Research Article Available online www.ijsrr.org ISSN: 2279–0543

International Journal of Scientific Research and Reviews

Structural, Optical and Thermal Investigations OFL- Arginine Ammonium Bromide Single Crystal for NLO Applications

S. Sivasakthi[1] and R. Suresh Babu[2]

[1,2]PG and Research Department of Physics, Muthurangam Govt. Arts College (A), Vellore-632 002. India
sivashakthi73@gmail.com[1*],rsb_7@yahoo.com[2]

ABSTRACT:

The homogeneous solution of L– Arginine Ammonium Bromide (LAAB) crystal was prepared for 1:1 ratio and good optical crystals were grown by slow evaporation method. The grown Crystal was subjected to various characterizations such as single, powder X-ray diffraction, Fourier Transform Infrared (FTIR) spectroscopy, UV-Vis Absorption Spectroscopy, Thermo gravimetric(TGA), Differential Scanning Calorimetery (DSC) and Second Harmonic Generation. The cell parameters were determined by single crystal X-ray diffraction such as a = 16.40 Å, b = 15.81 Å, c = 8.79 Å, Volume (V) = 2281 Å^3; α = ɤ = 90º β =90.65º confirmed that it belongs to monoclinic crystal system. The characteristics of the grown crystal were discussed in detail i.e., cell parameters, optical, functional group analysis, thermal studies and SHG result.

KEYWORDS: LAAB, slow evaporation method, single crystal, SHG

***Corresponding Author**

S. Sivasakthi[1]

PG and Research Department of Physics,

Muthurangam Government Arts College (A),

Vellore-632 002. India

sivashakthi73@gmail.com

INTRODUCTION

In recent times, fabrication of non-linear optical (NLO) materials plays a predominant role in the field of optoelectronic devices like laser diode, optical switching, optical computing, optical memory storage, electro-optical modulation, optical information processing etc. Fascinatingly, organic NLO materials are involved much attention due to the huge non-linear response over a wide range of frequency. Also, these materials exhibit practical difficulties in the production of bulk crystals for various potential applications. To overcome, this difficulties the synthesis of new hybrid semi-organic crystal are introduced with various organic and inorganic materials[1,2].

Based on this background, the combination of L-arginine with inorganic materials like ammonium bromide might enhance the non symmetric behaviors which pave the path towards the nonlinear optical properties. In addition, the proper combination of L-arginine with ammonium bromide could leads to alternate approach for potassium dihydrogen orthophosphate (KDP) crystals[3-6].

This works mainly focuses on the L– Arginine Ammonium Bromide (LAAB) crystal growth by slow evaporation method. In order to understand the structural, optical and thermal properties of LAAB crystals, various investigations have been carried out such as single, powder X-ray diffraction, Fourier Transform Infrared (FTIR) spectroscopy, UV-Vis Absorption Spectroscopy, Thermogravimetric (TGA), Differential Scanning Calorimetery (DSC) and Second Harmonic Generation (SHG).

EXPERIMENTAL DETAILS

The structure of L– Arginine Ammonium Bromide (LAAB) is shown in Figure 1 and the Table 1 shows the various properties of L-Arginine and Ammonium Bromide.

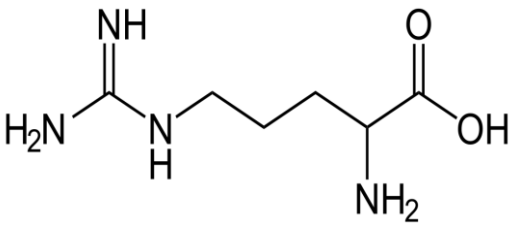

Figure 1. L-arginine structure

Table 1. Properties of L-Arginine and Ammonium Bromide

Properties	L-Arginine	Ammonium Bromide
Chemical formula	$C_6H_{14}N_4O_2$	NH_4Br
Molar mass	174.2 g·mol^{-1}	97.94 g·mol^{-1}
Appearance	white powder	white powder
Density	1.42 g/cm^3	2.429 g/cm^3
Melting point	260 °C	235 °C
Solubility in water	14.87 g/L	60.6 g/ 100ml

.

Synthesis and Crystal Growth

The L – Arginine and Ammonium Bromide materials were taken in equimolar ratio. In adduct is formed according to the following reaction.

$$C_6H_{14}N_4O_2 + NH_4Br \rightarrow NH_4(C_6H_{14}N_4O_2)Br$$

The distilled water and stirred at room temperature for 5 hours to achieve the homogenous condition. The L-Arginine Ammonium Bromide material was synthesized by slow evaporation method (L-AAB) tiny crystals also grown. The L-AAB material was purified by repeated recrystallization. After purification the solution was prepared for super saturation condition and filtered with Whatmann filter paper. The crystal clear solution carefully transferred to 50 ml beaker and closed with pinholes plastic sheet for natural evaporation. After 4 weeks, optically clear crystal was harvested with good dimension 14×3×2 mm^3. Good dimension crystals are very essential for device fabrications and optical applications. The grown crystal is shown in Figure 2.

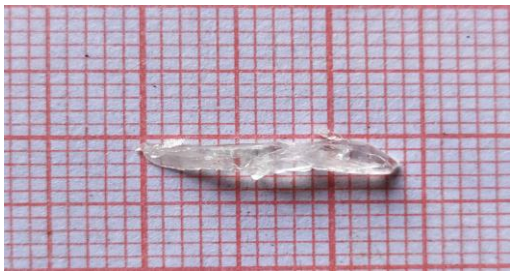

Figure 2. Photograph of grown LAAB crystal.

RESULT AND DISCUSSION

Powder x-ray diffraction

The good optical L-AAB crystal was powdered finely and subjected powder X-ray diffraction characteristics using the Bruker D8 Advanced powder X-ray diffractometer with Cu Kα (λ = 1.5418Å). The study was carried in the range of 10˚ to 90˚. The recorded X-ray pattern is shown in Figure 3. The good crystalline nature was confirmed from the single sharp peak[7].

The tiny crystal of LAAB was subjected to single crystal X-ray diffraction analysis. Using the Bruker instrument the cell parameter and space group ($P_{21\ 21\ 21}$) were found. The cell parameters of LAAB are given in Table 2.

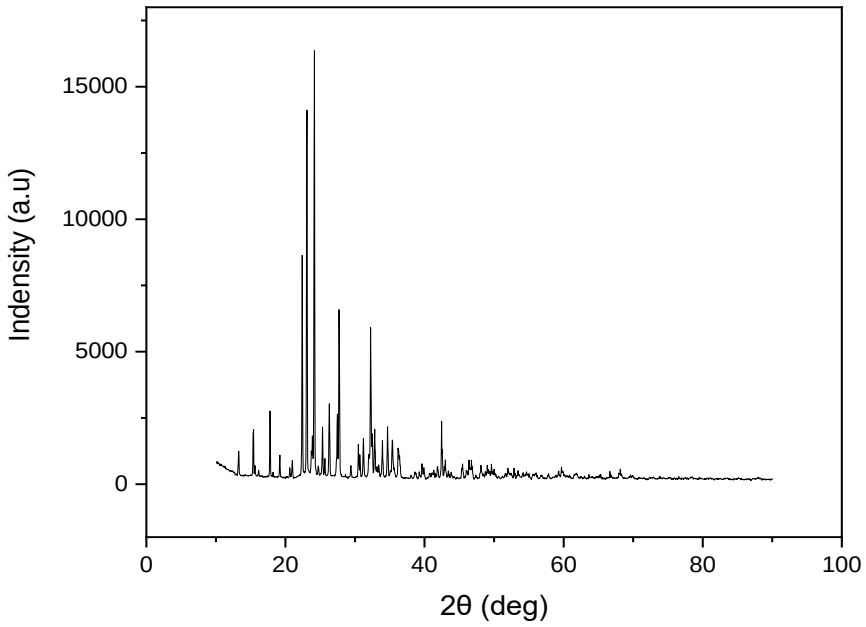

Figure 3. PXRD Pattern of LAAB Single Crystal

Single x-ray diffraction

Table 2. Lattice parameters of LAAB.

SAMPLE	LATTICE PARAMETER			VOLUME v(Å³)	α = γ≠ β	STRUCTURE
	a(Å)	b(Å)	c(Å)			
LAAB	16.40	15.81	8.79	2281	90º=90º≠ 90º	Monoclinic

FTIR spectral studies

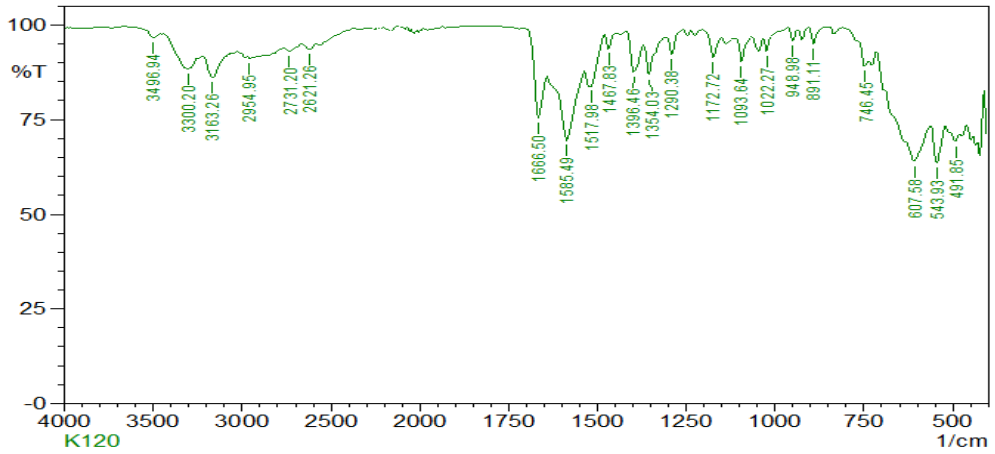

Figure 4. FTIR spectrum of LAAB crystal

The FTIR spectroscopy studies are effectively used to identify the functions groups presents in the crystal. The FTIR spectral analysis for the grown crystal has been recorded in the range of 400 – 4000 cm^{-1} as shown in Figure 4.

In the high energy region peak at 3496 cm^{-1} is due to -OH stretching. The peak at 3300 cm^{-1}, 2954 cm^{-1} is assigned to C-H stretching vibration. The peak at 3163 cm^{-1} is assigned to O-H stretching vibration. The peak at 2731 cm^{-1} indicates N-H stretching. It is clearly seen that the existence of carboxylic acids (COOH) function groups. The fact that some of the COOH groups are ionized implicates an appearance of the NH_3^+ group in arginine molecule. The strong band 1585 cm^{-1} in the infrared spectrum is attributed to N–H bending vibration of NH_3^+ group. The peak at 1660 cm^{-1} indicates NH_3^+ bending[8].

The peak 1467 cm^{-1},948 cm^{-1} and 746 cm^{-1} are assigned to C-H bending. The peak at 1354 cm^{-1} represents the CH_2 wagging vibration. The peak at 1172 cm^{-1} indicates Asymmetric of COO^- vibration. The stretching frequency around at 1093 cm^{-1} is characteristics of C-N stretching. The peak at 543 cm^{-1} is assigned to C-Br stretching. The

observed peaks in the spectrum are assigned to their corresponding bonds and functional groups and tabulated in Table 3.

Table 3. FTIR Functional Group Assignments of the Grown LAAB Crystal

Wave number (cm^{-1})	Bond Assignments
3496	-OH stretching
3300	C–H stretching
2731	N-H stretching
1666	NH_3^+ bending
1467	C-H bending
1290	C-O stretching
1172	COO^- vibration
1093	C-N stretching
543	C–Br stretching

UV-Vis spectral studies

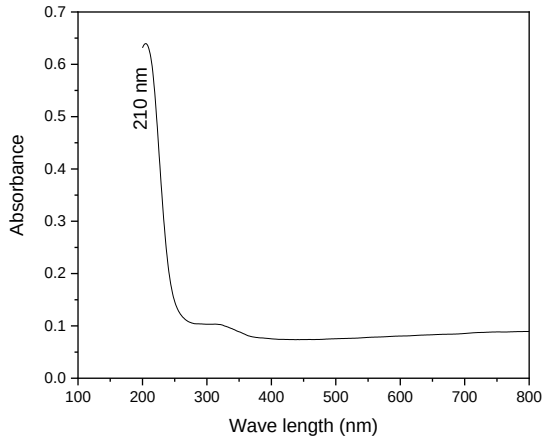

Figure 5. UV-Vis spectrum of LAAB crystal

The UV-Visible spectral study is a useful tool to determine the transparency, which is an important requirement for a material to be optically active. The optical transmission spectrum of the LAAB single crystal was recorded in the range of 100-800 nm and is shown in Figure 5.

A large absorption was found of 210 nm and drastic variation occurs the crystal has very low absorbance in the entire visible and IR region. The UV spectrum reveals that the

cut off wavelength of LAAB is 210 nm and the grown crystal has wide transparency in the entire visible region. This is optimized for the suitability of opto-electronic applications [9].

Band gap energy

The energy gap for a grown LAAB crystal was calculated for using the Tauc equation

$$(\alpha h\gamma) = A(h\gamma - E_g)^n$$

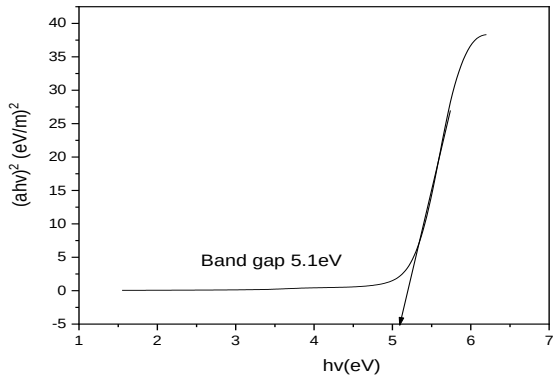

Figure 6. Band gap of LAAB crystal

Where *'α'* is the absorption coefficient, *'h'* is the Plank's constant, *'ν'* is the frequency of the incident photon and *A* is constant. The linear portion of the plot of $(\alpha h\nu)^2$ versus $h\nu$ where extrapolated to the energy axis which gives the exact band gap value. A plot of $(\alpha h\nu)^2$ versus $h\nu$ is shown in Figure 6. From the intercept of straight line on the energy axis, the band gap was found to be 5.1 eV. Large value of band gap indicates that the material is a good insulator and can provide large transmission in visible region.

Thermal gravimetric analysis

In order to study the thermal stability of the grown crystal, thermo gravimetric analysis (TGA) have been carried out using a SDT Q600 V20.9 Built 20 model thermal analyzer in an inert nitrogen atmosphere.

The thermal studies such as TGA studies were carried out for L– Arginine ammonium bromide crystal in the temperature range 28–800°C at the heating rate of 20°C per min. The recorded TGA thermal curves for L – Arginine ammonium bromide crystal are

shown in the Figure 7. The TGA trace shows, there is no weight loss below 154.5ºC, hence the crystal is completely devoid of any entrapped solvent in the lattice of the crystal. The major weight loss occurs at four stages. First stage weight loss of about 6.856% (0.1528 mg) observed between 85.5 ºC to 154.5 ºC is due to the decomposition of L-Arginine. Second stage weight loss of about 11.42% (0.2547 mg) observed between 155.2 ºC to 300 ºC this is due to step by step decomposition and release of volatile substances in the Compound, probably ammonia and carbon dioxide. The third stage gradual weight loss of about 51.53% (1.149 mg) observed for wider range of temperature between 301.5 ºC to 450 ºC is due to the decomposition of potassium (760 ºC). The fourth stage weight loss of about 7.919% (0.1765 mg) of wider range of temperature between 450^0C to 800^0C is due to decomposition of LAAB. These four different stages weight loss indicates the decomposition of the substance. The final residue weight left was 22.28% (0.4967 mg) after heating 800 ºC for LAAB crystal[10-12].

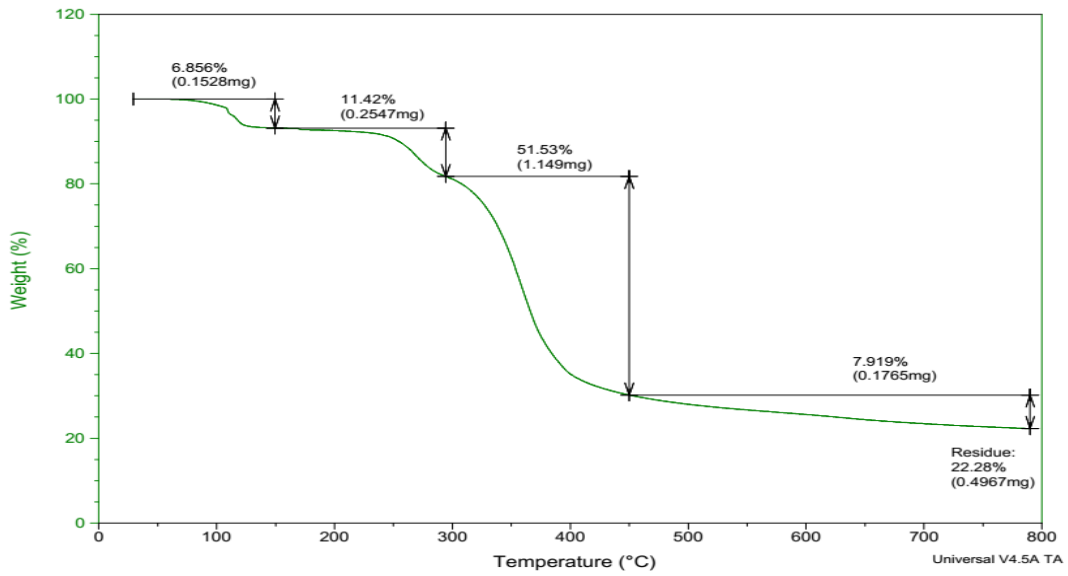

Figure 7. TGA curve for LAAB crystal

Differential scanning calorimetry

The DSC analysis of the grown crystal was carried out between 28 °C and 800 °C which is shown in Figure 8. There is a sharp endothermic peak starting at 111.47 °C to 122.39 °C, which corresponds to the decomposition as observed in TGA analysis. Again it also confirms absence of melting and any entrapped solvent in the lattice. DSC curve shows the sharp endothermic peak indicates the crystal has good crystallinity and decomposition point of as grown LAAB crystal is 122.39 ºC.

The TGA-DSC result shows that the grown crystal is thermally stable up to 111.47 ºC and establishes its suitability to withstand the high temperature for laser experiments.

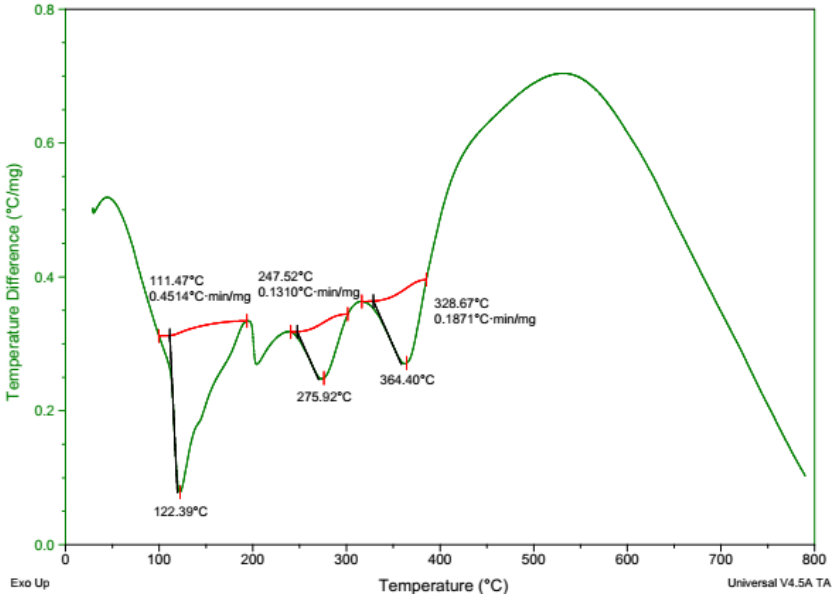

Figure 8. DSC curve for LAAB crystal

Second harmonic generation

In order to confirm the nonlinear optical property, powdered sample of LAAB was subjected to a Kurtz and Perry powder techniques, which remains a powerful tool for initial screening of materials for SHG. A Q switched High Energy Nd:YAG Laser (QUANTA RAY Model LAB – 170 - 10) operating at the fundamental wavelength of 1064 nm with pulse width 8 ns and repetition rate of 10 Hz and input energy as 0.701 J was used. The NLO property of the sample was confirmed by the sample was emission of bright green light as output with wavelength of 532 nm. The KDP sample was used as the reference material. The efficiency of second harmonic generation of L – Arginine and Ammonium Bromide crystal was found to be 1.76 times greater than the reference material KDP [13,14]. Thus LAAB crystal can be used as an effective candidate for nonlinear optical applications.

CONCLUSION

The good optical quality single crystal of LAAB has been grown by slow evaporation solution growth technique (SESGT). The sharp and well defined Bragg's peaks of powder XRD pattern at specified 2θ angles shows the crystalline nature and purity of the crystal. The lattice parameters of LAAB are determined by single crystal XRD. It belongs to monoclinic crystal system. The presence of functional groups was confirms by FTIR. The optical

absorption studies confirmed that the LAAB crystal has good optical transmission in the complete UV-VIS-NIR region in the electromagnetic spectrum. The TGA measurement reveals that the crystal is thermally stable upto 111°C and there is no structural phase transition in low temperature region. SHG efficiency of the grown crystal was measured by Kurtz and Perry powder techniques and its efficiency was found to be 1.76 times greater than the KDP. Thus LAAB crystal can be used as an effective candidate for non-linear optical applications.

REFERENCES

1. Sivasakthi S, Pasupathi G, Rajababu S. Growth And Characterization Of L-Histidine Sodium Bromide A Semiorganic Nonlinear Optical Crystal. International Journal of Scientific Research and Engineering Studies. 2016; 3 : 2349-8862.
2. Sivasakthi S, Pasupathi G, Thirunavukkarasu P. Growth and Characterization of Non-Linear Optical Studies On L-Alanine Ammonium Bromide Single Crystals. International Journal of Scientific Research and Engineering Studies. 2016; 3: 2349-886.
3. Anandan P, Saravanan T, Parthipan G, Mohan Kumar R et al. Crystal growth, structural and thermal studies of amino acids admixture L-arginine phosphate monohydrate single crystals. Solid State Sciences. 2011; 13: 915-22.
4. Yasotha P Sagunthala P. Growth and Charac terization Studies of L-Arginine Doped Zinc Sulphate Mono Hydrate Single Crystals. Materials Today. 2019; 9: 674-79.
5. VijayanMahakVij N, Naghma K T Khan,D. HaranathRajnikant, Jayalakshmy M S.Investigation on the key aspects of l-arginine paranitrobenzoate monohydrate single crystal: A non-linear optical material. Chinese Journal of Chemical Engineering. 2019; 27: 701 -08.
6. FelicitaVimala J, Thomas J, Joseph Prakash. A study on the growth and characteristic properties of L-Arginine doped ZTSsingle crystal. Elixir Crystal Growth. 2013; 56: 13350-354.
7. Tanusri Pal, TanusreeKar, Gabriele Bocelli, and Lara Rigi. Synthesis, Growth, and Characterization of L-Arginine Acetate Crystal: A Potential NLO Material. CrystalGrowth & Design. 2003; 3: 13-16.
8. Petrosyan A M, Sukiasyan R P, KarapetyanH A , Terzyan S S , Feigelson R S. Growth and investigation of new non-linear optical crystals of LAP family. Journal of Crystal Growth. 2000; 213: 103-11.

9. Preema, Thomasa C, Lanka Bhushan Kumara, Anuradhab A, Arunaa S, Ginson Josepha P, Sagayaraj P. Growth and characterization of nonlinear optical single crystals of L-arginine diiodate. Journal of Crystal Growth. 2006; 290: 560–64.
10. HajaHameed A S, Ravi G Hossain MD M, Ramasamy P. Growth and characterisation of L-arginine phosphate family crystals. Journal of Crystal Growth. 1999 ;204: 333-40.
11. Arjunan S , Bhaskaran A, Mohan Kumar R , Mohan R , Jayavel R. Effect of rare-earth dopants on the growth and structural, optical, electrical and mechanical properties of l-arginine phosphate single crystals. Journal of Alloys and Compounds. 2010; 506: 784-87.
12. Renuka N, Vijayan N , BrijeshRathi , Ramesh Babu R , Nagarajan K , Haranath D, Bhagavannarayana G. Synthesis, growth and optical properties of semi organic non linear optical single crystal l-Arginine acetate. Optik . 2012; 123 : 189–92.
13. Srinivasan P, Vidyalakshmi Y, and Gopalakrishnan R. Studies on the Synthesis, Growth, Crystal Structure, and Nonlinear Optical Properties of a Novel Nonlinear Optical Crystal: L-Argininium-4-nitro Phenolate Monohydrate (LARP). Crystal Growth & Design. 2008; 8: 2329-334.
14. Geetha P, Krishnan S, Jeromdas S, Chithambaram V. Growth and characterization of urea ammonium bromide nonlinear optical single crystals by slow evaporation technique. Optik. 2015; 126: 3962-964.