

Original Research Article

Synthesis, growth and characterization of amino acid based semiorganic crystal bis-thiourea l-lysine monohydrochloride

R. Tamilselvi, K. Arunadevi, D. Sivavishnu, P. Ramadoss*

Post Graduate and Research Department of Physics, Government Arts College, Tiruvannamalai, Tamil Nadu, India

Received: 01 March 2017

Accepted: 20 March 2017

***Correspondence:**

Dr. P. Ramadoss,

E-mail: dossrpg@yahoo.co.in

Copyright: © the author(s), publisher and licensee Medip Academy. This is an open-access article distributed under the terms of the Creative Commons Attribution Non-Commercial License, which permits unrestricted non-commercial use, distribution, and reproduction in any medium, provided the original work is properly cited.

ABSTRACT

Background: We report on synthesis, growth and characterization of Bis-thiourea L-lysine monohydrochloride (BTLM) crystal.

Methods: Bis-thiourea L-lysine monohydrochloride (BTLM) crystal were grown by solution growth method in the molar ratio 1:1 at room temperature.

Results: Transparent and defect free crystal of BTLM were harvested in the period of 40-45 days with dimension 7mm × 4mm × 2mm. Single crystal XRD analysis revealed that the crystal system belongs to Orthorhombic with cell parameters a= 14.41 Å, b= 5.89 Å and c= 15.52 Å. The sharp and well defined Bragg peaks observed in the powder XRD pattern confirm the crystalline nature of BTLM crystal. The presences of functional groups in the grown crystal BTLM were identified by FT-IR analysis. The fluorescence spectral study was carried out in the range of 280–500 nm. Second harmonic generation (SHG) of powdered BTLM sample was tested using Nd: YAG laser and is found to be 0.55 times that of potassium dihydrogen orthophosphate. The mechanical strength of the BTLM crystal was evaluated and it describes that the Vickers hardness number of BTLM is found to be increase with the applied load. The work hardening co-efficient (n) has been calculated from the slope of straight line between log P and log d. The dielectric study of BTLM was carried out as a function of frequency at different temperature.

Conclusions: From the result we confirm that the BTLM crystals have good physicochemical properties. So, the grown BTLM crystal was suitable candidate for nonlinear optical applications.

Keywords: Solution growth method, XRD, Fluorescence spectral study, SHG, Hardness

INTRODUCTION

The search for new non-linear optical materials for tailor made device application had been increasing from the last few decades because of their potential industrial applications especially in the field of photonics for optical switching, optical modulators, data storage devices, telecommunication and high density optical data storage.^{1,2} The importance of amino acids and their salts belongs to a family of organic materials that have wider NLO applications.^{3,5} Amino acids contain a deprotonated

carboxylic acid group (COO⁻) and protonated amino group (NH₃⁺). This dipolar nature exhibits peculiar physical and chemical properties in amino acids, thus make them ideal candidate for NLO applications.⁶

Thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and its ability to form an extensive network of hydrogen bonds⁷. The nonlinear optical properties of some of the complexes of thiourea, such as bis-thiourea cadmium chloride (BTCC), bis-thiourea zinc chloride (BTZC), and potassium thiourea bromide (PTB) have gained significant attention

in the last few years because both organic and inorganic components in it contribute to the process of second harmonic generation.^{8,9} The centrosymmetric thiourea molecule, when combined with inorganic salt yield non-centrosymmetric complexes which has the nonlinear optical properties.¹⁰

Owing to this basic nature L-lysine monohydrochloride form a number of salts with different organic and inorganic salts, which also showed NLO properties.¹¹ Hence L-arginine, L-histidine, L-threonine, L-alanine and L-valine have been subjected for the formation of salts with different inorganic acids. As a result very good semiorganic materials such as L-arginine phosphate monohydrate¹², L-histidine hydrochloride¹³, L-alanine cadmium chloride¹⁴, L-valine hydrochloride¹⁵ are some of example which proved very suitable material for NLO applications. In the organic class α -amino acids exhibit some specific features such as molecular chirality, weak vanderwaals, hydrogen bonds and the absence of strongly conjugated bonds, wide transparency ranges in visible and UV spectral region and zwitterionic nature of the molecule which favours crystal hardness.¹⁶ The present research article focused on synthesis, growth and characterization of Bis-thiourea L-lysine monohydrochloride crystal by solution growth method.

METHODS

Synthesis of BTLM

BTLM single crystals were synthesized using Bis-thiourea (AR Grade, Merck) and L-lysine monohydrochloride (AR grade, Merck) in deionized water by stoichiometric incorporation of Bis- thiourea and L-lysine monohydrochloride in the ratio 2:1 according to the following chemical reaction,

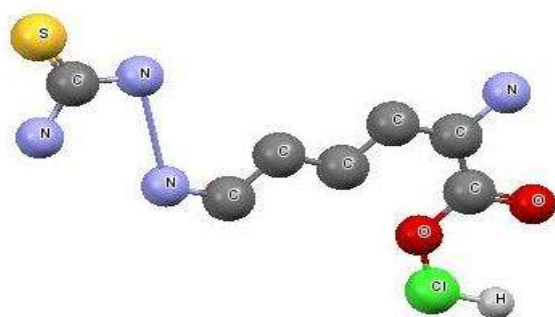
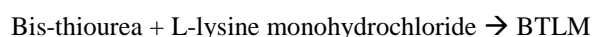
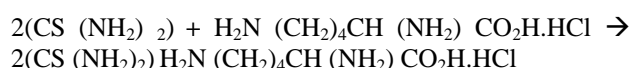


Figure 1: Structural diagram of BTLM.

The mother solution was thoroughly stirred using magnetic stirrer to form a homogeneous solution. Since

thiourea has the coordinating capacity to form different phases, the mixture of the reactants had to be stirred well to avoid co-precipitation of multiple phases. Purity of the synthesized salt was improved by successive recrystallization process. The molecular structural diagram of BTLM is shown in Figure 1.

Crystal growth of BTLM

The prepared BTLM solutions were stirred vigorously for 8 hours using magnetic stirrer. High degree of purity of synthesized salts was achieved by successive recrystallization process and filtration. Whatmann filter paper of micron pore size was used for filtration. The filtered solutions were poured into a beaker and covered with porous paper and housed for slow evaporation of the solvent at room temperature. After a time span of 40 to 45 days, good quality BTLM crystals of size 7mm \times 4mm \times 2mm were harvested. The photography of as grown crystal of BTLM is shown in Figure 2.



Figure 2: As grown crystal of BTLM.

RESULTS

Characterization

Single crystal X-ray diffraction analysis of BTLM crystal

A tiny crystal of BTLM was subjected to single crystal X-ray diffraction analysis using ENRAF NONIUS CAD 4-F single X-ray diffractometer with MOK_α ($\lambda=0.717\text{\AA}$) radiation. The calculated lattice parameter values are $a = 14.41\text{\AA}$, $b = 5.89\text{\AA}$ and $c = 15.52\text{\AA}$, $\alpha = 90.00^\circ$, $\beta = 90.13^\circ$, $\gamma = 89.98^\circ$ and Volume $V = 1317.258\text{\AA}^3$, which reveals that the grown BTLM crystal crystallizes in orthorhombic crystal system with non-centrosymmetric space group $P2_12_12_1$.

Powder X-ray diffraction analysis of BTLM crystal

A powder sample of Bis-thiourea L-lysine monohydrochloride (BTLM) was analyzed using BRUCKER Germany (Model D8 advance) X-ray diffractometer $\text{CuK}\alpha$ ($\lambda=1.5405\text{\AA}$) radiation. The powder XRD pattern is shown in Figure 3. From the powder XRD pattern, a well-defined Bragg's peak confirms the crystalline nature of the grown BTLM

crystal. The (hkl) values are indexed for corresponding intensity value using INDX software.

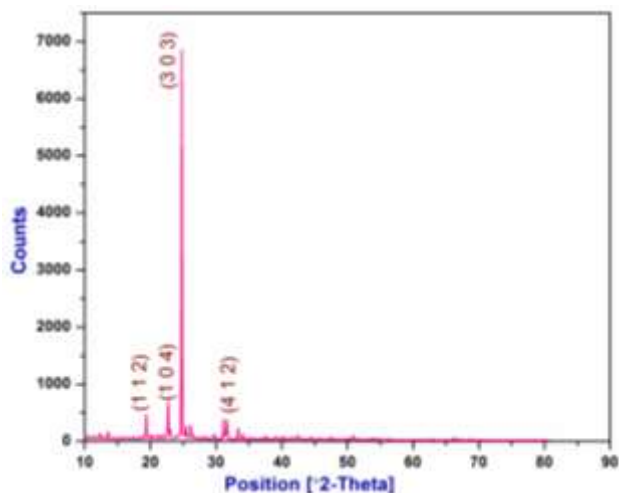


Figure 3: Powder XRD pattern of BTLM crystal.

FTIR spectral analysis

A freshly crushed powder of BTLM crystal was subjected to FTIR studies using thermo Nicolect v-200 FTIR spectrometer by KBr pellet method in the range 500-4000 cm^{-1} . The presences of functional groups are identified by FTIR spectrum which is shown in Figure 4. The absorbed frequencies and their assignment of 2APKHP crystals are shown in the Table 1. The broad band in the higher energy region around 3381 cm^{-1} is due to NH_2 asymmetric stretching. The strong but broad peaks observed at 3108 cm^{-1} due to presence of C-H symmetric stretching. The C-N stretching and bending identified at 2016 cm^{-1} and respectively. The absorption band at 1575, 1525 and 914 cm^{-1} is due to the N-C-N stretching. The peak at 1144 cm^{-1} is attributed to C=H bending. The C-C-N symmetric stretching is found at 791 cm^{-1} . The band appearing at 736 cm^{-1} infers the C-O-H stretching. The COO^- symmetric stretching was observed at 653 cm^{-1} . The absorption peak at 555 cm^{-1} is due to the C-Cl stretching. The S-C-N symmetric stretching was found at 478 cm^{-1} . The assignments confirm the presence of various functional groups present in the material.

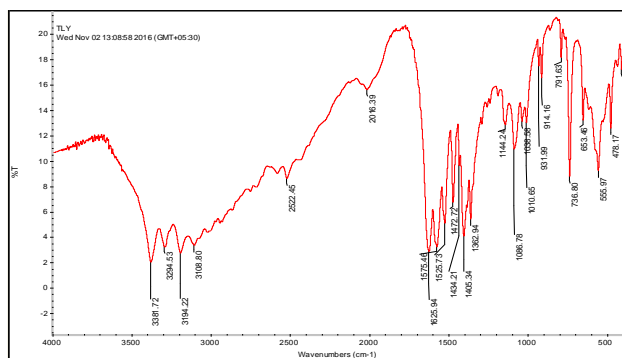


Figure 4: FTIR spectrum of BTLM crystal.

Table 1: Wavenumber assignments of BTLM crystal.

Wavenumber cm^{-1}	Assignments
3381	NH_2 asymmetric stretching
3294,3108	NH_2 symmetric stretching
2522	C-H stretching
2016	C-N stretching
1575	NCN stretching
1625	NH_2 bending
1525,1472	N-C-N stretching vibration
1434	C=S asymmetric stretching
1406,1038	C=S stretching
1362	C=H bending
1144	CH_3 symmetric stretching
1010	C-C stretching
931	C-H symmetric stretching
791	C-C-N symmetric stretching
736	C-O-H stretching
653	COO^- symmetric stretching
555	C-Cl stretching
478	S-C-N symmetric bending

Photoluminescence study

The excitation and emission spectra of 2APKHP was recorded using Cary Eclipse spectrophotometer. The PL study finds wide applications in the field of medical, biochemical and chemical research fields for analyzing compounds. Photoluminescence in solids is the phenomenon in which electronic states of solids are excited by light of particular energy and the excitation energy is released as light. The photon energies reflect the variety of energy states that are present in the material. Figure 5 shows PL emission spectrum recorded in the range of 280–500 nm with an excitation wavelength of 260 nm. The highest emission peak from the spectrum was observed to be at 484.85 nm. Other peaks observed are due to anionic and cationic nature of the sample. From this wavelength it is concluded that BTLM emits blue fluorescence.

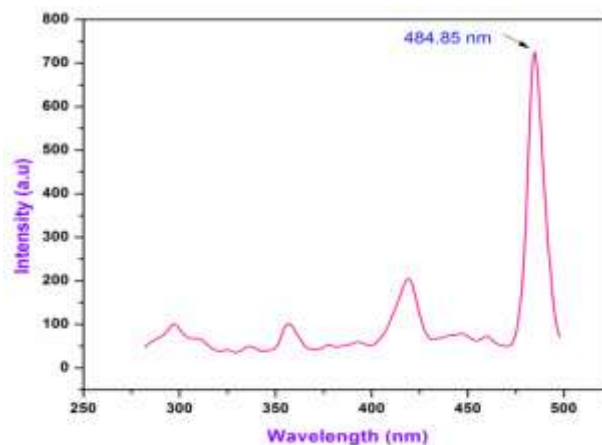


Figure 5: PL emission spectrum of BTLM crystal.

Nonlinear optical study

The powder sample of BTLM was subjected to KURTZ and PERRY techniques. A Q-switched Nd: YAG laser emitting 1.06 μm with power density up to 1 GW/cm^2 was used as a source to illuminate the powdered sample. The sample of good graded crystalline powder with average particle size of about $90\mu\text{m}$ sand witted between two glass slides using copper spices of 0.4mm thickness. A laser was produced as a continuous laser pulses with repetition rate of 10Hz. The input power was fixed at 0.68 J and the output power was measured as 4.4mJ, which was compared to output 8.8 mJ of standard KDP. The diffusion of bright green radiation of wave length $\lambda=532 \text{ nm}$ ($P_2\omega$) by the sample confirms second harmonic generation (SHG). The powder SHG efficiency of Bis-thiourea L-lysine monohydrochloride crystal was about 0.55 times of KDP. The good second harmonic generation efficiency indicates that the BTLM crystals can be used as a suitable material for non-linear optical devices.

Vicker's microhardness test

Mechanical strength of the materials plays a key role in device fabrication. According to Jiang et al.¹⁷, during an indentation process, the external work applied by the indenter is converted to a strain energy component which is proportional to the volume of the resultant impression. The hardness of a material is influenced by various parameters such as the lattice energy, Debye temperature, and heat of formation and inter atomic spacing. The Vickers hardness indentations were made on the cut and polished samples of BTLM of the crystals grown by slow evaporation method. At room temperature, the load was varied as, 25, 50 and 100 g and the several indentations were made for each load and the diagonal lengths (d) of the indented impressions were measured using Vickers hardness tester (LEITZ WETZLER) fitted with Vickers diamond indenter and attached to an incident light.. Vicker's hardness number was determined using the formula $H_v=1.8544 P/d^2 \text{ Kg/mm}^2$.^{18,19} The variation of hardness H_v with load P for BTLM crystal are shown in Figure 6. A plot between log p vs. log d for the grown crystal is shown in Figure 7.

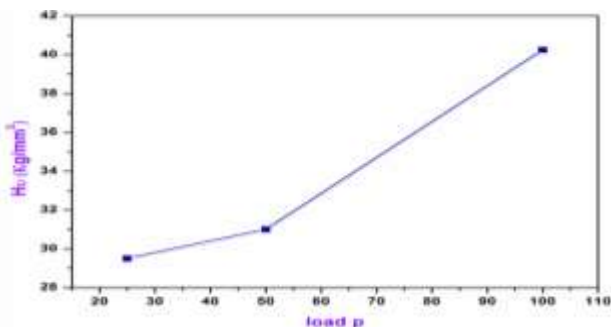


Figure 6: The variation of hardness H_v with load P for BTLM crystal.

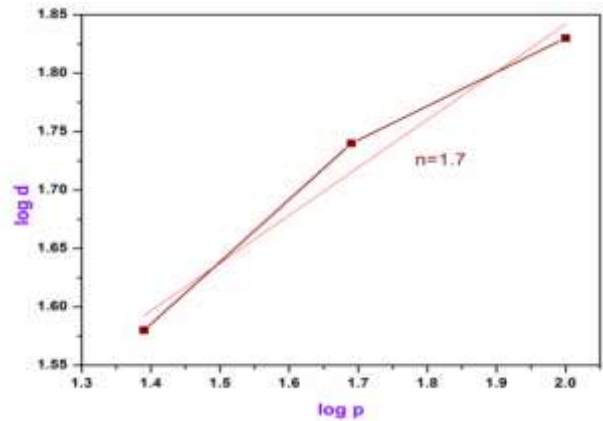


Figure 7: A plot between log p vs. log d for BTLM crystal.

The plot between log p and log d yields a straight line graph, and its slope gives the work hardening index n, which is found to be $n = 1.7$ for grown BTLM crystal. According to Onitsch, the value of 'n' should lie below 1.6 for comparatively hard materials, whereas it is above 1.6 for softer ones.²⁰ The microhardness study indicates that the crystal belongs to the class of soft materials.

Dielectric studies

Dielectric properties were highly correlated with the electro-optic property of the crystals.²¹ The magnitude of the dielectric constant depends on the degree of polarization (charge displacement) in the crystals. The dielectric experiment is carried out within the frequency range of 50 Hz to 7 MHz at various temperatures using HIOKI 3532-50 LCR HITESTER. The cut and polished rectangular shaped BTLM crystal is subjected to dielectric studies. Silver coating is provided on the electrode and the two phases of the crystal to make firm electrical contact. The capacitance (C_{cryst}) across the sample and the dielectric loss ($\tan \delta$) is measured for various temperatures. The frequency dependence of the dielectric constant at different temperatures is shown in Figure 8. It is observed that the dielectric constant has high values at lower frequencies and further decreases with increase in frequency and become independent at higher frequencies. The dielectric constant of the materials is due to the contribution of electronic, ionic, dipolar or orientational and space charge polarizations which high relay upon on the frequencies.²² The higher dielectric constant at lower frequencies is due to all active polarizations. The space charge polarization is generally active at lower frequencies and high temperatures.²³ The variation of dielectric loss with logarithmic frequency (Figure 9) indicates the low value of dielectric loss at higher frequency which suggests that the sample has enhanced optical quality which is of vital importance for non-linear optical materials.

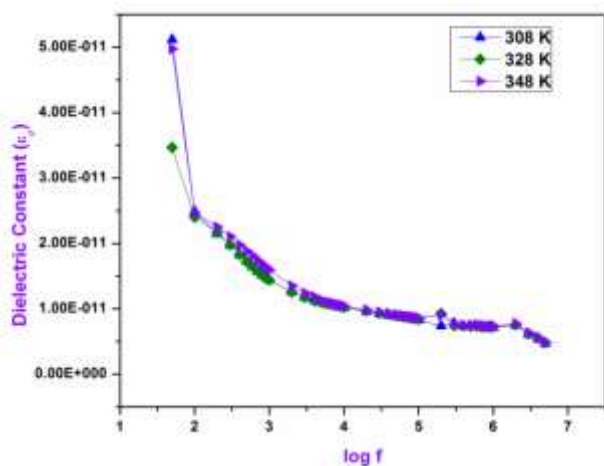


Figure 8: The variation of dielectric constant with log frequency of BTLM crystal.

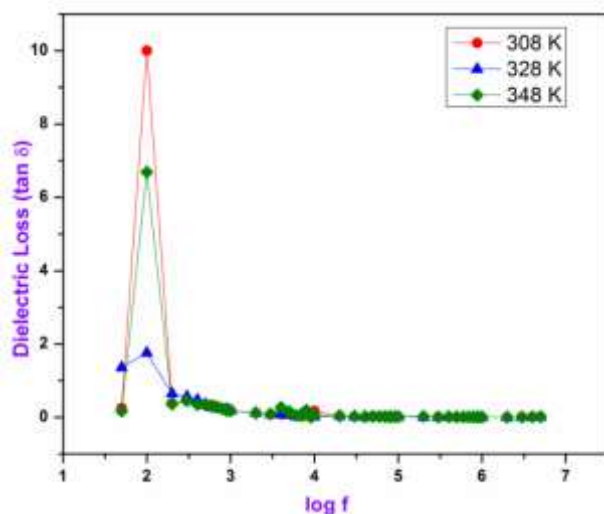


Figure 9: The variation of dielectric loss with log frequency of BTLM crystal.

CONCLUSION

A good quality, optically transparent BTLM crystal has been grown successfully by slow evaporation solution growth technique at room temperature. The unit cell parameters are calculated using Single crystal X-ray diffraction analysis. The grown BTLM crystal crystallizes in orthorhombic crystal system with non-centrosymmetric space group $P2_12_12_1$. Powder XRD shows good crystalline nature of the as grown crystal. The presences of various functional groups in the grown crystal are identified by FT-IR spectrum. PL emission spectrum recorded in the range of 280–500 nm with an excitation wavelength of 260 nm. The powder SHG efficiency analysis shows that the efficiency of BTLM crystal is 0.55 times than that of KDP. The mechanical behavior reveals that the BTLM crystal belongs to soft category. The dielectric studies show that the dielectric constant and dielectric loss of the crystal decreases

exponentially with increase in frequency and same trend were observed for different temperatures.

Funding: No funding sources

Conflict of interest: None declared

Ethical approval: The study was approved by the institutional ethics committee

REFERENCES

- Ledoux I. New advances in molecular engineering for quadratic nonlinear optics. *Synth Metal.* 1993;54:123-37.
- Iwai M, Kobayashi T, Furya H, Mori Y, Sasaki T. Crystal growth and optical characterization of rare-earth (Re) calcium oxyborate $\text{ReCa}_4(\text{BO}_3)_3$ (Re=Y or Gd) as new nonlinear optical material. *J Appl Phys.* 1997;36:L276–9.
- Chenthamarai S, Jayaraman D, Ushashree PM, Meera K, Subramanian C, Ramasamy P. Experimental determination of induction period and interfacial energies of pure and nitro doped 4-hydroxyacetophenone single crystals. *Materials Chemistry Physics.* 2000;64(3):179-83.
- Kitazawa M, Higuchi R, Takahashi M. Ultraviolet generation at 266 nm in a novel organic nonlinear optical crystal: 1-pyrrolidone-2-carboxylic acid. *Appl Phys Lett.* 1994;64:2477-9.
- Misoguti L, Varela AT, Nunes FD, Bagnato VS, Melo FEA, Filho JM, et al. Optical properties of L-alanine Organic Crystals. *Optical Materials.* 1996;6(3):147-52.
- Baraniraj T, Philominathan P. Growth and characterization of NLO based L-arginine maleate dihydrate single crystal. *Spectrochimica Acta Part A.* 2010;75:74-6.
- Zhang N, Jinang MH, Yuan DR, Xu D, Tao XT, Shao ZS, et al. The quality and performance of the organometallic complex nonlinear optical material Tri-allyl thiourea cadmium chloride (ATCC). *J. Crystal Growth.* 1990;102:581.
- Newman PR, Warren LF, Cunningham P, Chung TY, Copper DE, Burdge GI, et al. Semiorganics, a new class of NLO materials in advanced organic solid state materials. *Mater Res Soc Symp pro.* 1990;173:557.
- Ouarsaid M, Becker P, Nedelec CC. Raman And Infrared-Spectra Of Bis(Thiourea)Zinc Chloride $\text{Zn}[\text{Cs}(\text{Nh}_2)(2)](2)\text{Cl}_2$ Single-Crystal. *Phys. Stat. Sol (b).* 1998;207(2):499-507.
- Selvakumar S, Julius JP, Rajasekar SP, Ramanand A, Sagayaraj P. Microhardness, FTIR and transmission spectral studies of Mg^{2+} and Zn^{2+} doped nonlinear optical BTCC single crystals. *Mater Chem Phys.* 2005;89(2):244-8.
- Monaco SB, Davis LE, Velsko SP, Wang FT, Eimerl D, Zalkin A. A. Synthesis and characterization of chemical analogs of l-arginine phosphate. *Journal of Crystal Growth.* 1987;85(1-2):252-5.

12. Eimerl D, Velsko S, Davis L, Wang F, Loiacono G, Kennedy G. Deuterated L-arginine phosphate: a new efficient nonlinear crystal. *IEEEJ. Quantum Electron.* 1989;25(2):179-93.
13. Dhanuskodi S, Ramajothi J. Crystal growth, thermal and optical studies of L-histidine tetrafluoroborate: A semiorganic NLO material. *Cryst Res Technol.* 2004;39:592-7.
14. Dhanuskodi S, Vasantha K, PAA Mary. Structural and thermal characterization of a semiorganic NLO material: lalanine cadmium chloride. *Spectrochimica Acta A.* 2007;66:637-42.
15. Kirubavathi K, Selvaraju K, Valluvan R, Vijayan N, Kumaraman S. Synthesis, growth, structural, spectroscopic and optical studies of a new semiorganic nonlinear optical crystal: L-Valine hydrochloride. *Spectrochimica Acta A.* 2008;69:1283-6.
16. Nicoud JF, Twieg RJ, Chemla DS, Zyss JE (Eds). In *Nonlinear Optical Properties of Organic Molecules and Crystals.* Academic press, London. 1987:227-96.
17. Jiang MH, Fang Q. Organic and Semiorganic Nonlinear Optical Materials. *Adv Mater.* 1999;11:1147-51.
18. Subhadra KG, Rao KK, Sirdeshmukh DB. Systematic hardness studies on lithium niobate crystals. *Bull Mater Sci.* 2000;23:147-50.
19. Mukerji S, Kar T. Vicker's Microhardness Studies of L-arginine Hydrobromide Monohydrate Crystals (LAHBr). *Cryst Res Technol.* 1999;34:1323.
20. Onitseh EM. 'The present status of testing the hardness of materials', *Mikroskopie.* 1956;95:12-4.
21. Boomadevi S, Dhanasekaran R. Synthesis, crystal growth and characterization of L-pyrrolidone-2-carboxylic acid (L-PCA) crystals. *J Cryst Growth.* 2004;261:70-6.
22. Kirubavathi K, Selvaraju K, Valluvan R, Vijayan N, Kumararaman S. Studies on the growth aspects of semi-organic cadmium zinc thiourea acetate: A promising new NLO crystal. *J Mater Lett.* 2008;62:7-10.
23. Anandhababu G, Bhavannarayana G, Ramasamy P. Synthesis, Structure, Growth and Physical Properties of a Novel Organic NLO Crystal: 1,3-Dimethylurea Dimethylammounium Picrate," *Materials Research Bulletin. J Cryst Growth.* 2008;310:1228-38.

Cite this article as: Tamilselvi R, Arunadevi K, Sivavishnu D, Ramadoss P. Synthesis, growth and characterization of amino acid based semiorganic crystal bis-thiourea l-lysine monohydrochloride. *Int J Sci Rep* 2017;3(4):100-5.