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Synthesis, structural, thermal and NLO studies of organic nonlinear optical material- Tertiary butylammonium maleate monohydrate

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Abstract: An organic single crystals of Tertiary butylammonium maleate monohydrate (TBAMM), were grown by slow evaporation technique. The structure of the grown crystal was elucidated using single crystal X-ray diffraction analysis. XRD studies reveal that TBAMM crystal belongs to the monoclinic crystal system with space group P2₁/n. The presence of functional groups in TBAMM crystal was identified by FTIR spectral study. The molecular structure of the grown crystal was analyzed by NMR spectral analysis. Thermal behavior and stability of TBAMM were studied by TG/DTA analyses. UV-Vis -NIR spectral study shows wide transmission range with lower cut-off wavelength as 341nm. The optical band gap was found to be 3.13 eV from the Tauc's plot. The Second Harmonic Generation (SHG) efficiency of the TBAMM crystal was found to be 1.5 times more than that of KDP crystal.

Keywords: X-ray diffraction, Biomaterials, growth from solutions, organic compounds.

Introduction

Many active pharmaceutical compounds contain nitrogen atoms which can be protonated resulting in the pharmaceutical activity. As a result, these types of materials are having the desirable properties like hygroscopicity and physico chemical stability^{1,2,3}. These types of crystals are also capable of modifying the mechanical properties. The deprotonation of acid molecules results in the formation of counter ions which is the important step in drug formulation^{4,5}. In recent years, researches on organic crystals have been made at a rapid pace because of their potential applications in the fields of material science, molecular biology, electro optics and pharmaceutical applications^{6,7,8}. Organic nonlinear optical (NLO) materials are attracting a great deal of attention due to their high nonlinearity and rapid response in the electro-optic effect compared to inorganics. New organic compounds with one or more conjugated bond positions, leading to highly efficient charge transfer systems have been actively studied. Most of the organic crystals are composed of carboxyl groups, which are responsible for strong electron acceptors and they exhibit high intermolecular charge transfer resulting in high SHG efficiency.

Organic compounds formed by weak van der Waals and hydrogen bonds possess high degree of delocalization⁹. Hence they are optically more nonlinear than inorganic materials. Some of the advantages of organic materials include flexibility in the methods of synthesis, scope for altering the properties by functional substitution, inherently high nonlinearity and high damage threshold¹⁰. Organic materials with delocalized π electrons usually display a large NLO response which makes it most resourceful for various optical applications

including communication, computing, information processing, disk data storage. It can also be used for laser fusion reactions and laser remote sensing¹¹. Organic materials contain delocalised π electrons, a protonated amine group (NH₃⁺) and deprotonated carboxylic acid group (COO⁻). The dipolar nature of the materials exhibits peculiar physical and chemical properties in amines which make them ideal candidates for NLO applications^{12–14}. Recently, the crystal engineering considers the carboxylic acids as attractive substrates for synthesis because of their ability to generate predictable supramolecular modes with the hydrogen bonding interactions among themselves¹⁵⁻¹⁸. The main direction of the research is to find recurring packing patterns(motifs) adopted by certain functional groups¹⁹. Such repetitive motifs are called supramolecular synthess²⁰. The connections of dicarboxylic acid and amines serve as building blocks that self assemble via O-H-----O and N-H-----O hydrogen bonds when crystallized²¹.

The study of structural chemistry of maleic acid and related substances is quite interesting due to the presence of highly strained hydrogen atoms ²². The intramolecular hydrogen bond in maleic acid is very strong and most of the complexes of maleic acid are in monoionised state. Maleic acid is basically a dicarboxylic acid with large π -conjugation has attracted a great deal of attention²³. Maleic acid is a part of well known pharmaceutical antibiotic drugs like Chlorophenaramine maleate, Prochlorperazine maleate, Fluroxamine maleate, Pheniramine maleate etc., Tertiary butyl amine moieties are present in drugs for hypertension, heart failure and anticancer diseases and also in the field of crop protection and rubber vulcanization.

In the present investigation, tertiarybutylammonium maleate monohydrate (TBAMM) was synthesized by slow evaporation method. The grown crystals were characterized by single crystal XRD, FT-IR, NMR, UV-vis-NIR, TG/DTA analyses and SHG also be studied for this title crystal.

2. Experimental procedure

2.1 Synthesis and Growth of TBAMM

Single crystals of Tertiary butyl amino maleate monohydrate (TBAMM) were grown by slow evaporation solution growth method at room temperature. Tertiary butyl amine(2-amino-2-isopropane) and Maleic acid(But-2-ene-1,4-dioic acid) were dissolved in deionized water with 1:1 mole ratio to get a clear solution and the solution was stirred well for homogeneity. The resulting solution was filtered using a Whattman filter paper and the beaker containing the filtrate was kept in a dust free environment for crystallization. After a period of 23 days, colourless crystals of the title compound were obtained. The purity of the synthesized crystal was improved considerably by repeating the crystallization process three times. Fig.1 shows the as-grown single crystal of the title compound.



Fig.1. As grown single crystal of TBAMM

3. Characterization techniques

Single crystal XRD data of the grown crystal were obtained using a Enraf Nonius CAD4-MV31 single crystal X-ray diffractometer with MoKα (0.7107 Å) radiation at room temperature. The ORTEP view of the molecule was drawn at 50% probability thermal displacement ellipsoids with the atom numbering scheme. The crystal structure was solved by a direct method with the SHELXS-97 program^{24,25}. The UV-vis-NIR spectrum was recorded in the range of 200-800nm using Perkin-Elmer Cary 5E spectrometer. The FT-IR spectrum of the title compund was obtained using JASCO FT-IR 410 spectrometer by the KBr pellet method. The ¹H and ¹³C NMR spectra of the title compound were recorded on a Brucker AVANCE III 500 MHz (AV 500) instrument at 23°C (300 MHz for ¹H NMR and 75 MHz for ¹³CNMR) to confirm the molecular structure. The TG-DTA of the title compound has been analysed by using a TGA Q50V20.13 Build 39 Perkin-Elmer Diamond TG-DTA

instrument. A platinum crucible was used for heating the sample and the analysis was carried out in an atmosphere of nitrogen at a heating rate of 10° C/min in the temperature range of 23-600°C. The SHG efficiency of the grown crystal was determined with help of modified Kurtz and Perry technique using Nd:YAG laser with pulse repetition rate of 10Hz and wavelength 1064nm.

4. Results and discussion

4.1. Single crystal X-ray diffraction method -Structural data

Single crystal X-ray diffraction measurements were made at 293 K using title crystal for data collection. Accurate lattice parameters were determined from least squares refinements of well-centered reflections in the range of 2.91 to 26.02°. XRD data reveal that the synthesized complex, TBAMM belongs to the monoclinic crystal system with space group P2₁/n. The lattice parameters obtained are a = 6.0911(8) Å, b =19.077(2) Å, c = 9.6850(11) Å, α =94.465(7)° β =94.465(7)° and γ =90°, unit cell volume(V) = 1122.0(2) Å³ and Z = 4.The total number of reflections collected/unique is17721/2575.The crystallographic data and structure refinement parameters are given in Table 1. The grown crystal is a new compound (CCDC no. 996278). The asymmetric unit consists of maleate anion and tertiary butyl ammonium cation and a water molecule. Fig.2 shows the ORTEP representation of the molecule with atom numbering scheme. The crystalline packing shows the interactions between tertiary butyl amine, maleate anions and water molecule. The anion pairs are hydrogen bonded (N-H...O) to the cations and the motif is connected to its b-translation equivalents to form a one dimensional hydrogen bonded chain parallel to b-axis.



Fig.2 ORTEP diagram of the TBAMM

The single crystal X-ray structure of the proton transfer complex of the title compound shows the presence of protonated tertiary butyl ammonium cation and deprotonated maleate anion and also a water molecule with the intermolecular hydrogen bonding associations as shown in ORTEP diagram (Fig.2, Table 2). The single crystal X-ray structure of the proton-transfer complex of TBAMM shows the presence of mono protonated tertiary butyl ammonium cation and deprotonated maleate anion resulting in the formation of intermolecular hydrogen bonding associations. The maleate anion possesses a short intramolecular distance O-H....O hydrogen bond, with an O......O distance of 2.4045(16) Å, which forms nearly planar seven membered ring structure as typically found in other hydrogen maleate anions²⁷ and other inter and intra molecular hydrogen bondings as shown in Table 2. The loss of a proton from maleic acid is confirmed from the elongated bond length of C(1)-O(5) from 1.22(17) Å to 1.23(17) Å. The deprotonation of maleic acid is further confirmed from hydrogen bond table 2. The bond angle of the carboxylate ion in maleate anion show characteristic value for O(5)-C(1)-O(4) as 122.11(14)° which is higher when compared to O(2)-C(4)-O(3) angle of 121.11(14)°.

Table 1. Crystallographic data and structure refinement parameters for TBAMM

Empirical formula	C ₈ H ₁₇ N O ₅
Formula weight	207.23
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, P ₂ 1/n

Unit cell dimensions	$a = 6.0911(8)$ Å; $\alpha = 90$ deg.		
	$b = 19.077(2)$ Å; $\beta = 94.465(7)$ deg.		
	$c = 9.6850(11)$ Å; $\gamma = 90$ deg.		
Volume	1122.0(2) Å ³		
Z	4		
Calculated density	1.227 Mg/m ³		
Absorption coefficient(μ)	0.101 mm ⁻¹		
F(000)	448		
Crystal size	0.30 x 0.25 x 0.20 mm		
Theta range for data collection	2.14 to 27.52 deg.		
Reflections collected / unique	17721/2575 [R(int) = 0.0538]		
Completeness to theta	27.52 - 99.9 %		
Absorption correction	Semi-empirical from equivalents		
Max. and min. transmission	0.9869 and 0.9694		
Refinement method	Full-matrix least-squares on F ²		
Data / restraints / parameters	1575 / 3 / 150		
Goodness-of-fit on F^2	1.073		
Final R indices	R1 = 0.0454, wR2 = 0.1191		
R indices (all data)	R1 = 0.0717, wR2 = 0.1325		
Extinction coefficient	0.1610(4)		
Limiting indices	-7<=h<=7, -23<=k<=24, -11<=l<=12		
Identification code	shelxl		
CCDC No.	996278		

Moreover, the elongated bond length of C(5)-N(3) from 1.48 Å to 1.50 Å for tertiary butyl amine, causes the Vander Waals bond between N-H...O also to stretch the C-N bond of tertiary butylamine which proves the protonation of tertiary butyl amine in TBAMM. It is found that among three protons H(3A), H(3B) and H(3C) bonded with nitrogen atom, H(3B) is the protonated hydrogen and this is proved by the bond lengths N(3)-H(3B) is 0.955(18) Å whereas N(3)-H(3C) is 0.92(2) Å and N(3)-H(3A) is 0.906(18) Å. These differences are attributed to the loss of a carboxylic proton at C1, leading to the conversion from the neutral to the anionic state.

Table 2.Bond lengths [A] and angles [deg] of Hydrogen atom for TBAMM

D-HA	d(D-H)	d(HA)	d(DA)	<(DHA)
C(6)-H(6C)O(3)#1	0.96	2.54	3.455(2)	159.2
O(3)-H(3D)O(4)	0.82	1.59	2.4045(16)	176.4
O(1)-H(1A)O(5)#2	0.886(16)	1.948(17)	2.8144(17)	166(2)
O(1)-H(1B)O(2)	0.911(16)	1.938(16)	2.8444(17)	173(2)
N(3)-H(3A)O(2)#1	0.906(18)	2.026(19)	2.9126(18)	165.7(14)
N(3)-H(3B)O(5)#3	0.955(18)	1.913(19)	2.8557(18)	168.6(15)
N(3)-H(3C)O(1)#4	0.92(2)	1.89(2)	2.803(2)	176.7(16)

4.2 FTIR analysis

The recorded FTIR spectrum of the TBAMM in the range of 4000-400 cm⁻¹ is shown in Fig 3. The peak at 3455 cm⁻¹ is assigned to N-H streching vibration and hence the t-butyl amine nitrogen is protonated in the crystal as shown in ORTEP diagram (Fig 2). The peaks at 2988 cm⁻¹ and 2919 cm⁻¹ are due to C-H stretching vibration of t-butyl amine and maleic acid.



Fig.3 FT-IR spectrum of TBAMM

The C=C stretching vibration of maleic acid group occurs at 1639 cm⁻¹. The peak at 1575cm⁻¹ is assigned to C=O vibration of the acid group and the peak at 2115 cm⁻¹ is due to C-N stretching vibration. The peak at 2532 cm⁻¹ is due to combination mode of COO⁻ group. The peak at 1010 cm⁻¹ corresponds to C-O stretching which has been deprotonated. The peak at 875 cm⁻¹ is due to C-H plane out of bending vibration. The peaks corresponding to 709 cm⁻¹ is due to NH wagging and 567 cm⁻¹ is due to C-C out of plane ring deformation^{28,29}.

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Frequency Cm ⁻¹	Assignments		
3455cm ⁻¹	N-H asymmetric stretching and symmetric		
	stretching vibration		
$2988 \text{ cm}^{-1} \text{ and } 2919 \text{ cm}^{-1}$	C-H asymmetric stretching and symmetric		
	stretching vibration		
2532 cm^{-1}	COO ⁻ vibration mode		
2115cm ⁻¹	C-N stretching vibration		
1639cm ⁻¹	C=C stretching vibrations		
1575 cm ⁻¹	C=O stretching vibration		
$1436 \text{ cm}^{-1} \text{ and } 1321 \text{ cm}^{-1}$	asymmetric and symmetric stretching		
	vibration of the nitro		
1010 cm ⁻¹	C-O stretching vibration		
875 cm ⁻¹	C-H out of plane bending vibration		
709cm ⁻¹	NH wagging		
567 cm ⁻¹	C-C out of plane ring deformation[24,25].		

Table 3. shows the various functional modes present in the molecular structure. Hence, the IR spectrum confirms the presence of functional groups and characteristics of amine and acid groups.

4.3 NMR spectroscopy

The ¹H NMR and ¹³C NMR spectral analyses are the two important analytical techniques used to study the molecular structure of title compound. Fig.4a shows the structure of title compound with different number of protons and carbons present in the chemical environments involved in the structure.



Fig.4a Structure of TBAMM

4.3.1. ¹H NMR spectrum

Fig.4b shows the recorded ¹H NMR spectrum of grown crystal which shows five different signals due to five distinct proton environments including solvent signal. The peaks at δ 2.5ppm correspond to solvent peaks. The signal at δ 6.066 ppm is due to CH protons of maleate ion. The signal at δ 7.8ppm is assigned to NH₃⁺ protons in t-butylamine which are deshielded due to the decreasing absorbing powers of COO⁻ atoms. As a result, the δ value is increased from 2-3ppm to 7.8ppm. Hence the signal at δ 7.8ppm confirms the deshielding effect of COO⁻ atoms on NH₃⁺ proton. The peak at δ 1.2ppm is due to CH₃ groups in t-butyl part of the amine group. The peak at δ 3.5ppm reveals the moisture protons like water and O--H---O protons.



Fig.4b ¹H NMR spectrum of TBAMM

4.3.2.¹³ C NMR spectrum

Fig.4c shows the ¹³C NMR spectrum of the title compound. The appearance of 5 distinct carbon signals in the spectrum including the solvent peak unambiguously confirms the molecular structure of the title compound. The signal at δ 167.50 ppm has been assigned to the C6 carbon (C-O) atom in the maleate ion. The signal at δ 136.19ppm is due to CH=CH of maleate ion. The signal at δ 51.19ppm corresponds to methyl groups attached to carbon atom in tertiary butylamine, while δ 124.58ppm corresponds to C2 and C4 aromatic carbon atoms of maleate anion. The signal at δ 27.18 ppm shows the methyl group in tertiary butyl group. The solvent peaks are shown at δ 40.02 ppm. It is concluded that the spectrum provides the useful information about the various types of carbon atoms involved in the molecular structure of the title compound.



Fig.4c ¹³C NMR spectrum of TBAMM

4.4 UV-vis- NIR spectral analysis

The UV-vis-NIR absorption spectrum of the grown crystal was recorded in the wavelength range of 200-800 nm (Fig.4a). The higher intensity of the absorption band observed in the UV region may be due to conjugated systems present in the grown crystal TBAMM. The absorption is very low in the near infrared region entire visible region and UV-region with lower cut-off wavelength 341nm. The optical band gap (Eg) was evaluated using Tauc's relation given by

$$\alpha hv = A(hv - E_g)^2$$

(1)

where α is the absorption coefficient, A is a constant, E_g is the optical band gap, h is the Planck constant and v is the frequency of the incident photons.



Fig.4a UV- visible-NIR spectrum of TBAMM

The value of band gap energy was estimated from the plot of $(\alpha hv)^2$ against hv (Fig.4b) by extrapolating the linear portion of the curve to zero absorption.



Fig.4b Plot of $(\alpha hv)^2$ versus photon energy

The optical band gap was measured as 3.13 eV from the plot. The higher value of optical band gap suggests that material is dielectric in nature. Only the dielectric material will have wide transparency. The material with wide transparency is required for the fabrication of optical electronic devices.

4.5. Thermal analysis

The Thermogravimetric (TG) and Differential thermal analysis (DTA) were carried out in the nitrogen atmosphere at a heating rate of 10°C min ⁻¹ from 0 °C to 700 °C. It is observed from TG curve that the weight loss is negligible (3.00%) at 102.6°C and it may be due to evaporation of water molecules and the major weight loss starts from 106.8°C onwards. The major weight loss is confirmed by the endothermic peak of DTA analysis at 106.8°C (Fig 5).



Fig.5. TGA and DTA curve of TBAMM

Hence, the crystal can be used in devices with more thermal stability up to 145 °C. The decomposition is almost completed at 409 °C. The sharpness of the peaks shows the good degree of crystalline quality of the crystal^{30,31}.

NLO efficiency of the TBAMM crystal was measured by the Kurtz and Perry technique³². A Q-switched Nd:YAG laser was used as light source. A laser beam of fundamental wavelength 1064nm. The sample was ground well and tightly packed in a micro capillary tube. The relative SHG efficiency of the grown crystal was measured by comparing the SHG output from the standard material KDP (Potassium dihydrogen phosphate) of same particle size. The relative efficiency was found to be 1.5 times that of standard KDP. The SHG was confirmed from the emission of green radiation (532nm) by the crystal. On a molecular scale the extent of charge transfer (CT) across the NLO Chromophore determines the level of SHG efficiency. Even though the grown crystal belongs to centrosymmetric group, it exhibits considerable amount of NLO behavior Rieckoff et al., ³³, Ghazaryan et al., ³⁴, Shakir et al., ³⁵, Wensheng et al., ³⁶, Dhanabal et al³⁷, P.Pandi et al ³⁸ and Sagadevan Suresh et al., ³⁹ have studied the SHG efficiency of some centrosymmetric crystals due to strong hydrogen bonds.

In the TBAMM study, the strong proton donor maleic acid transfers a proton to the strong proton acceptor tertiary butyl amine. Intermolecular hydrogen bonding is formed between the hydrogen of the protonated nitrogen atom of tertiary butyl amine and the negatively charged oxygen atom of the maleate ion ⁴⁰. In the present case, the donor–acceptor strength would be considerably high due to the intermolecular hydrogen bonding. The SHG efficiency of the title complex may due to the presence of intermolecular hydrogen bonding through N-H-O and C-H-O bonds. This indicates that the synthesized complex can be used as a promising NLO material with SHG efficiency more than that of KDP.

5. Conclusion

Single crystals of TBAMM were synthesized and crystallized from tertiary butyl amine and maleic acid by slow evaporation method. The structure of the grown crystal was solved using SHELXS-97 program. It is observed from the crystallographic data that the grown crystal belongs to monoclinic system with P2₁/n space group. The absence of absorption in the visible UV–NIR region is confirmed and the high optical band gap indicates that the TBAMM can be useful for optoelectronic applications. The cut-off wavelength and optical band gap were measured as 341nm and 3.13eV respectively. The presence of various functional groups and the protons and carbon atoms of various chemical environments present in the grown crystal was confirmed by FT-IR and NMR spectral analyses. The thermal stability and decomposition pattern of the TBAMM were studied using TG–DTA analyses. Thermal studies reveal that the grown crystal is thermally stable up to 106.8°C. The TBAMM possesses SHG efficiency 1.5 times more than that of KDP.

References

- 1. Z. Rahman, A.S. Zidan, R.Samy, V.A. Sayeed, M.A. Khan, Improvement of physicochemical properties of an antiepileptic drug by salt engineering, AAPS Pharm. Sci. Technol. 13 (2012) 793-801.
- T. Kojima, K. Sugano, S. Onoue, N. Murase, M. Sato, Y. Kawabata, T. Mano, Solid form selection of zwitter ionic 5-HT4 receptor agonist, Int. J.Pharm, 350 (2008) 35.
- 3. P. Guerrieri, K. Jarring, L.S. Taylor, Impact of counterion on the chemical stability of crystalline salts of procaine, J. Pharm. Sci. 99 (2010) 3719.
- 4. S.E. David, M. Ramirez, P. Timmins, B.R. Conway, Comparative physical, mechanical and crystallographic properties of a series of gemfibrozil salts, J. Pharm. Pharmacol. 62 (2010) 1519.
- 5. P.H. Stahl, C.G. Wermuth, Handbook of Pharmaceutical Salts: Properties, Selection and Use, Wiley-VCH, Zürich, 2002.
- 6. C.B. Aakeröy, M.E. Fasulo, J. Desper, Cocrystal or salt: does it really matter? Mol. Pharm. 4 (2007) 317–322.
- 7. S.L. Childs, K.I. Hardcastle, Cryst. Growth Des. 7 (7) (2007) 1291–1304.
- 8. J.G. Zeikus, M.K. Jain, P. Elankovan, Succinate production in *Escherichia coli* Appl. Microbiol. Biotechnol. 51 (1999) 545–552.
- M. Narayan Bhat, S.M. Dharmaprakash, Effect of solvents on the growth morphology and physical characteristics of nonlinear optical γ-glycine crystals, J. Cryst. Growth 242 (2002) 245-252.

- 10. B. Narayana Moolya, S.M. Dharmaprakash, Growth and characterization of nonlinear optical diglycine hydrobromide single crystals, Mater. Lett. 61 (2007) 3559-3562.
- 11. T. Pal, T. Kar, G. Bocelli, L. Rigi, Cryst, Morphology, Crystal Structure, and Thermal and Spectral Studies of Semiorganic Nonlinear Optical Crystal LAHClBr, Growth Des. 4 (2004) 743-747.
- 12. J.J. Rodrigues Jr, L. Misogutti, F.D. Nunes, C.R. Mendonca, S.C. Zilio, Optical properties of L-threonine crystals, Opt. Mater. 22 (2003) 235.
- 13. E. Ramachandran, S. Natarajan, Crystal growth of some urinary stone constituents: III. In-vitro crystallization of L-cystine and its characterization, Cryst. Res. Technol. 39 (2004) 308.
- 14. Tapati Malik, Tanusree Kar, Gabriele Bocelli, Amos Musatti, Structural and thermal characterization of L-arginine dihydrate a nonlinear optical material Cryst. Res. Technol.41 (2006) 280-284.
- D.N. Chin, J.A. Zerkowski, J.C. MacDonald, G.M. Whitesides, in: J.K. Whitesell (Ed.), Organised Molecular Assemblies in the Solid State, Wiley, New York, 1999, pp. 185–253.
- B.M. Foxman, D.J. Guarrera, L.D. Taylor, D. van Engen, J.C. Warner, Environmentally Benign Synthesis Using Crystal Engineering: Steric Accommodation in Non-Covalent Derivatives of Hrdroquinones, Cryst. Eng. 1(1998) 109–118.
- 17. J.C. MacDonald, G.M. Whitesides, Solid-state structures of hydrogen-bonded tapes based on cyclic secondary diamides, Chem. Rev. 94 (1994) 2383–2420.
- 18. G.T.R. Palmore, T.J.M. Luo, M.T. McBride-Weiser, E.A. Picciotto, C.M. Reynoso-Paz, Engineering crystalline architecture with diketopiperazines: An investigation of the strength of hydrogen-bonded tapes based on the cyclic dipeptide of (S)-aspartic acid ,Chem. Mater. 11 (1999) 3315–3328.
- 19. G.R. Desiraju, Nature Chemistry beyond the molecule, 412 (2001) 397–400.
- 20. G.R. Desiraju, Supramolecular Synthons in Crystal Engineering—A New Organic Synthesis. Angew. Chem. Int. Ed. Engl. 34 (1995).
- 21. J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang, Hydrogen Bond pattern functionality and graph sets, Angew. Chem. Int. Ed. Engl. 34 (1995) 1555–1573.
- 22. James and Williams, A refinement of the crystal structure of maleic acid, Acta crystallographica sec B,30(1974) 1249.
- 23. S.Natarajan, S.A.M.Britto, E.Ramachandran. Growth, Thermal, Spectroscopic, and Optical Studies of L-Alaninium Maleate, a New Organic Nonlinear Optical Material ,Crystal growth and Design, Vol.6, (2006) pp 137-140.
- 24. M.N. Burnett, C.K. Johnson, ORTEP III, Report ORNL-6895, Oak Ridge.
- 25. G.M.Sheldrick, A short history of *SHELX* Acta Crystallography, Section A:Foundations of Crystallography 64 (2008)112-122.
- M. Vimalan, T. Rajesh Kumar, S. Tamilselvan, P. Sagayaraj, C.K. Mahadevan, Growth and properties of novel organic nonlinear optical crystal: L-alaninium tartrate (LAT), Physica B 405 (2010) 3907– 3913.
- 27. D.Madsen, S.Larsen, Methylamine and Dimethylamine Salts of the Hydrogen Maleate Ion, Acta Crystallogr. C54 (1998) 1507 -1511.
- 28. P.Srinivasan, T.Kanagasekaran, R.Gopalakrishnan, G.Bhagavannarayana, P. Ramasamy, Studies on the Growth and Characterization of L-Asparaginium Picrate (LASP) A Novel Nonlinear Optical Crystal, J. Crys. Growth Design. 6 (2006) 1663.
- 29. T.Uma Devi, N. Lawrence, R. Ramesh Babu, K. Ramamurthi, Growth and characterization of Lprolinium picrate single crystal: A promising NLO crystal *J*. Cryst. Growth 310 (2008) 116–123.
- M.M.C. Chou, L. Chang, C. Chen, W.Fu Yang, Growth behavior of non polar GaN on the nearly lattice-matched (100) γ-LiAlO₂ substrate by chemical vapor deposition ,J. Cryst. Growth 311 (2009)448-451.
- 31. D.R. Hang, Mitch M.C. Chou, L. Chang, Y. Dikme, M. Heuken, Growth and characterization of *m*-plane GaN-based layers on LiAlO₂ (1 0 0) grown by MOVPE, *J.* Cryst. Growth 311 (2009) 452-455.
- 32. S.K.Kurtz, T.T. Perry, A Powder Technique for the Evaluation of Nonlinear Optical Materials *J*.Appl. Phys. 39 (1968) 3798-3813.
- K. E. Rieckoff, W. L. Peticoals, Optical second harmonic generation in crystalline amino acids, Science 147 (1965) 610-611.
- V.V,Ghazaryan, M. Fleck, A. M. Petrrosyan, Glycine glycinium picrate—Reinvestigation of the structure and vibrational spectra, Spectrochim. Acta A 78(2011) 128-132

- 35. M. Shakir, S. K.Kushwaha, K. K. Maurya, M. Arora, G. Bhagavannarayana, Growth and characterization of glycine picrate—Remarkable second-harmonic generation in centrosymmetric crystal, *J.* Cryst. Growth 311(2009) 3871-3873.
- 36. Guo. Wensheng, Guo. Fang, Wei. Chunsheng, Liu. Qitao, Zhou. Guangyong, Wang. Dong, Shao. Zhongsheu, Growth and Characterization of Guanidinium Trifluoroacetate Second Harmonic Generation from a Centrosymmetric Crystal, Sci. China Ser. B: Chem. 45 (2002) 276–280.
- 37. T.Dhanabal,M.Sethuraman,G.Amirthaganesan,SamarK.Das, Spectral, thermal, structural, optical and antimicrobial activity studies on 2-imethylimidazolinium picrate An organic charge transfer complex*J*. Molecular Structure 1045(2013) 112-123.
- P.Pandi, G.Peramaiyan, S.Sudhahar, G.Chakkaravarthi, R.Mohankumar, G.Bhagavanarayana, R.Jayavel, Studies on synthesis, growth, structural, thermal, linear and nonlinear optical properties of organic picolinium maleate single crystals, Spectrochimica Acta Part A 98 (2012) 7-13.
- Sagadevan suresh, Growth, optical, mechanical, dielectric and theoretical properties of picolinium maleate NLO single crystal Optik International Journal for Light and Electron Optics 125-12(2014) 2826-2829.
- 40. H. Alyar, Z. Kantarci, M. Bahat, E. Kasap, Investigation of torsional barriers and nonlinear optical (NLO) properties of phenyltriazines *J.* Mol. Struct. 834 (2007) 516–520.
