



Synthesis, Growth and Physicochemical Properties of a New Semiorganic Nonlinear Optical Crystal: L-Arginine Monohydrochloride Barium Chloride (LAMBC)

J. Hepsiba^a and M. Murugan^{a,*}

^a Department of Physics, Ponnaiya Ramanujam Institute of Science and Technology University, Puducherry-600005, India.

*Corresponding Author

murugan.munuswamy@yahoo.com

(M. Murugan)

Tel.: +91 44 2533 3381

Received : 20-05-2018

Accepted : 29-05-2018

ABSTRACT: Appropriate amounts of l-arginine monohydrochloride and barium chloride were dissolved in double distilled water at room temperature. Transparent and defect less bulk crystal of LAMBC with dimension $6 \times 5 \times 3 \text{ mm}^3$ have been grown by solution growth method. Single crystal X-ray diffraction study reveals that LAMBC crystal belongs to orthorhombic crystal system and the measured lattice parameters values are $a=8.28 \text{ \AA}$, $b=9.37 \text{ \AA}$, $c=14.938 \text{ \AA}$, $\alpha=\beta=\gamma=90^\circ$ and volume $V=1158.94 \text{ \AA}^3$. In Powder XRD, the powdered sample was scanned over in the range of 10 to 80° at a scan rate of 1° per minute. Thus the powder XRD pattern observed well defined Bragg's peaks reveal that the LAMBC crystal is in good crystalline nature. FT-IR analysis was carried out to identify the various functional groups present in LAMBC. In the recorded optical transmission spectrum, the UV transparency cut-off wavelength at 307 nm and high transmission percentage of LAMBC crystal from 307 nm to 1000 nm are observed. The powder SHG efficiency of LAMBC crystal is 0.55 times that of standard inorganic KDP. Microhardness study of grown crystal of LAMBC reveals that the grown crystal possesses high mechanical strength. The dielectric properties of LAMBC crystal shows high dielectric constant in lower frequency region and decreases with increase in frequency. The surface of the grown crystal LAMBC has examined by chemical etching analysis.

Keywords: Solution growth; XRD; FTIR; UV; Hardness; Dielectric Studies; Chemical etching.

1 Introduction

Nonlinear optics plays an important role in the emerging photonic and optoelectronic technologies. Nonlinear optical materials find wide applications in the area of laser technology, optical communication and the data storage technology [1]. Non-linear optical (NLO) crystals with high conversion efficiency for second harmonic generation (SHG) and transparent in the visible and ultra violet ranges are required for various devices in field of optoelectronics and photonics [2-4].

Some complexes of the amino acids with simple organic and inorganic salts appear to be promising for optical second harmonic generation (SHG). This research is extended to semi-organic NLO material crystal so as to obtain superior NLO crystal by combining the advantages of organic and inorganic materials [5]. Hence Semi-organic

single crystals are attracting great attention in the field of non linear optics because of their high optical nonlinearity, chemical flexibility of ions, high mechanical strength, thermal stability and excellent transmittance in the UV-Vis region [6-9].

Among the various process of semi organic non-linear optical materials, metal complexes have received potentials interest, because they can be effectively used as the better alternatives for KDP crystals in the frequency doubling process and laser fusion experiments [10, 11]. Materials of amino acids possess particular feature, such as weak Vander waals and hydrogen bonds, wide transparency range in the visible region and zwitterionic nature of the molecules [12, 13]. The potentials NLO properties of L- arginine phosphate mono hydrate

crystals[14], and its deuterated compound[15], have stimulated a wide interest in the complexes of L-arginine and other amino acids[16,17].

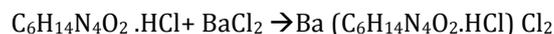
One of the three basic amino carboxylic acid [18], L-lysine reacted with other carboxylic acids has also been studied for its intrinsic polarities. Several crystals composed of L-lysine with NLO properties have been grown and characterized [19, 20]. In this present investigation we report on synthesis, growth and physicochemical properties of l-arginine monohydrochloride barium chloride (LAMBC) nonlinear optical crystal using slow evaporation method.

The grown crystals were characterized using single crystal XRD, Powder X-ray diffraction, Fourier transform infrared (FT-IR) analysis, UV-vis spectroscopy, dielectric studies, Microhardness and etching analysis have been determined.

2. Experimental Procedure

2.1 Synthesis of LAMBC

A analytical reagent (AR) grade of L -Arginine monohydrochloride and barium chloride taken in equimolar ratio at room temperature with Millipore water (18.2 mΩ cm resistivity) as a solvent. The solution was stirred using magnetic stirrer for 8 hours to obtain the homogeneous solution. The synthesized LAMBC salt has been achieved by the following chemical reaction.



L-Arginine monohydrochloride + Barium chloride → LAMBC

2.2 Synthesis of LAMBC

A material to grow as a crystal, determination of its solubility in a particular solvent is an essential criterion because the solubility is the driving force for the rate of crystal growth. The recrystallized synthesized salt was used to measure the solubility of LAMBC in Millipore water. A 250 ml capacity glass beaker containing 100 ml of Millipore water was placed in the constant temperature bath. The initial temperature of the bath was set at 30 °C. The synthesized powder sample of LAMBC prepared as a solution by a motorized stirrer and it was continuing till the excess salt at the bottom of the beaker completely dissolved.

The stirring was further continued, to ensure homogeneous temperature and concentration throughout the entire volume of the solution. After confirming the

saturation, the content of the solution was analyzed gravimetrically. A 20 ml of the saturated solution of the sample was withdrawn by means of a warmed pipette and the same was poured into a cleaned, dried and weighed petri dish. The solution was then kept for slow evaporation in a heating mantle till the solvent was completely evaporated.

The mass of LAMBC in 20 ml of solution was determined by weighing the petri dish with salt and hence the quantity of LAMBC salt (in gram) dissolved in 100 ml of water was determined. The solubility of LAMBC salt in double distilled water was determined further for five different temperatures (35, 40, 45, 50 and 55 °C) by adopting the same procedure. Figure 5.1 shows the solubility curve of LAMBC. The positive slope of the solubility curve of LAMBC enables growth by slow evaporation method.

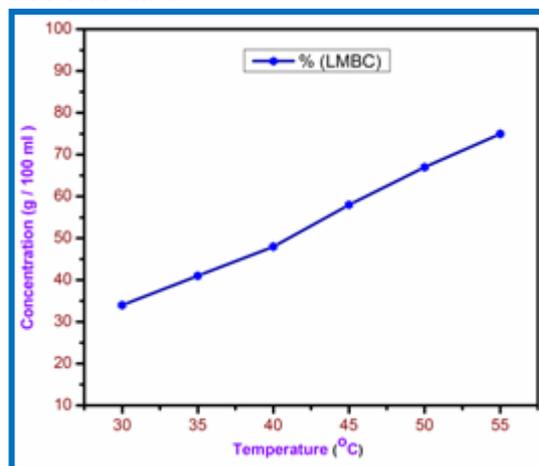


Figure 1 Solubility curve of LAMBC crystal.

2.3 Crystal growth of LAMBC

Solution method with slow evaporation technique was implemented to grow crystal of the synthesized LAMBC salt. According to solubility data, the saturated solution of l-arginine monohydrochloride barium chloride (LAMBC) sample was prepared and constantly stirred for about 6 hours using magnetic stirrer. The solution was filtered using Whatman filter paper. Then the filtered solution (pH = 4) was poured into a beaker and covered by perforated cover for controlled evaporation. The seed crystals of LAMBC were grown within a few days by spontaneous nucleation. After a span of 30-35 days the quality LAMBC crystal with dimension 6 mm × 5 mm × 3 mm was harvested. As grown crystal of LAMBC crystal is

shown in the Figure 2. The optimized growth conditions are presented in the Table 1.

Table 1 Optimized growth condition of LAMBC

Growth method	Slow evaporation
Solvent used	De-ionized water
Molecular formula	Ba (C ₆ H ₁₄ N ₄ O ₂ .HCl) Cl ₂
Molar ratio (1:1)	L-arginine monohydrochloride +
Temperature	Room temperature
Period of growth	30 – 35 days
Dimension of the	6 mm × 5 mm × 3 mm



Figure 2 As grown crystal of LAMBC.

3. Characterization

3.1 Single crystal X-ray diffraction analysis of LAMBC crystal

Single crystal X-ray diffraction analysis of l-arginine monohydrochloride barium chloride (LAMBC) crystal was recorded using ENRAF NONIUS CAD-4 diffractometer. The calculated unit cell parameters of the LAMBC crystal are a=8.28 Å, b=9.37 Å, c=14.938 Å, α=β=γ=90° and volume V=1158.94 Å³, which reveals that the crystal belongs to orthorhombic crystal system.

3.2 Powder X-ray diffraction analysis of LAMBC crystal

Powder sample of LAMBC crystal was subjected to powder X-ray diffraction studies with CuKα (λ=1.5406 Å) radiation. The powdered sample was scanned in the range 10-80 °C at a scan rate of 1° per minute. A well defined Bragg's peaks observed in the powder XRD pattern reveals that the grown crystal has highly crystalline nature. The recorded powder XRD pattern of the grown LAMBC crystal is shown in Figure 3.

3.3 FT-IR Spectrum Analysis of LAMBC crystal

The FTIR spectral analysis of Ba(NH₂NHCSNH₂)Cl₂ was carried out between 4000 and 500 cm⁻¹. The observed spectrum is shown in the figure 4. In the high energy region, there is a broad band between 2100 and 3500 cm⁻¹. The intense sharp peak was observed at 3166 cm⁻¹ due to O-H (-H₂O) vibration. The involvement of NH₃⁺ ion in hydrogen bonding is evident by the fine structure of band in the lower energy region. The bands appear in the region 1641 and 1616 cm⁻¹ is assigned for C=S. The peak at 1641 is due to asymmetrical NH₃⁺ bending mode. The resolved sharp peak at 1485 cm⁻¹ is due to symmetrical NH₃⁺ bending. The narrow bands at 797,642,456 cm⁻¹ and wide split band at 1485, 1314,1281 cm⁻¹ correspond to the vibration of Cl groups.

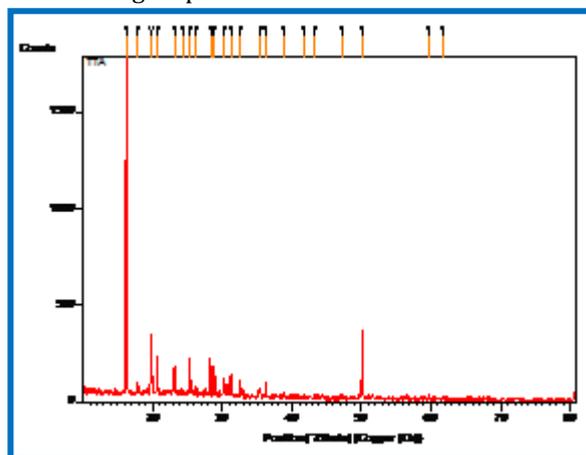


Figure 3 The powder XRD pattern of LAMBC.

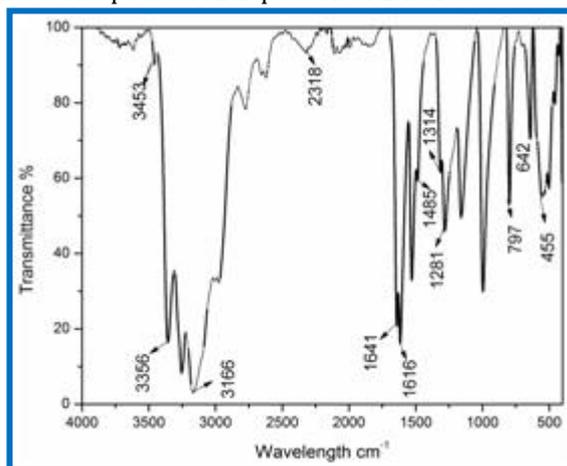


Figure 4 FTIR spectrum of grown crystal LAMBC.

Table 2 Wave assignments of grown LAMBC crystal

Wavenumber cm ⁻¹	Assignments
3166	O-H Stretching Vibration

2318	C-H stretching
1641	NH ₃ ⁺ Asymmetrical bending
1616	NH ₂ Deformation
1485	NH ₃ ⁺ Symmetrical bending
1314	C-H Stretching Vibration
1281	Wide Band
797, 456	Narrow Band
642	C-Cl stretching

3.4 Optical transmission study of LAMBC crystal

The optical transmission spectrum was recorded using DOUBLE BEAM UV-Vis Spectrophotometer:2202 in the region 200-1000 nm and the optical transmission spectrum of l-arginine monohydrochloride barium chloride (LAMBC) crystal is shown in Figure 5. The transmission is maximum in the entire visible region and infrared region. In LAMBC crystal, the UV transparency cut-off wavelength lies at 307 nm and the percentage of transmission is high in the entire visible region from 307 nm to 1100 nm. The absence of absorption in the entire visible region makes the triglycine of l-arginine monohydrochloride barium chloride (LAMBC) crystal as a potential candidate for second harmonic generation and various applications [18].

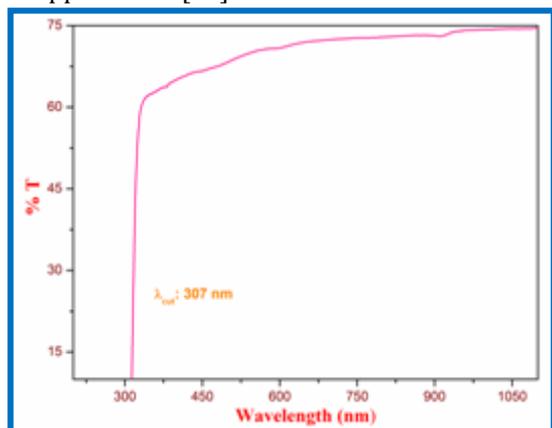


Figure 5 Optical transmission spectrum of LAMBC crystal.

3.5 SHG efficiency of LAMBC crystal

In order to confirm the non-linear optical property of powdered sample of LAMBC crystal was subjected to KURTZ and PERRY techniques, which remains powerful tool for initial screening of materials for SHG efficiency [21]. A Q-switched Nd: YAG laser emitting 1.06μm with power density up to 1 GW/cm² was used as a source of illuminating the powder sample. The sample was

prepared by sandwiching the graded crystalline powder with average particle size of about 90μm between two glass slides using copper spices of 0.4 mm thickness. A laser was produced a continuous laser pulses repetition rate of 10Hz. The experimental setup uses a mirror and 50/50 beam splitter. Here well known NLO crystal KDP is taken as a reference material.

The fundamental beam was splitted into two beams by the beam splitter (BS); one of them was used to illuminate the powder under study and the other constituted the reference beam of power Pω. Half-wave plate (HW) placed between two parallel polarizers (P) and was used to pump the beam power. The input power was fixed at 0.68 J and the output power was measured as 4.8 mJ, which was compared to output 8.8 mJ of standard KDP. The diffusion of bright green radiation of wave lengthλ=532 nm (P2ω) by the sample confirms second harmonic generation (SHG). The powder SHG efficiency of LAMBC crystal was about 0.55 times of KDP. The good second harmonic generation efficiency indicates that the LAMBC crystals can be used as a suitable material for non-linear optical devices.

3.6 Microhardness studies of LAMBC crystal

The mechanical properties of the crystal are evaluated by mechanical testing which reveals certain mechanical characteristics. The fastest and simplest type of mechanical testing is the hardness measurement. Among the different testing methods, the Vicker’s hardness test method is more commonly used. In the present study, Vicker’s hardness test was carried out on the grown crystal using SHIMADZU HMV microhardness tester fitted with a diamond pyramidal indenter. Microhardness measurements were done on LAMBC for the applied load (p) varying from 25 to 100g for a constant for indentation time 10s. Several indentations were made for each load and the diagonal length (d) of the indentation was measured.

Vicker’s hardness number was determine using the formula $HV = 1.8544 P/d^2$ (Kg/mm²). A graph was plotted between Hv and load (p) (Figure 6). It is observed that Hv increases with applied load which is known as reverse indentation size effect (RISE). For an indentation load of 100 g, crack was initiated on the crystal surface, around the indenter. This is due to the release of internal

stress locally initiated by indentation. The work hardening coefficient (n) has been calculated from the slop of straight line between $\log p$ and $\log d$ (Figure 7) and it is found to be 1.27 which indicates moderately hard nature of material [22].

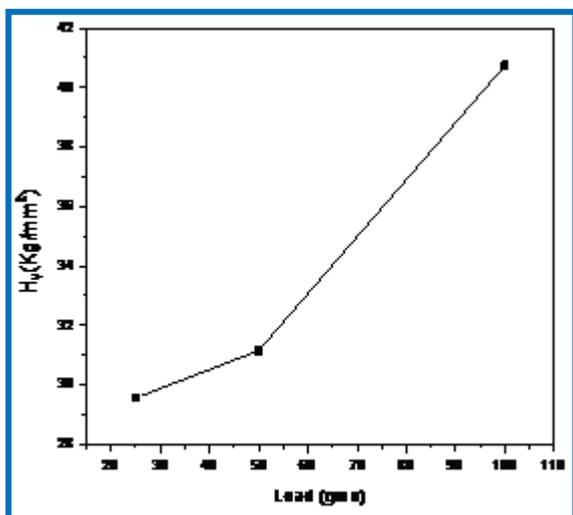


Figure 6 Plot of load (p) Vs hardness (HV) for LAMBC crystal

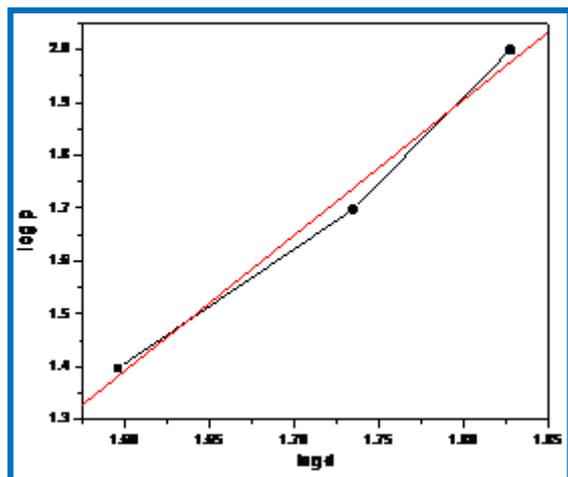


Figure 7 Plot of $\log d$ Vs $\log p$ for LAMBC crystal.

3.7 Dielectric studies of LAMBC crystal

The dielectric constant and the dielectric loss of the LAMBC sample were measured using HIOKI 3532-50 LCR HITESTER. Dielectric constant and dielectric loss of the sample have been measured for different frequencies (100 Hz to 5 MHz) at different temperatures (308 to 368 K). Figure 8 and Figure 9 show the variations of dielectric constant and dielectric loss respectively as a function of frequency at different temperatures. It is observed from Figure 8 that the dielectric constant (at 308 K) decreases with increase in frequency from 100 Hz to 10 kHz and

then attains a constant value of 27.82. The same trend is observed for other temperatures too. It is also observed that the value of dielectric constant increases with temperature. Such variations at higher temperature may be attributed to the blocking of charge carriers at the electrodes. The decrease of dielectric constant at low frequency region may be due to space charge polarization. Figure 9, indicates that as the frequency increases, the dielectric loss decreases exponentially and then attains a lower value of 0.049 at 308 K. The low value of dielectric loss confirms that the sample possesses lesser defects.

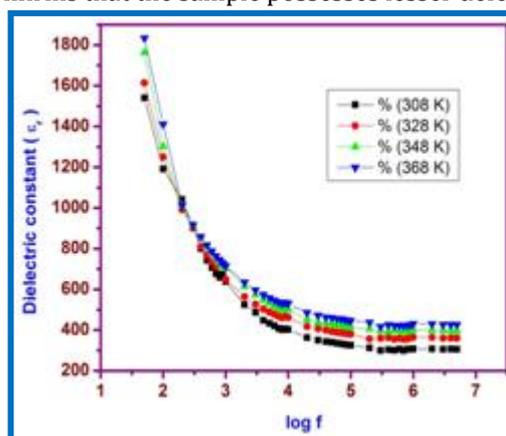


Figure 8 Variation of dielectric constant with \log frequency at different temperatures for LAMBC crystal.

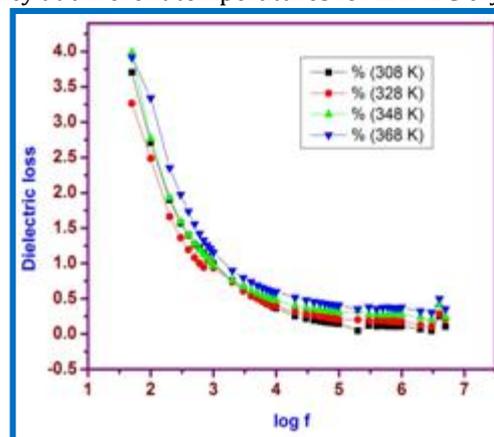


Figure 9 Variation of dielectric loss with \log frequency at different temperatures for LAMBC crystal.

3.8 Chemical Etching analysis of LAMBC crystal

Crystals with lesser defects are most wanted for device fabrications [23]. Growth defects can be easily identified by the chemical etching analysis [24]. The performance and properties of materials are mainly depends on the defects present in the sample. Therefore, analyzing and identifying the defects is most important. Here, the chemical etching was made using water at room

temperature. The etched surface was cleaned using good quality filter paper and the inspected immediately using microscope. The etching study was demonstrated for 10 s and 15 s, and the observed etch patterns are shown in Figure 10a and 10b.

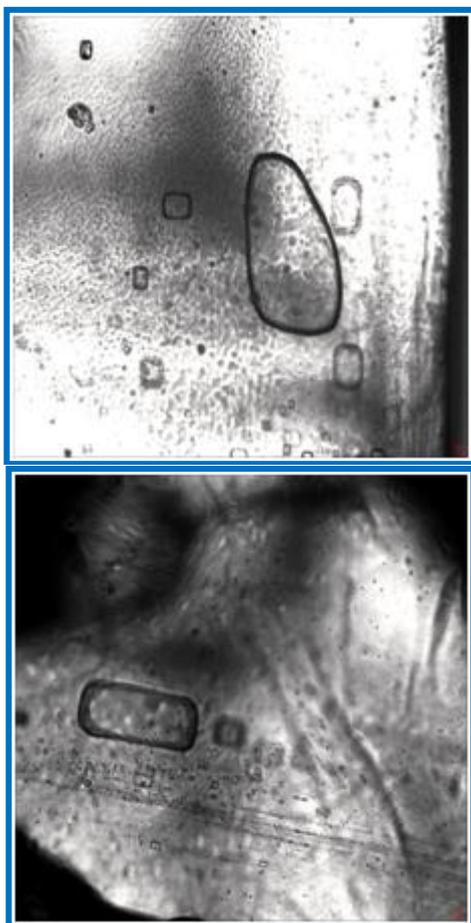


Figure 10 (a) & (b) Etch pattern of LAMBC crystal for 10s and 15s.

From the figure, it is observed that there is a smooth surface and rectangle shape etch pits observed on the surface of the sample when etch pattern was taken with in 10s. In the etch pattern for 15 s, there are some rectangle shape etch pits (small size) and also the dark spot is observed. These etch pits due to the chemical impurities and crystal undergoes selective dissolution during growth.

4. Conclusions

Optical good quality LAMBC crystal was grown successfully by slow evaporation technique at room temperature. Unit cell parameters and crystal system were determined by single crystal X-ray diffraction technique, which reveals that the crystal belongs to orthorhombic crystal system. Powder XRD shows good crystalline of the grown LAMBC crystal. The various functional groups presence in the grown crystal of LAMBC was identified by FTIR study. The UV cut off wavelength of LAMBC crystal was found to be 307 nm and, which reveals grown crystals are potential candidate for NLO applications. The second harmonic generation (SHG) efficiency of LAMBC crystal is about 0.55 times that of KDP. The temperature dependent dielectric constant and dielectric loss as grown LAMBC crystal were measured. From the microhardness test, the value of n was found to be 1.27, which indicates the hard nature of LAMBC crystal. The surface micrograph of grown LAMBC crystal was analysed by etch pattern.

References

- [1] H.S Nalwa, S. Miyata, (1997) Nonlinear optics for organic molecules and polymers, CRC press, New York.
- [2] M. Krishnakumar, S. Karthick, K. Thirupugalmani, B. Babu, G. Vinitha, Growth, spectral, optical, laser damage threshold and DFT investigations on 2-amino 4-methyl pyridinium 4-methoxy benzoate (2A4MP4MB):A potential organic third order nonlinear optical material for optoelectronic applications, *Optics and Laser Technology*, 101 (2018) 91–106.
- [3] B. Babu, J. Chandrasekaran, R. Thirumurugan, V. Jayaramakrishnan, K. Anitha, Experimental and theoretical investigation on 2-amino5-bromopyridinium L-tartrate-A new organic charge-transfer crystal for optoelectronics device applications, *Journal of Material Science: Materials in Electronics*, 28 (2017) 1124–1135.
- [4] S. Dinakaran, S. Verma, S. Jerome Das, G. Bhagavannarayana, S. Kar, K.S. Bartwal, Determination of crystalline perfection, optical indicatrix, birefringence and refractive-index homogeneity of ZTS crystals, *Applied Physics B*, 103 (2011) 345-349.
- [5] I. Ledoux, J. Badan, J. Zyss, A. Migus, D. Hulin, J. Etchepare, G. Grillon, and A. Antonetti, Generation of high-peak-power tunable infrared femtosecond pulses in an organic crystal: application to time resolution of weak infrared signals, *Journal of the Optical Society of America B*, 4 (1987) 987–997.

- [6] S. Boomadevi, H.P. Mittal, R. Dhasekaran, Synthesis, crystal growth and characterization of 3-methyl 4-nitropyridine 1-oxide (POM) single crystals, *Journal of Crystal Growth*, 261 (2004) 55–62.
- [7] M.D. Aggarwal, J. Choi, W.S. Wang, K. Bhat, R.B. Lal, A.D. Shields, B.C. Penn, D.V. Frazier, Solution growth of a novel nonlinear optical material: L-histidinetetrafluoroborate, *Journal of Crystal Growth*, 204 (1999) 179–182.
- [8] G.Xing, M.Jiang, Z.Shao, D.Xu, Bis(thiourea)cadmium chloride (BTCC) a novel nonlinear optical crystal of organometallic complex, *Chinese Journal of Lasers*, 14 (1997) 302-308.
- [9] S.Velsko, (1990) Laser program annual report, Lawrence, Lawrence Livermore, National laboratory, Livermore CA.
- [10] S.R.Batten, R.Robson, Interpenetrating Nets: Ordered, Periodic Entanglement, *Angewandte, Chemie International Edition*, 37(1998) 1460-1494.
- [11] O.M.Yaghi, H.Li, C.Davis, D.Richaedson, T.L.Groy, Synthetic Strategies, Structure Patterns, and Emerging Properties in the Chemistry of Modular Porous Solids, *Accounts of Chemical Research*, 31(1998) 474- 484.
- [12] T. Balakrishnan and K. Ramamurthi, Growth, structural, optical, thermal and mechanical properties of glycine zinc chloride single crystal, *Materials Letters*, 62 (2008) 65-68.
- [13] S. Balaprabhakaran, J. Chandrasekaran, B. Babu, R. Thirumurugan, K. Anitha, Synthesis, crystal growth and physicochemical characterization of new organic crystal: L-ornithiniumdipicrate (LODP), *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 136 (2015) 700-706.
- [14] S.Palaniswamy and O.N. Balasundaram, Growth and characterization of semi-organic nlo material: glycine potassium chloride (GPC), *Rasayan Journal of Chemistry*, 2 (2009) 28-33.
- [15] S. Palaniswamy and O.N. Balasundaram, Effect of ph on the growth and characterization of glycine sodium chloride (GSC) single crystal, *Rasayan Journal of Chemistry*, 1 (2008) 782-787.
- [16] Suresh Sagadevan and R. Varatharajan, Studies on the mechanical properties of glycine lithium chloride NLO single crystal, *International Journal of Physical Sciences*, 8 (2013) 1892-1897.
- [17] J. Qin, D. Liu, C. Dai, C.Chen, B. Wu, C.Yang, C.Zhan, Influence of the molecular configuration on second-order nonlinear optical properties of coordination compounds, *Coordination Chemistry Reviews*, 188 (1999) 23-34.
- [18] M.D. Aggarwal, J. Choi, W.S. Wang, K. Bhat, R.B. Lal, A.D. Shields, B.G. Penn, D.V. Frazier, Solution growth of a novel nonlinear optical material: L-histidinetetrafluoroborate, *Journal of Crystal Growth*, 204 (1999) 179-182
- [19] Malcolm L. H. Green, Seth R. Marder, Mark E. Thompson, Judith A. Bandy, David Bloor, P. V. Kolinsky & R. J. Jones, *Nature*, 330 (1987) 360-362.
- [20] S.R. Marder, B.G. Terman et al. materials for nonlinear optics chemical perspective (American Chemical society Washington). 1991..
- [21] S.K. Kurtz, T.T. Perry, A Powder Technique for the Evaluation of Nonlinear Optical Materials, *Journal of Applied Physics*, 9 (1968) 3798-3813.
- [22] E.M.Onitsch, The Present Status of Testing the Hardness of Materials, *Mikroskopie*, 95 (1956) 12-14.
- [23] B. Babu, J. Chandrasekaran, B. Mohanbabu, Yoshitaka Matsushita and M. Saravanakumar, Growth, physicochemical and quantum chemical investigations on 2-amino 5-chloropyridinium 4-carboxybutanoate – an organic crystal for biological and optoelectronic device applications, *RSC Advances*, 6 (2016) 110884-110897.
- [24] K. Owezarek, Sangwal, Effect of impurities on the growth of KDP crystals: Mechanism of adsorption on (101) faces, *Journal of Crystal Growth*, 102 (1990) 574-580.

Competing Interests:

The authors declare that they have no competing interests.

About The License



Attribution 4.0 International (CC BY 4.0)

The text of this article is licensed under a Creative Commons Attribution 4.0 International License.