GROWTH AND CHARACTERIZATION OF A NEW NON LINEAR OPTICAL MATERIAL L-LEUCINE THIOUREA CRYSTAL

B. Ravindran[a], S. Malini[b], N. Menaka[b], S. Ambikavathy[b] S. Kamali[c],
[a]Assistant Professor, PG and Research Department of Physics, Thiru.Vi. Ka. Government Arts College, Thiruvarur-610 003, Tamil Nadu, India.
[b]Research Scholar, PG and Research Department of Physics, Thiru.Vi. Ka. Government Arts College, Thiruvarur-610 003, Tamil Nadu, India
[c]Assistant Professor, Department of Science & Humanities,University College of Engineering,Thirukkuvalai-610 204, Tamil Nadu, India.

ABSTRACT

New organic crystals of L-leucine thiourea were grown by slow evaporation method from the aqueous solution. Different characterization studies were carried out for the grown crystals, such as UV-Vis, FTIR, XRD, TG-DSC and SHG. Identification of materials can be done by the FTIR and X-ray diffraction analysis. The grown crystal belongs to monoclinic was determined using XRD. Using TG-DSC analysis the thermal stability can be determined and it was absorved that the crystal was stable upto 205° C. The SHG efficiency of the grown crystal was found to be noted that highly pronounced on compared with urea and KDP.

Keywords: L-leucine thiourea, XRD, UV-Visible Spectroscopy, XRD, FTIR, NLO

1. Introduction

An intense effort has been focused to design and develop a new organic nonlinear optical (NLO) material with large optical susceptibility. That type materials may in found of widespread applications, such as optoelectronic modulators, high speed signal processing, optical switching and frequency convertors [1-3]. The properties of the material like transparency, refractive index, chemical and thermal stability determines the field of applications. Interest has been witnessed on amino acids for optical applications [4, 5]. The optical activity of the amino acid is determined by the tetrahedral array of different groups about the α-carbon atom. Because of the presence of de protonated carboxyl group and protonated amino group (Zwitter ionic nature) the nonlinear polarization property increased [6, 7]. L-leucine is an essential branched chain of L-amino acid. Earlier reports on the growth and NLO studies of L-leucine shows that SHG efficiency of L-leucine is twice that of Urea [8]. Only few of the L-leucine derivatives were reported earlier such as L-leucine nitrate [9], L-leucine oxalate [10], L-leucine perchoralate [11] and L-leucine L-leucinium picrate [12]. So far zinc tris thiourea seems to be a promising NLO material among the large number of semi

organic material. Recently amino acids such as L-leucine [14], L-serine [15], L-lysine [16] and γ-glycine [17] doped zinc thiourea sulphate were identified as promising NLO active materials [13]. In this present investigation we are reporting the growth and NLO studies of L-leucine thiourea crystals for the first time. Detailed analysis on the grown crystals by XRD, FTIR, TG-DSC, UV-Vis and NLO studies were carried out.

2. Experimental details

To check the suitability of the grown crystal as a nonlinear optical material, the optical properties of L-leucine thiourea crystal were studied by measuring its optical absorption in the UV-Vis-NIR region and SHG. Optical spectra for the grown crystal was measured by a UV-Vis-NIR spectrometer (VARIAN carry 5000) in the range 150-800nm.

Using Kurtz and Perry powder technique the SHG efficiency was measured. On irradiation the sieved powder sample of grown crystal by Nd-YAG laser of output λ = 1064 nm of energy 2.5 mj per pulse, the second harmonic signal was generated. Due to the emission of green radiation (λ = 532 nm) from the sample the SHG which was displaced in the CRO through photomultiplier tube. It is of immense importance to know about the thermal behaviour of crystals for device fabrications. For that we have performed the TG-DSC studies for L-leucine thiourea crystals using the thermal analyzer STAR system (METTLER TOLEDO). The FTIR spectra is recorded by using Perkin Elmer FT-IR Spectrometer to confirm the functional groups of the grown crystals from 4000-400 cm^{-1}

2.1 Synthesis and growth

On dissolving high purity AR grade (Merk) L-leucine and thiourea in double distilled water with a molar ratio 1:1 to synthesize L-leuecine thiourea. Whatmann filter paper is used to filter the mixture of super saturated solution of L-leucine thiourea which is prepared at room temperature by constant stirring up to 6hours. Good quality, transparent, colourless crystal was harvested after allowing it to evaporate the filtered solution in a dust free space in a period of 5 days. Photograph of L-leucine thiourea crystal **(Fig.1)**

Fig.1 Morphology of L-leucine thiourea crystal

3. Results and discussion

3.1 FTIR Spectral studies

The FTIR spectrum of L-leucine thiourea crystal is shown in the Fig.2. KBr is mixed with the powder of the grown crystals and the produced spectrum was recorded in the region 4000-400 cm^{-1}. An observed sharp peak at 2955.83 cm^{-1} indicates the symmetric stretching band is due to NH_3^+ ions. The characteristic absorption band at 1571.06 and 1294.17 cm^{-1} are related to asymmetric stretching vibration of carboxylic group COO^- and NH_3^+ bending, which reveals the protonation of amino groups. Evidence for the presence of thiourea is confirmed from its characteristic peak 1404.85 cm^{-1} ($\gamma_{C=S}$ stretching) 1237.70 cm (γ_{CN} streching) 768.21 cm^{-1} ($\delta_{C=S}$ bending). The peak at 1609.16 cm^{-1} ($\gamma_{C=S}$ stretching) of L-leucine. The observed spectra were found to be in good agreement with the recorded wave number confirms the existence of L-leucine compound with thiourea. **(Fig.2)**

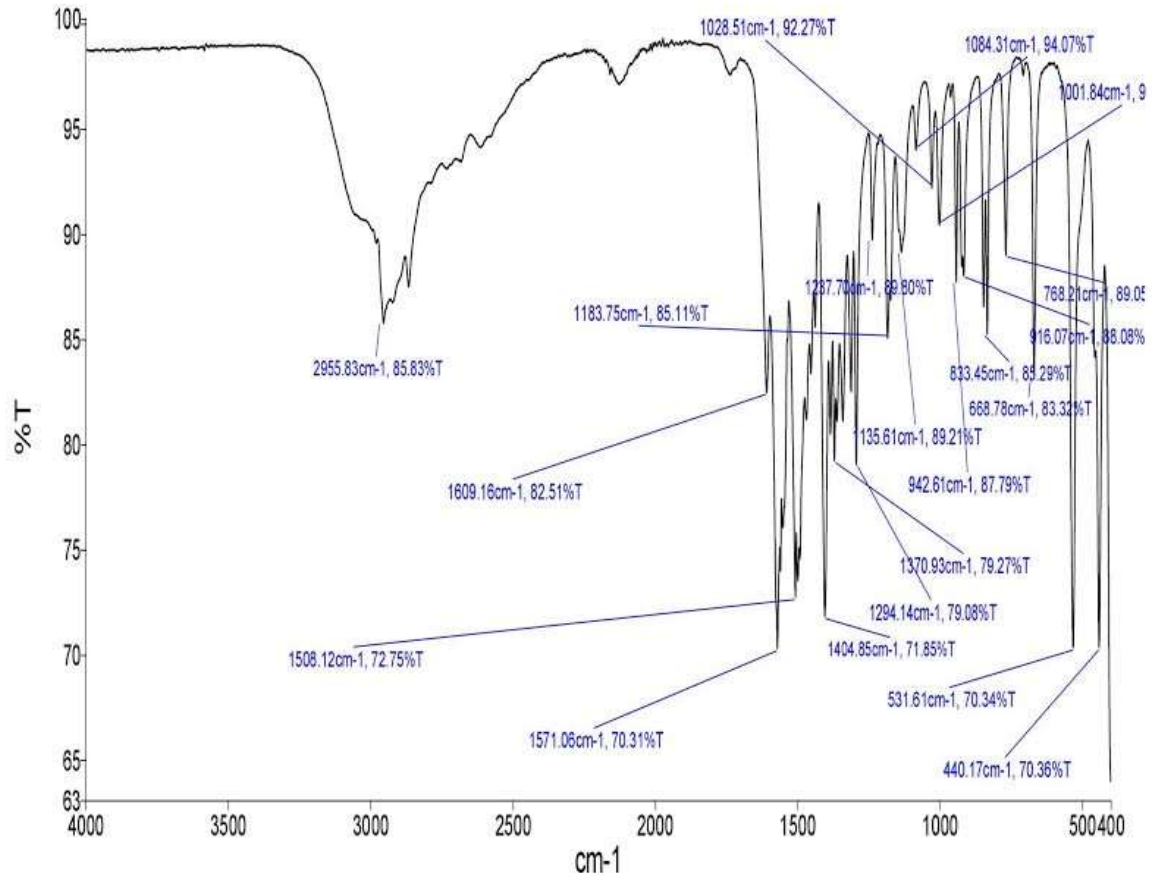

Fig. 2 FTIR Spectrum of L-leucine thiourea

3.2 Optical Absorption Studies

Using VARIAN carry 5000 spectrometer the optical absorption spectrum of the grown crystal was recorded in the range of 200 -800 nm. Fig.3 shows the recorded spectrum. No absorption of light is found in the entire visible region of the recorded spectrum. In the region of 236.32 nm to 800 nm a widened transparency is observed. List of some L-leucine family crystals are given below. From that it is observed that the transparency of L-leucine thiourea was lowered on compared with L-leucine leucinium picrate and L-leucine nitrate. (**Table 1) Fig. 3**

Table 1

UV-Visible cutoff wavelength of the reported L-leucine family crystals

Crystals	UV cutoff wavelength in nm
L-leucine `	220 [8]
L-leucine nitrate	310 [9]

L-leucine L-leucinium picrate	480	[12]
L-leucine phthalic acid potassium iodide	227	[18]
L-leucine thiourea	236.32*	

* Present work

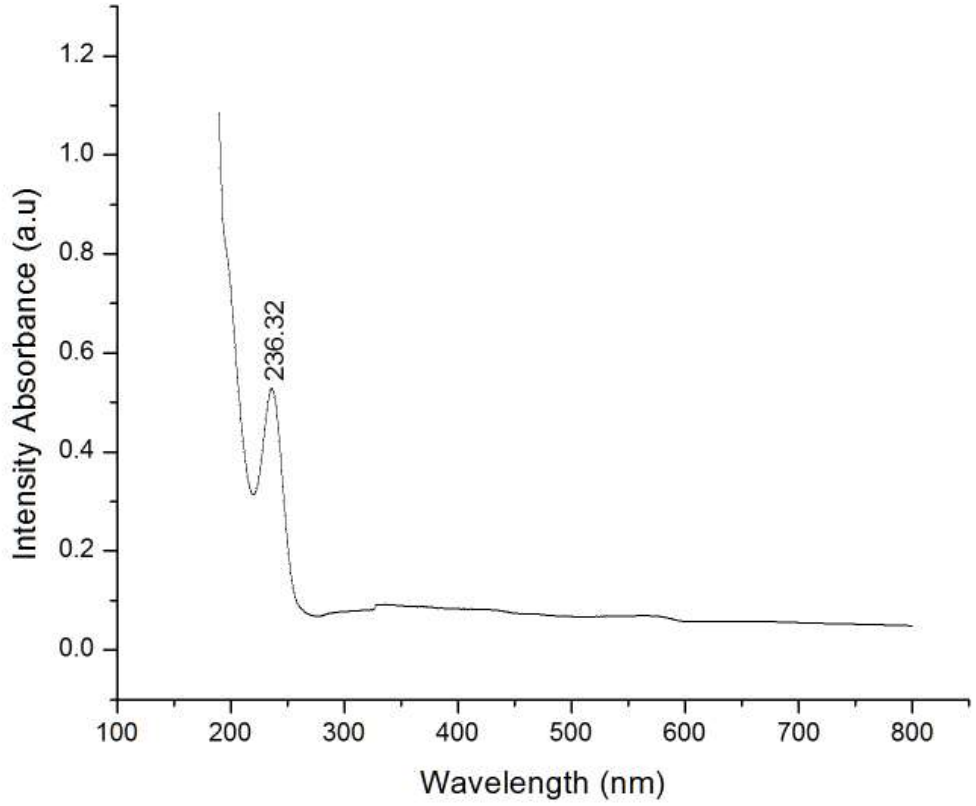

Fig. 3 UV-Visible spectrum of L-leucine thiourea

3.3 Thermal Studies

Thermo gravimetric analysis of the title compound is used to reveals the thermal properties. By using simultaneous thermal analyzer METTLER TOLEDO TG-DSC was carried out and the resulting curve is shown in the Fig.4. 3.1490 mg of sample is taken as initial mass to carry the experiment. The observed curve indicates that there was single stage decomposition. No weight loss is occurred up to 205.61°C and the compound starts to decompose from 205.61° C to 337.25° C. Due to dissociation of L-leucine thiourea sudden weight loss occurs between 205-337.25° C. The dissociation may probably accounts for the evolution of gases like N_2 and ammonia etc., from the thermal analysis it may be confirmed that L-leucine thiourea will be thermally stable and can be utilized for optical device fabrication up to 205.61° C. For the comparative study some of the reported thermal stability data of the L-leucine famiy is shown. **(Table 2) Fig. 4**

Table 2

Thermal stability of some of the reported L-leucine family crystal

Crystals	Thermal stability in˚C
L-leucine `	268 [8]
L-leucine nitrate	159.7 [9]
L-leucinium oxalate	203 [10]
L-leucine L-leucinium picrate	195 [12]
L-leucine phthalic acid potassium iodide	192 [18]
L-leucine thiourea	205.61*

*Present work

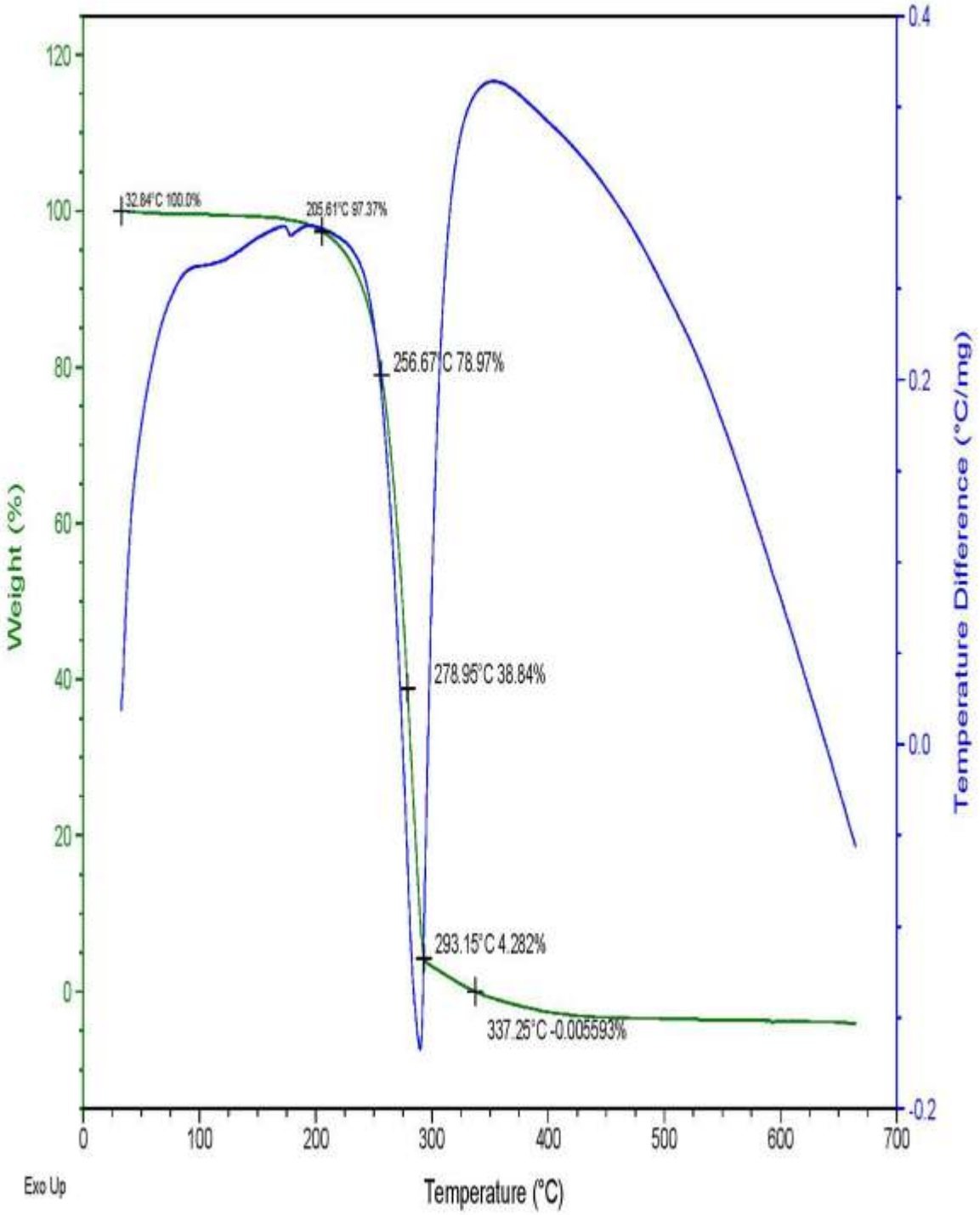

Fig. 4 TG-DSC of L-leucine thiourea

3.4 X-ray diffraction studies

The X-ray powder diffraction data for L-Leucine thiourea crystals were recorded to determine the purity, crystalline nature and identity. The powder XRD pattern is shown in the Fig.4 and the resulting diffraction pattern confirms the grown crystal structure by the computer program. Lattice parameters were calculated

by taking two-theta values as the input data using POWDERX refinement software and are found to be matched with the reported data. **Fig. 5**

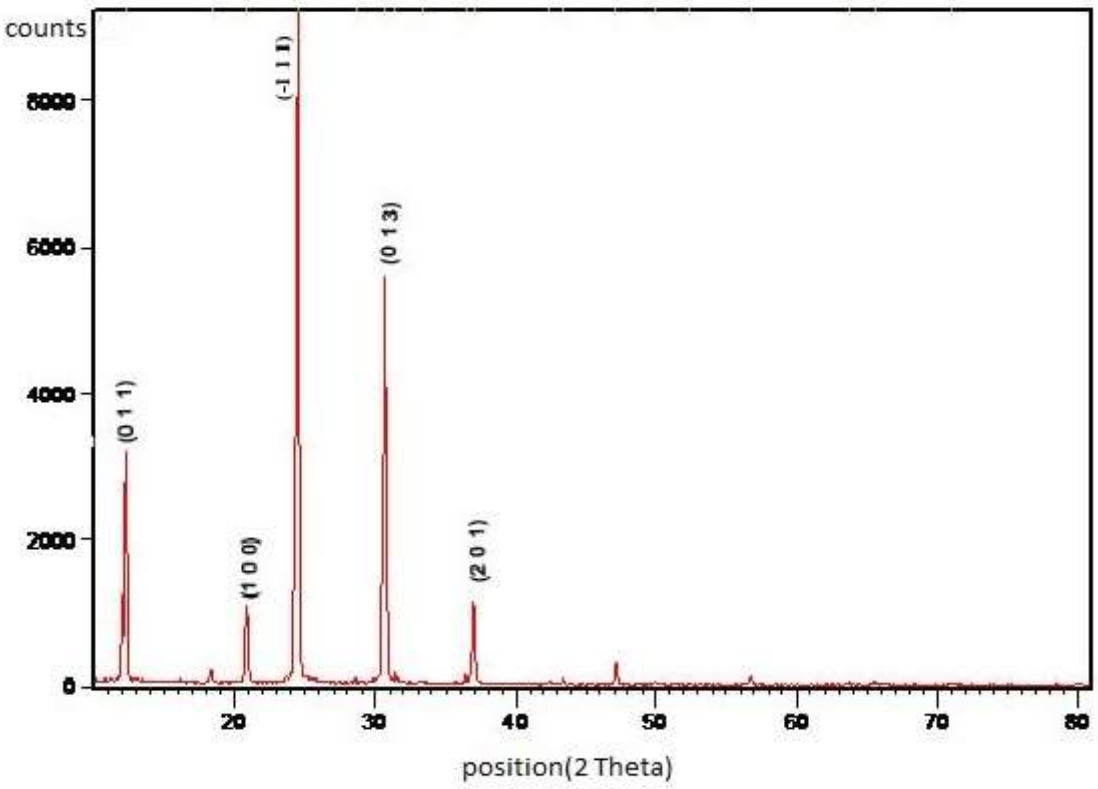

Fig. 5 XRD pattern of L-leucine thiourea

3.5 SHG

A source of Q-switched Nd-YAG laser with a wavelength of 1064 nm in 90̊ scattering geometry with an input energy of 3.6 mj pulse^{-1}, 8 ns pulse duration and repetition rate of 10 Hz with a spot size of 1mm diameter was used to measure the SHG efficiency of L-leucine thiourea placed in a micro capillary tube. The packed sample was irradiated by the source and the emerged output green radiation of wavelength λ = 532 nm from the specimen was detected. It was observed that the SHG efficiency of L-leucine thiourea crystal is more pronounced on compared with KDP and urea.

4. Conclusion

A new good quality, transparent crystal nonlinear optical crystal L-leucine thiourea was grown by slow evaporation method at constant temperature. FTIR analysis confirms the presence of functional groups. Optical absorption studies UV-Visible shows the transparency of the crystals. Crystal identification was done by XRD. TG-DSC studies confirm that there is no water of crystallization in L-leucine thiourea crystal and is stable up to 205.61°C. Kurtz and Perry method confirms the SHG efficiency of the grown L-leucine thiourea crystal and was found to be more pronounced on compared with KDP and urea. So it may be confirmed that the grown crystal will be a promising one for the NLO device fabrication.

References

[1] G. Madhurambal, B. Ravindran, M. Mariappan, K. Ramamurthi, S.C. Mojumdar, Growth and characterization of cinnamic acid-urea single crystal, J. Therm. Anal. Calorim. 104 (3) (2011) 875.
[2] B. Ravindran, G. Madhurambal, M. Mariappan, K. Ramamurthi, Growth and characterization of mercury cinnamate single crystal, J. Therm. Anal. Calorim. 104 (3) (2011) 909.
[3] G. Madhurambal, B. Ravindran, M. Mariappan, S.C. Mojumdar, Growth and characterization of tris thiourea chromium (III) sulphate, J. Therm. Anal. Calorim. 108 (3) (2012) 905.
[4] S. Dhanuskodi, K. Vasantha, P.A. Angeli Mary, Structural and thermal characterization of a semiorganic NLO material: L-alanine cadmium chloride, Spectrochimica Acta Part A 66 (2007) 637.
[5] K. Meera, R. Muralidharan, R. Dhanasekaran, Prapun Manyum, P. Ramasamy, Growth of nonlinear optical material: L-arginine hydrochloride and its characterization, J. Cryst. Growth 263 (2004) 510.
[6] J. Madhavan, S. Aruna, K. Prabha, J. Packium Julies, Ginson P. Joseph, S. Selvakumar, P. Sagayaraj, Growth andcharacterization of a novel NLO crystal L-histidine hydrofluoride dihydrate, J. Cryst. Growth 293 (2006) 409.
[7] A. Joseph Arul Pragasam, J. Madhavan, M. Gulam Mohamed, S.Selvakumar, K. Ambujam, P. Sagayaraj, Growth and characterization of amino acid (glycine and valine) substituted L-arginine diphosphate single crystals, Opt. Mater. 29 (2006) 173.
[8] S. Adhikari, T. Kar, Bulk single crystal growth and characterization of L-leucine – A nonlinear optical material, Mater. Chem. Phys. 133 (2012) 1055.
[9] S. Adhikari, T. Kar, Experimental and theoretical studies on physicochemical properties of L-leucine nitrate – a probable nonlinear optical material, J. Cryst. Growth 356 (2012) 4.
[10] A. Anbuchezhiyan, S. Ponnusamy, C. Muthamizhchelvan, Synthesis and characterization of nonlinear optical studies of L-leucinium oxalate: a single crystal, Optoelectron. Adv. Mat. 3 (2009) 1161.
[11] P. Baskaran, M. Vimalan, G. Bakiyaraj, K. Kirubavathi, K. Selvaraju, Synthesis, Growth and characterization of a nonlinear optical crystal: L-leucinium perchlorate, J. Taibah Univ. Sci. 11 (2017) 11.
[12] G. Bagavannarayana, B. Riscob, M. Shakir, Growth and characterization of L-leucine L-leucinium picrate single crystal: A new nonlinear optical material, J. Mater. Chem. 126 (2011) 20.
[13] S.S. Gupte, C.F. Desai, Vickers hardness anisotropy and slip system in ZTS crystals, Cryst.

Res. Technol. 34 (1999) 1329.
[14] N.N. Shejwal, R.B. Kulkarni, S.S. Hussaini, Mahindra D. Shirsat, Influence of L-leucine on structural, thermal, fluorescence and nonlinear optical properties zinc thiourea sulphate single crystal, Bionano Frontier 8 (3) (2015) 70.
[15] F. Helen, G. Kanchana, Investigation on the properties of L-serine doped zinc tris (thiourea) sulphate crystal for NLO application, Indian J. Pure and Appl. Phys. 52 (2014) 821.
[16] J. Prakash, M. Lawrence, Growth and characterization of pure and L-lysine doped zinc (tris) thiourea sulphate crystals, International Journal of Computer Applications, 8.3 (2010) 36.
[17] N.R. Dhumane, S.S. Hussaini, V.G. Dongre, Mahendra D. Shirsat, Influence of glycine on the nonlinear optical (NLO) properties of zinc (tris) thiourea sulphate (ZTS) single crystal, 31 (2008) 328.
[18] M.R. Jagadeesh, H.M. Suresh Kumar, R. Ananda Kumari, Growth and characterization of NLO crystal: L-leucine phthalic acid potassium iodide, Mater. Sci - Poland, 33 (3) (2015) 529.