwell, D. Bloor (Eds.), *Organic Materials for Non-linear Optics III*, Royal Society of Chemistry, Cambridge, 1993.
- [6] J. Messier, F. Kajzar, P. Prasad, D. Ulrich (Eds.), *Nonlinear Optical Effects in Organic Polymers*, Kluwer Academic Publishers, Dordrecht, 1989.
- [7] J. Messier, F. Kajzar, P. Prasad (Eds.), *Organic Molecules for Nonlinear Optics and Photonics*, Kluwer Academic Publishers, Dordrecht, 1991.
- [8] T. Kobayashi (Ed.), *Nonlinear Optics of Organics and Semiconductors*, Springer-Verlag, Berlin, 1989.
- [9] M. Ardoino, L. Zeng, C. Razzetti, M. Zha, L. Zanotti, M. Curti, *Mater Chem Phys*, 66 (2000), 299-302.
- [10] E. de Matos Gomes, V. Venkataramanan, E. Nogueira, M. Belsley, F. Proenc, A. Criado, M.J. Dinez, M.D. Estrad, S. Perez-Garrido, *Synth Met*, 115 (2000), pp. 225-228.
- [11] V.K. Dixit, S. Vanishri, H.L. Bhat, E. de Matos Gomes, M. Belsley, C. Santinha, G. Arunmozhi, V. Venkataramanan, F. Proena, A. Criado, *J. Cryst. Growth*, 253 (2003), pp. 460-466.
- [12] https://pubchem.ncbi.nlm.nih.gov/compound/1_3-dimethylurea
- [13] Halbout JM, Sarhangi A, Tang CL. *Appl Phys Lett* 1980; 37:864–866.
- [14] Pratik M.Wankhade, Gajanan G.Muley, *Results in Physics*, 3, 2013, 97-102.
- [15] Muley GG, Rode MN, Pawar BH., *Optoelectron. Adv. Mater-Rapid Commun.* 2009; 3:704–705.
- [16] Kurtz SK, Perry TT. *J Appl. Phys.* 1968; 39:3798–813.
- [17] H. Lipson, H. Steeple, *Interpretation of X-ray Powder Diffraction Patterns*, Fifth ed., Macmillan, New York, 1970.

- [18] Ravi U, Srinivasan K, Anbukumar S, Ramasamy P. J. Cryst. Growth 1994; 137:598–604.
- [19] Robert M. Silverstein, Francis X. Webster, David J. Kiemle, Spectrometric Identification of Organic Compounds, 7th ed., Wiley & Sons, INC., 2005.
- [20] K.J.Arun, S. Jayalekshmi, J. Miner. Mater. Charact. Engg, 8 (2009) 599.
- [21] M.A.Gaffara, A.Abu El-Fadl, Bin Anooz, Physica B, 327 (2003)43–54.
- [22] <http://en.wikipedia.org/wiki/EDAX>
- [23] M.E.Brown, Thermal Analysis: Techniques and Applications, Chapman and Hall, New York (1988).
- [24] J.R.Macdonald, Impedance Spectroscopy-Solid Materials and Systems, John Wiley & Sons, 1987.
- [25] A. Shanthi, C. Krishnan, P.Selvarajan, Spectrochimica Acta Part A: Molecular and Bimolecular Spectroscopy, 122 (2014) 521–528.
- [26] M. Sheik-Bahae, A.A. Said, and E.W. Van Stryland, Opt. Lett., 14,955(1989).