Growth and Spectral properties of NLO Single Crystals: L-Tyrosine and L-Tyrosine Succinate Hydrobromide

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Abstract

A Novel nonlinear optical, L-Tyrosine and L-Tyrosine Succinate Hydrobromide (LTSHB) single crystals have been grown by slow evaporation method with rotoevaportor. The powder X-ray diffraction pattern shows a high degree of crystallinity of the grown crystals. UV–Vis spectrum indicates the transparency of the crystals in the entire visible region. The presence of functional group has been identified by FTIR analysis. The second harmonic generation efficiency of the grown LTSHB crystal is found to be 1.2 times that of standard KDP crystal.

KEYWORDS: Powder XRD, UV-Vis, FTIR, NLO.

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1 Introduction

In the modern world, the development of science in many areas has been achieved through the growth of single crystals. Nonlinear optical materials play a vital role in the technology of photonics including optical information processing. Many research efforts are undertaken to synthesize and characterize new molecules for second-order NLO applications such as high-speed information processing, optical communication and optical data storage [1–12]. These applications depend on the various properties of the materials, such as transparency, birefringence, refractive index, dielectric constant and chemical stability. Among NLO materials, organic NLO materials are generally believed to be more versatile than their inorganic counterparts due to their more favourable nonlinear response. In the organic class, amino acids exhibit some specific features such as molecular chirality, weak Van der Waals and hydrogen bonds, wide transparency range in the visible and UV spectral regions, and zwitterionic nature of the molecule which favours crystal hardness. Other advantage of organic compounds apart from the above include amenability for synthesis, multifunctional substitutions, higher resistance to optical damage and maneuverability for device applications etc. [13–16]. Due to the fact that amino acids contain chiral carbon atom and crystallize in the noncentrosymmetric space groups, they are usually potential candidates for optical second harmonic generation.

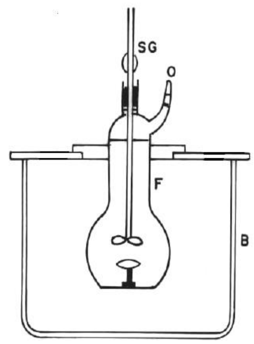

Fig. 1 Roto Evaporator. SG- Stirring Gland, O- Opening, S-Stirrer, F-Flask, B-Bath

Roto evaporator designed indigenously has been used in this study to enhance nucleation and is shown in Fig.1. In this apparatus, a glass flask of 1 litre capacity containing the solution is kept at the centre of the water bath of 20 litre capacity which is heated using heating coils. Water bath was continuously stirred by stirring paddles which prevents rapid temperature fluctuations and hence ensures very good temperature control. Temperature is maintained constant to an accuracy of ± 0.01º C by a digital controller setup. The solution was stirred using stirring gland which helps to increase the growth rate. Recently, several complexes of Succinic acid crystals have been reported: L-Alaninum Succinate [17], L-Valine Succinate [18], L-Proline Succinate [19] and Urea Succinic acid [20], which posses NLO properties. But no work is cited on LTSHB single crystal in the literature so far and for the first time growth of LTSHB single crystal by slow evaporation method is reported in this article

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2 Experimental Technique

L-Tyrosine single crystal was grown from L-Tyrosine (AR grade) dissolved in double distilled water. The solution was stirred continuously for 3 hours to get the saturated solution. To remove impurities such as solid and dust particles, the saturated solution was filtered using whatmann No 1 filter paper twice. Then the solution was transferred to crystal growth vessels and crystallization was allowed to take place by slow evaporation at a temperature of 45ºC in a constant temperature bath. Then the filtered solution was covered by polythene paper in which holes were made for slow evaporation. Optically good quality L-Tyrosine single crystals of size 1.4 x 0.5 x 0.6 cm^3 were grown by slow evaporation method within one week and is shown in Fig.2.

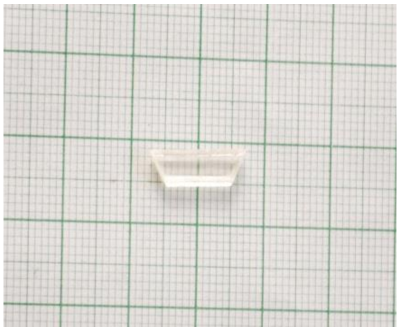

Fig. 2 Photography of the grown LT crystal

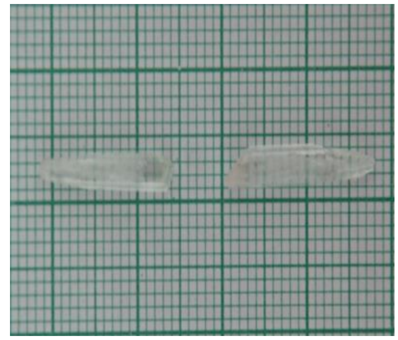

Fig. 3 Photography of the grown LTSHB crystal

LTSHB was synthesised from L-Tyrosine, Succinic and Hydrobromic acid (HB) taken in the equimolar ratio (1:1:1) in aqueous solution. The solution was stirred well at a constant rate for 3 hours to get homogeneous mixture. Prepared solution was filtered twice using Whatmann No 1 filter paper and the solution was allowed to evaporate using rotoevaporator in a constant temperature water bath at 45°C for one days. Then the filtered solution was taken in a beaker and covered by a perforted sheet for controlled evaporation. The seed crystals of LTSHB were obtained in the time interval of 10 days by spontaneous nucleation. Good quality seed crystals were placed in the supersatured solution and the solution was allowed to evaporate slowly at room temperature to obtain pure crystals by recrystallization process. Colourless and transparent LTSHB crystals of size 1.5 x 0.3 x 0.6 cm^3 were obtained after 3 weeks which is shown in Fig. 3.

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The grown crystals of LT and LTSHB have been analyzed by different characterization techniques. Powder X-ray diffraction studies was performed using PANalytical powder X-ray diffractometer with CuKα radiation (λ= 1.5418Å). The optical absorption spectrum was recorded in the range 200-800 nm with Shimadzu-160 spectrometer. The functional groups were identified by using the SHIMADZU FTIR Spectrophotometer in the range 400–4000 cm^{-1} with KBr pallet. The NLO efficiency of the grown LTSHB crystal was measured by KURTZ powder technique using ND: YAG laser of wavelength 1064nm.

3 Results and Discussion

3.1 Powder X-ray diffraction analysis

The powder X-ray diffraction pattern was obtained for the range 10°- 80° with a scan speed of 2°/min. The XRD pattern is shown in the Fig. 4(a) and Fig.4 (b) respectively. The sharp well defined peaks obtained for both crystal ensures high degree of crystallinity [21]. The powder XRD data for LT and LTSHB crystals are given in Table A. 1 and Table A. 2 respectively.

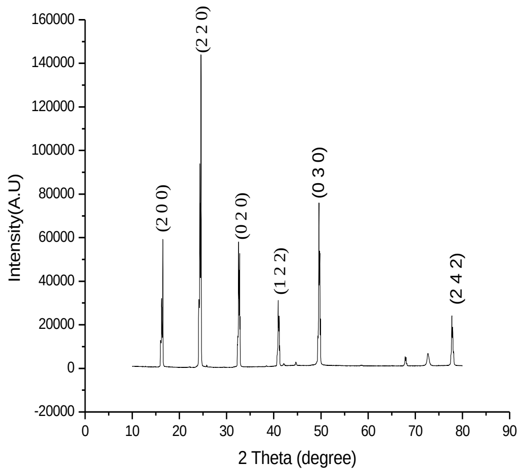

Fig .4(a) Powder XRD pattern of LT crystal

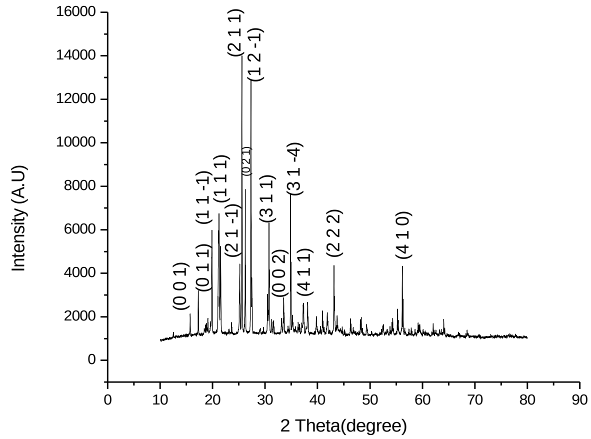

Fig. 4(b) Powder XRD pattern of LTSHB crystal

Table A. 1 Powder XRD data for LT crystal

Pos [º 2 Th]	FWHM[º 2 Th]	d- spacing [Aº]
16.4791	0.0669	5.37944
24.5574	0.0816	3.62209
32.5284	0.0408	2.75041
40.9277	0.0816	2.20327
49.7742	0.0612	1.83042
77.7379	0.0816	1.22749

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Table A.2 Powder XRD data for LTSHB crystal

Pos [º 2 Th]	FWHM[º 2 Th]	d- spacing [Aº]
17.2815	0.0669	5.13142
18.8336	0.0502	4.71189
21.1250	0.0669	4.20569
21.5323	0.0836	4.12705
25.1816	0.0669	3.53663
25.5763	0.0836	3.48294
26.2173	0.0502	3.39921
27.2955	0.0502	3.26734
30.7541	0.0502	2.90733

33.5496	0.0502	2.67120
34.9601	0.0408	2.57084
37.3661	0.0612	2.40468
43.1303	0.0612	2.09571
55.029	0.0674	1.66742

3.2 UV-Vis spectral analysis

The optical transmittance range and transparency cutoff wavelength are the main requirements for device applications. The recorded spectrum is shown in Fig.5.A and Fig.5.B respectively. The LT and LTSHB crystals have lower cut- off wavelength around 470nm and 245 nm which is comparable with LTHB crystal [22]. There is no absorption band beyond 245 nm for LTSHB, which confirms the absence of any overtones and absorbance due to electronic transitions. The transmittance window in the visible region enables good optical transmission of the second harmonic frequencies of Nd: YAG laser [23]. The optical band gap (Eg) is evaluated from the transmission spectra and the optical absorption coefficient (α) near the absorption edge is given by $\alpha h\gamma = A\,(h\gamma - E_g)^{1/2}$, where A is a constant, E_g the optical band gap,h the Planck's constant and γ the frequency of the incident photons. The band gap values of grown crystals are found to be 2.64 eV and 4.31eV for LT and LTSHB crystal respectively.

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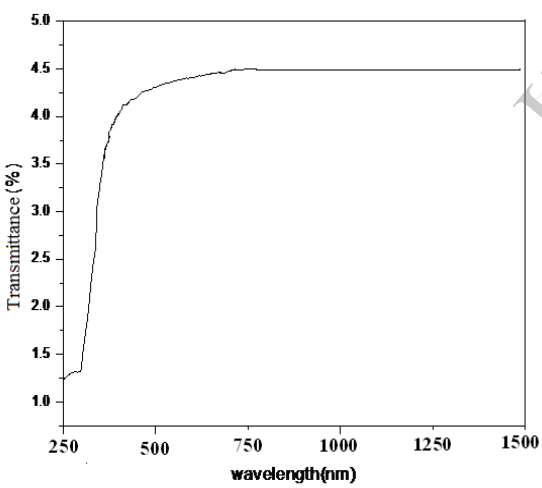

Fig. 5(a) Transmittance Spectrum of LT

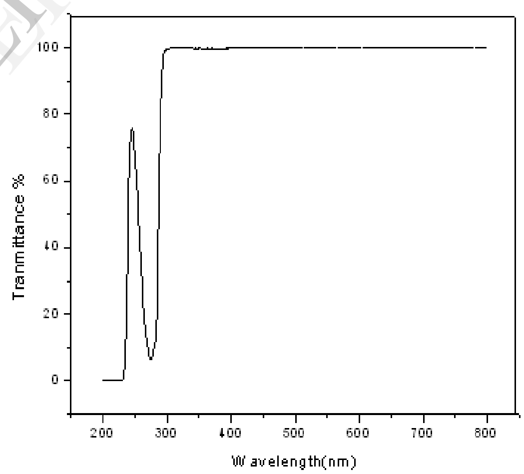

Fig. 5(b) Transmittance Spectrum of LTSHB crystal

3.3 FTIR Spectral studies

Functional groups present in the sample have been analyzed using Fourier transform infrared (FT-IR) spectrum. The FTIR absorption spectrum of LT and LTSHB are shown in Fig. 6.A & Fig. 6.B respectively. The broad and strong bands around 2600cm^{-1} are due to NH_3^+ stretching. The bands observed at 1600 cm^{-1} and 1512 cm^{-1} are assigned to asymmetrical and symmetrical NH_3^+ bending respectively for LTSHB. The strong band observed at 1720 cm^{-1} is assigned to protonated carbonyl group for LTSHB crystal [24].The bands at 1338, 1330cm^{-1} is assigned to C-N-H symmetrical bending for LT and LTSHB crystals and NH_3^+ torsional oscillation band is observed at 524 cm^{-1} for LTSHB crystal [25]. The FTIR assignments of LT and LTSHB crystals are listed in Table B.1 and Table B.2 respectively.

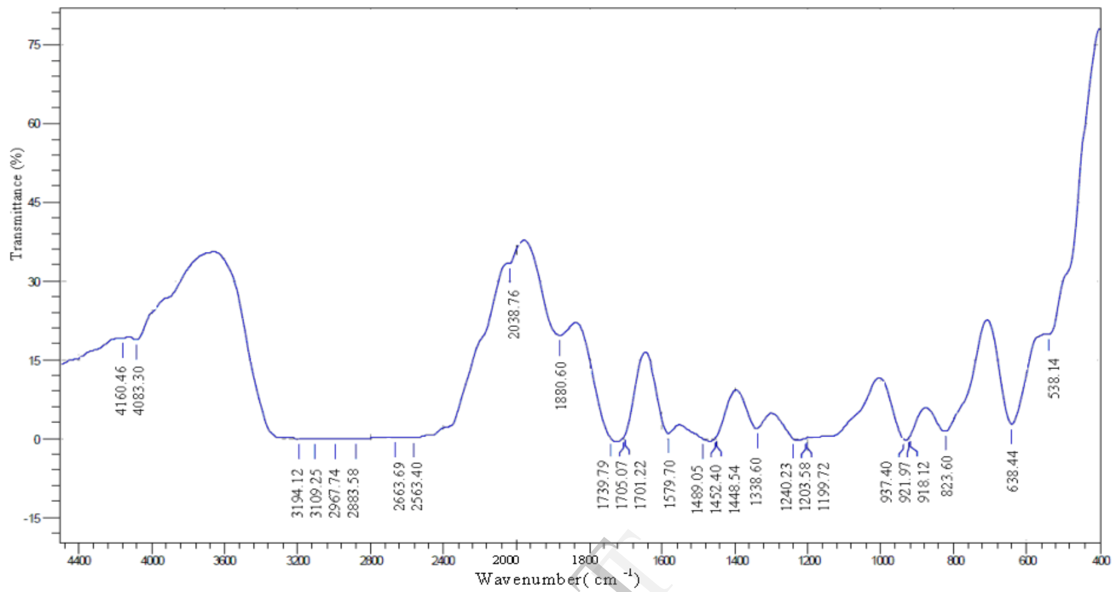

Fig. 6 (a) FTIR spectrum of LT crystal

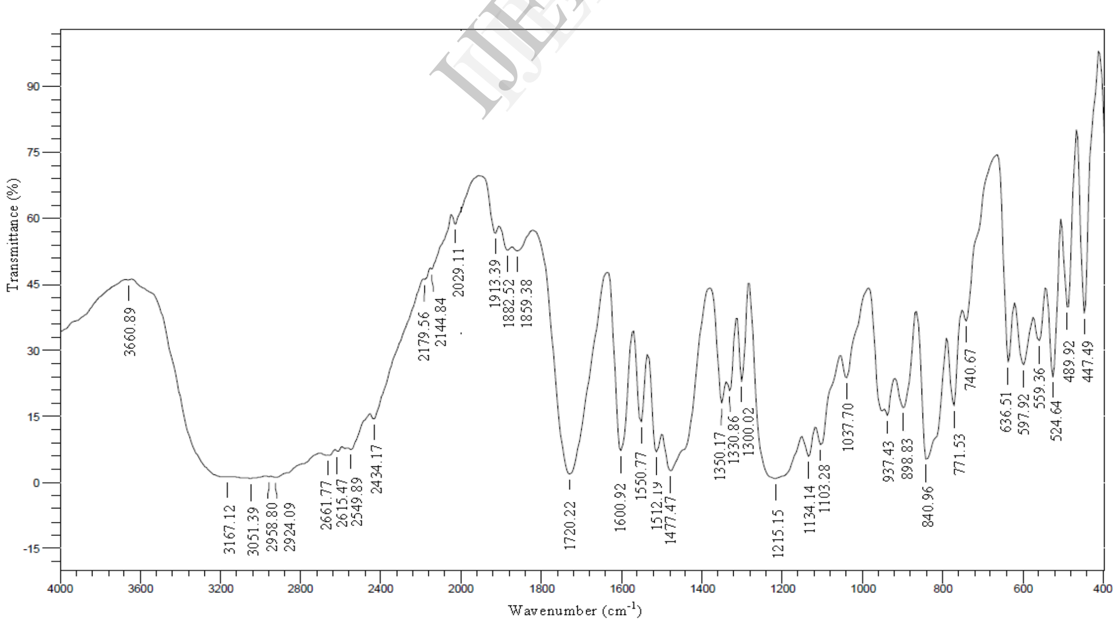

Fig. 6 (b) FTIR spectrum of LTSHB crystal.

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Table B.1 Assignment of vibrational frequencies in the FTIR spectra of LT crystal

Wavenumber (cm^{-1})	Assignment
1739	Protonated COO^-
1489	Aromatic C=C stretching
1338	C-N-H symmetric bending
1240	Phenolic C-O stretch
937	C-O-H out of Plane bending
823	C-CH_3 bending
638	Aromatic C-H out of Plane bending

Table B.2 Assignment of vibrational frequencies in the FTIR spectra of LTSHB crystal

Wavenumber (cm^{-1})	Assignment
2615	NH_3^+ symmetric stretching
1882	Combination band of substituted ring
1720	Protonated COO^-
1600	Asymmetric bending NH_3^+
1550	Aromatic C=C stretching
1512	Symmetric bending of NH_3^+
1477	Aromatic C=C stretching
1350	CH_2 Wagging
1330	C-N-H symmetric bending
1300	C-O stretching
1134	NH_3^+ rocking
1103, 1037	C-H in plane deformation (ring)
937	C-O-H out of Plane bending
898	CH_2 rocking
840	C-CH_3 bending
771, 636	Aromatic C-H out of Plane bending
524	NH_3^+ torsional
447	C-C torsional

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3.5 Second Harmonic Generation (SHG) studies

The second harmonic generation behaviour of the powdered material has been tested using the Kurtz powder technique. A high intensity Nd: YAG laser (λ = 1064 nm) with a pluse duration of 6ns was passed through the powdered sample. The SHG behaviour was measured from the output of the laser beam having the green emission. It is observed that the SHG efficiency of the grown LTSHB crystal is 1.2 times that of standard KDP crystal.

4 Conclusion

A new LTSHB single crystal has been successfully grown by the slow evaporation method using roto evaporator. The sharp well defined peaks confirm the crystalline nature of the grown crystals. The lower cut off wavelength (470nm and 245nm) ensures good optical transparency and use of LTSHB as suitable material for many biological and industrial applications. The FTIR spectral analysis confirms the presence of functional groups in the crystals. SHG efficiency tested using Nd: YAG laser shows that LTSHB can be utilised as a promising material for NLO applications.

Reference

[1] Krishnan, S.; Justin, C.; Jerome Das, S., (2008) Growth and characterization of novel ferroelectric urea-succinic acid single crystals. *J Cryst Growth.* **310**: 3313-3317.

[2] Gupte, S.S.; Desai, C.F., (1999) Vickers hardness anisotropy and slip system in zinc (tris)thiourea sulphate crystals. *Cryst Res Technol.* **34**: 1329-1332.

[3]Verma,S.;Singh,M.K.;Wadhavan,V.K.;Suresh,C.H.,(2000) Growth morphology of zinctris(thiourea)sulphate crystals. *J. Phys*. **54**: 879-888.

[4] Boomadevi, S.; Dhanasekaran, R.; Ramasamy, P., (2002) Investigation on nucleation kinetics of urea crystals from methanol. *Cryst. Res. Technol***. 37**: 159-168.

[5] Sangwal, K.; Mielniczek-Brzoska, E., (2004) Effect of impurities on metastable zone width for the growth of ammonium oxalate monohydrate crystals from aqueous solutions. *J. Cryst. Growth.* **267**: 662-675.

[6] Li, G.; Xue, L.; Su, G.; Li , Z.; Zhuang, X.; He, Y.; (2005) Rapid growth of KDP crystal from aqueous solutions with additives and its optical studies. *Cryst. Res. Technol.* **40**: 867-870.

[7] Gunasekaran, S.; Ponnusamy, S.; (2006) Growth and characterization of cadmium magnesium tetra thiocyanate crystals. *Cryst. Res. Technol*. **41**: 130-137.

[8] Udayalakshmi, K.; Ramamurthi, K. (2006) Optical, mechanical and thermal properties of p-bromoacetanilide,.*Cryst. Res. Technol.* **41**: 795-799.

[9] Kumar, K.; Ramamurthy, K., (2006) A novel growth method for zinc thiourea sulphate single crystals. *Cryst. Res. Technol.* **41**: 217-220 .

[10] Rajasekaran, R.; Rajendran, K.V., (2003) , Investigation on nucleation of cadmium thiourea chloride single crystals. *Mater. Chem. Phys***. 8:** 273-280.

[11] Angelimary, P.A.; Dhanuskodi, S., (2001) Growth and characterization of a new nonlinear optic Bisthiourea zinc chloride. *Cryst. Res. Technol*. **36:** 1231-1237.

[12] Haja Hameed, A.S. ; Ravi, G.; Dhanasekaran, R.; Ramasamy, P., (2000) Growth and characterization of KDP and KAP. *J. Cryst.Growth.* **212:** 227-237.

IJERT

[13] Kuznetsov, V.A.; Okhrimenko, T.M.; Rak, M., (1998) Growth promoting effect of organic impurities on growth kinetics of KAP and KDP crystals. *J. Cryst. Growth*. **193:** 164-173

[14] Zaitseva, N.P.; Rashkovich, L.N.; Bogatyreva, S.V., (1995) , Stability of KH2PO4 and K(H, D)2PO4 solutions at fast crystal growth rates. *J. Cryst. Growth.* **148:** 276-282.

[15] Nyvlt, J.; Rychly, R.; Gottfried, J.; Wurzelova, J., (1970) Metastable zone-width of some aqueous solutions. *J. Cryst. Growth.* **6:** 151-162.

[16] Ushasree, P.M.; Jayavel, R.;Ramasamy, P., (1999) Growth and characterization of phosphate mixed ZTS single crystals. *Mater. Sci. Eng. B.* **65:** 153-158.

[17] Ramachandra Raja, C.; Gokila, G.; Antony Joseph, A. (2009)Growth and spectroscopic characterization of a new organic nonlinear optical crystal: L-Alaninium succinate. *Spectrochim. Acta Part A.* **72:** 753-756.

[18] Jesintha John, C.; Xavier, T.S.; Lukose, G.; Hubert Joe, I., (2012) Electronic absorption and vibrational spectra and nonlinear optical properties of l-valinium succinate. *Spectrochim. Acta Part A.* 85: 66-73.

[19] Balamurugaraj, P.; Suresh, S.; Koteeswari, P.; Mani, P., (2013) Growth, Optical, Mechanical, Dielectric and Photoconductivity Properties of L-Proline Succinate NLO Single Crystal**.** *J. Mater. Phys. Chem*. **1:** 4-8.

[20] Singh, B.K.; Sinha, N.; Singh, N.; Kumar, K.; Gupta, M.K.; BinayKumar, (2010) Structural, dielectric, optical and ferroelectric property of urea succinic acid crystals grown in aqueous solution containing maleic acid**.** *J. Phys. Chem. Solids*. **71:** 1774 -1779.

[21] Anandan, P.; Vetrivel, S.; Jayavel, R.; Vedhi, C.; Ravi, G.;Bhagavannarayana, G., (2012) Crystal growth, structural and photoluminescence studies of L-tyrosine hydrobromide semi organic single crystal. *J. Phys. Chem. Solids.* **73:** 1296-1301.

[22] Natarajan, S.; Shanmugam, G.; Martin Britto Dhas, S.A.; (2008) Growth and characterization of a new semi organic NLO material: L-tyrosine hydrochloride**.** *Cryst. Res. Technol*. **43:** 561-564.

[23] Ashour, A.; El–Kadry, N.; Mahmoud, S.A., (1995) On the electrical and optical properties of CdS films thermally deposited by a modified source**.** *Thin Solid Films***.** **269:** 117-120.

[24] Anandan, P.; Saravanan,T.; Vasudevan,S.; Mohan Kumar, R.; Jayavel, R., (2010) Crystal growth and characterization of l-tyrosine bromide (LTB) nonlinear optical single crystals**.** *J. Cryst. Growth.* **312:** 837-841.

[25] Narayana Moolya, B., Dharmaprakash, S.M., (2006) Synthesis, growth and characterization of nonlinear optical crystal: L-tyrosine hydrobromide **.** *J.Cryst. Growth.* **290:** 498-503.

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