

# Crystallization, spectral, and thermal characterization of L-histidine methyl ester dihydrochloride (LHMED)

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**Abstract** A novel nonlinear optical semi-organic single crystal of L-histidine methyl ester dihydrochloride was grown by slow evaporation solution growth method at an ambient temperature. The grown crystal was characterized by single crystal X-ray diffraction. Functional groups and the modes of vibrations were identified by FT-IR spectroscopy. The chemical composition of the crystal was confirmed by Energy dispersive X-ray analysis. The optical behavior of the crystal was examined by UV spectral analysis, which shows the absence of absorption between the wavelengths ranging from 230 to 1000 nm. The optical band gap of the grown crystal was estimated and is found to be 5.35 eV. The thermal behavior of the crystal was investigated by thermogravimetric and differential thermal analyses. The nonlinear optical property of the grown crystal was confirmed by the powder technique of Kurtz and Perry.

**Keywords** Nonlinear optical property · UV · FT-IR · Energy dispersive X-ray analysis (EDAX) · TG · DTA

## Introduction

Numerous research activities have been in practice for the past three decades on nonlinear optical (NLO) crystals, owing to their wide applications in frequency conversion, data storage, optical image processing, optical

communication, optical switching, etc. [1–3]. Recently a number of semi-organic crystals for nonlinear optical applications have been explored [4–6]. Among these, complexes of amino acid with inorganic salts were found to be promising NLO material as they share the properties of both organic and inorganic materials. Marcy et al. [7] reported that the nonlinearity of L-histidine tetrafluoroborate was at least five times higher than that of KDP. In the light of this, a series of L-histidine analogs such as L-histidine hydrochloride monohydrate [8], L-histidine bromide [9], L-histidine hydrofluoride dihydrate [10], L-histidine perchlorate [11], L-histidine nitrates [12], L-histidine dihydrogen orthophosphate orthophosphoric acid [13], L-histidine tetrafluoroborate [14], L-histidine trifluoroacetate [15] have been reported.

In continuation of the above works, we have grown L-histidine methyl ester dihydrochloride (LHMED), a semi-organic nonlinear optical material by low temperature solution growth method with optimum size. The structure of LHMED was first solved by Vilchiz et al. [16] with tiny crystals. However, no other systematic studies have been made on the material characterization of this crystal. For material characterization, thermal, and spectral analyses are very significant and useful methods. Hence, several authors have used these techniques for various materials characterization [17–26]. In this article, we are reporting the growth, single crystal XRD, FTIR, EDAX, UV, thermal analyses (TG-DTA), and NLO property of the grown crystal.

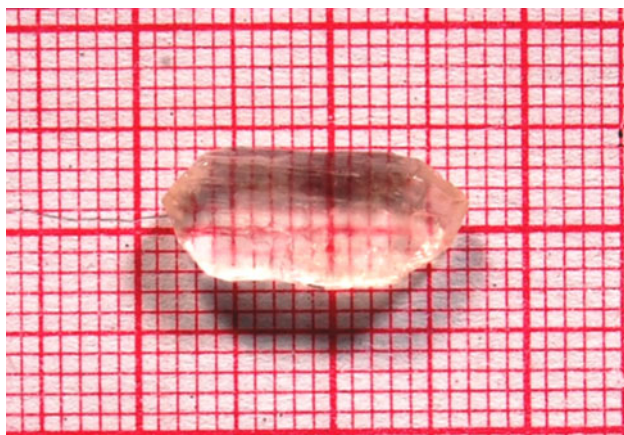
## Experimental

### Crystal growth

The starting material LHMED (AR grade) procured from Sigma-Aldrich Company was purified further by repeated

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**Fig. 1** Photograph of LHMED crystal

recrystallization in deionised water. Recrystallized LHMED was thoroughly dissolved in double distilled water at 32 °C and stirred well for about 2 h using magnetic stirrer. After obtaining homogeneous mixture of the solution over the entire volume, it was filtered twice using micro-whatman filter paper to eliminate the suspended impurities. Then, it was kept in a borosil beaker covered with perforated polyethylene sheet for controlled evaporation and placed in a constant temperature water bath kept at 32 °C. In this study, two drops of H<sub>2</sub>O<sub>2</sub> were added to the solution of LHMED to restrain the growth of micro-organism [27]. The crystal with good transparency was obtained after a period of 30 days. The photograph of as grown LHMED crystal is shown in Fig. 1.

## Results and discussion

### Single crystal XRD

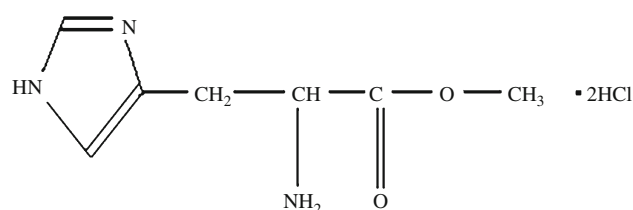
In order to determine the cell parameters of the LHMED crystal, the single crystal X-ray diffraction study was carried out using ENRAF–NONIUS CAD4 X-ray diffractometer with MoK $\alpha$  ( $\lambda = 0.7170 \text{ \AA}$ ) radiation. A small specimen of LHMED having dimensions  $0.10 \times 0.15 \times 0.35 \text{ mm}^3$  was cut out from the grown crystal and was then used for XRD analysis. From the X-ray diffraction data, it is observed that the LHMED crystal is monoclinic in structure with space group P2<sub>1</sub>. The lattice parameters are  $a = 8.215$ ,  $b = 7.105$ ,  $c = 9.512 \text{ \AA}$ ,  $\alpha = \gamma = 90^\circ$  and  $\beta = 94.54^\circ$ . These values are in good agreement with the reported values [16]. The crystallographic data is presented in Table 1. The molecular structure of LHMED is shown in Fig. 2.

### FT–IR Spectral analysis

The FTIR spectrum of LHMED was recorded in the KBr phase in the frequency region  $450\text{--}4000 \text{ cm}^{-1}$  using

**Table 1** Crystallographic data of LHMED crystal

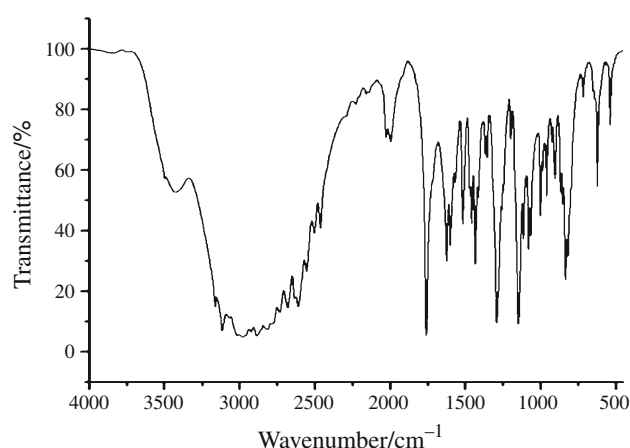
LHMED	Crystal data
Empirical formula	C <sub>7</sub> H <sub>11</sub> N <sub>3</sub> O <sub>2</sub> ·2HCl
Crystal system	Monoclinic
Space group	P2 <sub>1</sub>
Lattice parameters	$a = 8.221 \text{ \AA}$ $b = 7.108 \text{ \AA}$ $c = 9.505 \text{ \AA}$ $\beta = 94.56(2)^\circ$
Cell volume	$V = 555.42 \text{ \AA}^3$
Z	2
Molecular weight (gm)	242.10



**Fig. 2** Molecular structure of LHMED crystal

Perkin-Elmer spectrometer and is shown in Fig. 3. The assignments of various functional groups are given in Table 2.

The absorption band at  $3429 \text{ cm}^{-1}$  is due to the presence of hydrogen bond N–H stretching, characteristics of amino acids [28]. The stretching frequency at  $3115 \text{ cm}^{-1}$  shows the presence of NH<sub>3</sub><sup>+</sup> group in the crystal. The aromatic C–H stretching and aliphatic C–H stretching modes are resolved at  $3015$  and  $2886 \text{ cm}^{-1}$  [29]. Multiple fine structures at the lower energy mode indicate the strong hydrogen bonding interactions of NH<sub>3</sub><sup>+</sup> groups with the COO<sup>−</sup> group. The strongest band observed at  $1759 \text{ cm}^{-1}$



**Fig. 3** FTIR spectrum of LHMED crystal

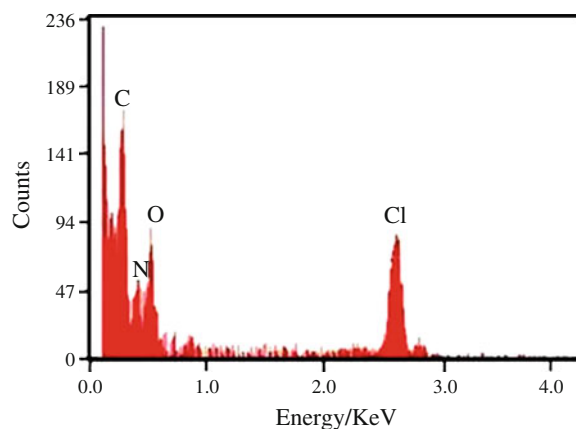
**Table 2** FT-IR frequency assignment for LHMED crystal

Wavenumber/cm	Assignment
3429	NH stretching
3162	NH <sub>3</sub> <sup>+</sup> stretching
3015	Aromatic CH stretching
2920	Aliphatic CH <sub>2</sub> stretching
2886	Aliphatic C–H stretching
1759	C=O Stretch of carbonyl group
1625	C=N Stretching of imidazole ring
1600	Aromatic C=C Stretching
1568	C=O asymmetric stretching
1515	NH <sub>3</sub> <sup>+</sup> Symmetric deformation
1458	CH <sub>2</sub> scissoring
1434	C–C Stretching
1418	C=O symmetric stretching
1291	C–O stretching
1257	CH <sub>3</sub> stretching
1148	C–O Stretching of Ester
1080	C–N stretching
1002	C–H out of plane bending
987	Ring asymmetric stretching
868	Ring symmetric
833	C–C–O stretch
718	CH <sub>2</sub> rocking
622	Ring deformation
537	Torsional oscillation of NH <sub>3</sub> <sup>+</sup>

indicates the presence of C=O stretching of carbonyl group. The peak at 1625 cm<sup>-1</sup> is assigned to C=N stretching of imidazole ring. Aromatic C=C stretching and C–C stretching are resolved at 1600 and 1434 cm<sup>-1</sup>. The presence of strong peak at 1291 cm<sup>-1</sup> is due to C–O stretching of carbonyl group. The strong peak appears at 1148 cm<sup>-1</sup> is due to the stretching vibration of C–O group of ester [30]. In the lower wavenumber region, the bands at 987, 868, and 622 cm<sup>-1</sup> are due to the ring asymmetric, symmetric stretching, and plane deformation.

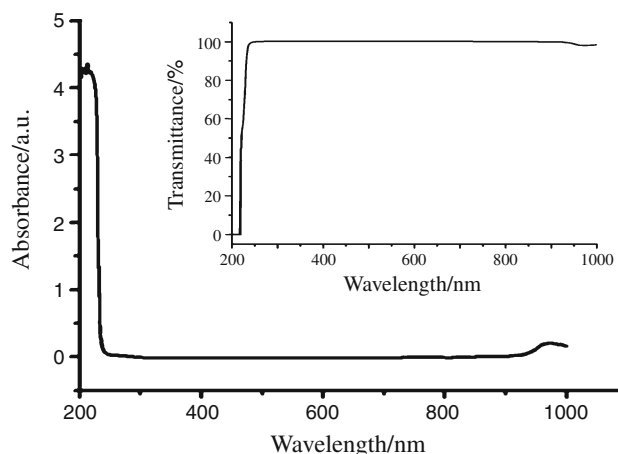
#### EDAX analysis

Energy dispersive X-ray analysis (EDAX) is a micro-analytical technique that uses the characteristic spectrum of X-rays emitted by the sample after excitation by high-energy electrons. This analysis is an important tool for characterizing the elements present in the given sample. In this study, the EDAX analysis was carried out for LHMED crystal by FEI QUANTA 200F energy dispersive X-ray micro analyzer. The result observed in the elemental analysis of LHMED is shown in Fig. 4. The EDAX spectrum confirms the presence of carbon, nitrogen, oxygen, and chlorine in the grown crystal.

**Fig. 4** EDAX spectrum of LHMED crystal

#### UV spectral analysis

In order to find the suitability of LHMED crystal for optical applications, UV–vis–NIR spectral study was performed with a Varian Carry-5E UV–vis spectrophotometer in the wavelength range 200–1000 nm. Optically transparent crystal of thickness about 2 mm was used for this study. The recorded absorption and transmission spectrum are shown in Fig. 5. From the absorption spectrum, it is clear that there is no significant absorption in the entire UV–visible–NIR region, which enables the crystal to be a good material for second harmonic generations from Nd:YAG laser and optoelectronic applications. A sharp fall in absorption is observed around 230 nm and this corresponds to the lower cut-off wavelength or fundamental absorption of the crystal. From the transmission spectrum, it is observed that the percentage of transmission is maximum in the wavelength range 230–1000 nm. The optical transparency of LHMED is larger than that of L-histidine hydrochloride monohydrate [8] and hence the presence of

**Fig. 5** Optical spectrum of LHMED crystal

methyl ester enhances the transparency window of the grown crystal.

The UV spectral study is also useful in understanding the electronic structure of the band gap of LHMED crystal. The optical band gap is one of the most useful aspects of the band structure, as it strongly influences the optical and electrical properties of the material. Absorption in the near UV region arises due to electronic transitions associated within the crystal. The optical energy gap of LHMED is ascertained from the absorption spectrum. By Tauc relation [31], the absorption coefficient  $\alpha$  for a material is given as

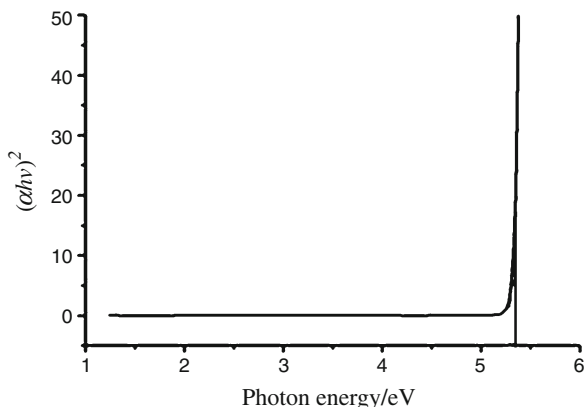
$$\alpha h\nu = A(h\nu - E_g)^n$$

where  $A$  is a constant which varies with transitions,  $E_g$  is the band gap of the material, and  $n$  is an index which can have the values  $1/2$ ,  $3/2$ ,  $2$ , or  $3$  depending on the nature of the electronic transition responsible for absorption. Here,  $n = 1/2$  is considered for an allowed direct transition. From the absorption spectrum, a graph is plotted between  $h\nu$  and  $(\alpha h\nu)^2$  and is shown in Fig. 6. The band gap of LHMED is estimated by exploring the straight line in the linear region of the graph at  $(\alpha h\nu)^2 = 0$  [32, 33]. The estimated band gap energy of LHMED crystal is 5.35 eV. Hence, the grown crystal has wide band gap energy and it can be utilized in applications in which high-temperature operation is essential.

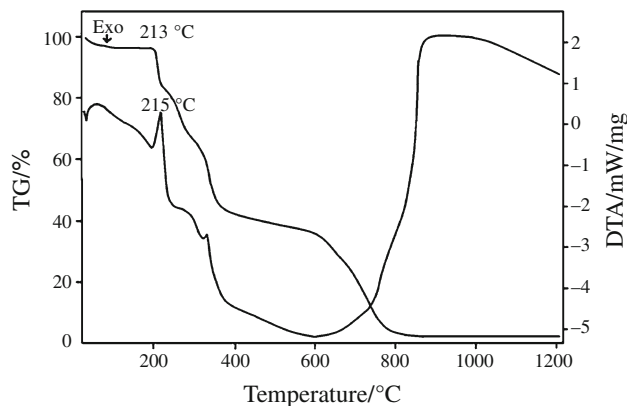
#### Thermal analyses

The thermogravimetric (TG) and differential thermal analysis (DTA) of LHMED crystal were carried out using the instrument NETSZCH STA 409 C/CD. The TG and DTA thermograms of LHMED were recorded between 25 and 1200 °C at a heating rate of 10 K/min in the nitrogen atmosphere. The simultaneously recorded TG and DTA traces are presented in Fig. 7.

The TG trace gives the complete picture of decomposition of the material. From the TG trace, it is observed that



**Fig. 6** Band gap calculation of LHMED crystal



**Fig. 7** TG-DTA curves of LHMED crystal

there is no significant weight loss up to 213 °C and there is a major weight loss between 213 and 332 °C. This confirms that the crystal is thermally stable up to 213 °C and suitable for possible device applications where the crystal is essential to endure high temperatures [34]. The DTA curve shows an intense sharp endothermic peak at 216 °C, which corresponds to the melting point of the LHMED crystal. The peak at 327.5 °C shows the major decomposition of the sample. The broad endothermic peak beyond 800 °C represents the release of the material as gaseous products.

#### Kurtz and Perry SHG test

The second-harmonic generation of LHMED was investigated by the Kurtz and Perry powder technique [35] using Q-switched, mode locked Nd:YAG laser operating at the fundamental wave-length 1064 nm, producing pulse width 8 ns with the repetition rate of 10 Hz. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered samples packed in a capillary tube. The output beam from the sample was filtered by an IR detector and then detected by a photomultiplier tube. The final output is displayed on the oscilloscope. The emission of second harmonic signal was confirmed by the emission of green radiation from the sample. For the SHG efficiency measurement, microcrystalline KDP was used as the reference material. The second harmonic efficiency of LHMED was found to be 1.6 times higher than that of KDP.

#### Conclusions

Single crystal of LHMED was grown by slow solvent evaporation method from aqueous solution at room temperature. Single X-ray diffraction study reveals that LHMED crystallizes in a monoclinic system with the space group  $P2_1$ . The presence of various functional groups and their modes of vibrations were identified by FTIR

spectroscopy. Chemical composition of LHMED was confirmed by EDAX analysis. The UV spectral analysis reveals that the crystal is completely transparent in the entire visible region with the lower UV cut-off wavelength around 230 nm and thus confirms the suitability of the material for NLO applications. The band gap of the crystal is estimated from the optical absorption spectrum and is found to be 5.35 eV. The SHG efficiency of LHMED is found to be 1.6 times higher than that of KDP. The TG and DTA analyses show that the crystal is thermally stable up to 213 °C.

## References

- Rajasekaran M, Anbusrinivasan P, Mojumdar SC. Growth, spectral and thermal characterization of 8-hydroxyquinoline. *J Therm Anal Calorim.* 2010;100:827–30.
- Moitra S, Kar T. Growth and characterization of L-valine- a nonlinear optical crystal. *Cryst Res Technol.* 2010;45:70–4.
- Krishnan C, Selvarajan P, Freeda TH. Growth and studies of pure and lithium bromide-doped zinc tris-thiourea sulfate (ZTS) single crystals. *Mater Manufact Process.* 2008;23:800–4.
- Lydia Caroline M, Kandasamy A, Mohan R, Vasudevan S. Growth and characterization of dichloro bis L-proline Zn(II): a semiorganic nonlinear optical crystal. *J Cryst Growth.* 2009;311:1161–5.
- Senthil A, Ramasamy P. Synthesis, growth and characterization of strontium bis (hydrogen L-malate) hexahydrate bulk single crystal: a promising semi-organic nonlinear optical material. *J Cryst Growth.* 2010;312:276–81.
- Kandasamy A, Siddeswaran R, Murugakoothan P, Suresh Kumar P, Mohan R. Synthesis, growth and characterization of L-proline cadmium chloride monohydrate (L-PCCM) crystals—a new nonlinear optical material. *Cryst Growth Design.* 2007;7:183–6.
- Marcy HO, Rosker MJ, Warren LF, Cunningham PH, Thomas CA. L-histidine tetrafluoroborate: a solution-grown semiorganic crystal for nonlinear frequency conversion. *Opt Lett.* 1995;20(3):252–4.
- Madhavan J, Aruna S, Thomas PC, Vimalan M, Rajasekar SA, Sagayaraj P. Growth and characterization of L-histidine hydrochloride monohydrate single crystals. *Cryst Res Technol.* 2007;42:59–64.
- Ramajothi J, Danuskodi S. Crystal growth, thermal and optical studies on a semiorganic nonlinear optical material for blue-green laser generation. *Spectrochim Acta A.* 2007;68:1213–9.
- Madhavan J, Aruna S, Praba K, Julius JP, Jinson J, Joseph P, Selvakumar S, Sagayaraj P. Growth and characterization of novel NLO crystal L-histidine hydrofluoride dihydrate (LHHF). *J Cryst Growth.* 2006;293:409–14.
- Aruna S, Vimalan M, Thomas PC, Thamizharasan K, Ambugam K, Madhavan J, Sagayaraj P. Growth and characterization of semi organic nonlinear optical crystals. *Cryst Res Technol.* 2007;304:180–5.
- Petrosyan HA, Karapetyan HA, Petrosyan AM. L-Histidine nitrates. *J Mol Struct.* 2006;794:160–7.
- Madhavan J, Aruna S, Ambujam K, Pragasa AJA, Ravikumar SM, Mohamed MG, Sagayaraj P. Crystallization and characterization of nonlinear optical L-histidinium dihydrogen orthophosphate orthophosphoric acid single crystal. *Cryst Res Technol.* 2006;41:997–1001.
- Jayaraman R, Sivasubramanian D. Optical and microhardness studies of semiorganic nonlinear optical material: L-histidine tetrafluoroborate. *Cryst Res Technol.* 2003;38:986–91.
- Sun GH, Sun XT, Sun ZH, Wang XQ, Liu XJ, Zhang GH, Xu D. Growth and characterization of a nonlinear optical crystal: L-histidine trifluoroacetate. *J Cryst Growth.* 2009;311:3904–10.
- Vilchiz VH, Norman RE, Chang SC. L-Histidine methyl ester dihydrochloride. *Acta Crystallogr C.* 1996;51:696–8.
- Madhurambal G, Mariappan M, Mojumdar SC. Thermal, UV and FTIR spectral studies of urea–thiourea zinc chloride single crystal. *J Therm Anal Calorim.* 2010;100:763–8.
- Madhurambal G, Ramasamy P, Anbusrinivasan P, Vasudevan G, Kavitha S, Mojumdar SC. Growth and characterization studies of 2-bromo-40-chloro-acetophenone (BCAP) crystals. *J Therm Anal Calorim.* 2008;94:59–62.
- Parthiban S, Murali S, Madhurambal G, Meenakshisundaram SP, Mojumdar SC. Effect of zinc(II) doping on thermal and optical properties of potassium hydrogen phthalate (KHP) crystals. *J Therm Anal Calorim.* 2010;100:751–6.
- Ramasamy G, Parthiban S, Meenakshisundaram SP, Mojumdar SC. Influence of alkali metal sodium doping on the properties of potassium hydrogen phthalate (KHP) crystals. *J Therm Anal Calorim.* 2010;100:861–5.
- Muthu K, Bhagavannarayana G, Chandrasekaran C, Parthiban S, Meenakshisundaram SP, Mojumdar SC. Os(VIII) doping effects on the properties and crystalline perfection of potassium hydrogen phthalate (KHP) crystals. *J Therm Anal Calorim.* 2010;100:793–9.
- Meenakshisundaram SP, Parthiban S, Madhurambal G, Mojumdar SC. Effect of chelating agent (1,10-phenanthroline) on potassium hydrogen phthalate crystals. *J Therm Anal Calorim.* 2008;94:21–5.
- Mojumdar SC, Sain M, Prasad RC, Sun L, Venart JES. Selected thermoanalytical methods and their applications from medicine to construction. *J Therm Anal Calorim.* 2007;60:653–62.
- Varshney G, Agrawal A, Mojumdar SC. Pyridine based cerium(IV) phosphate hybrid fibrous ion exchanger: Synthesis, characterization and thermal behaviour. *J Therm Anal Calorim.* 2007;90:731–4.
- Madhurambal G, Ramasamy P, Anbusrinivasan P, Mojumdar SC. Thermal properties, induction period, interfacial energy and nucleation parameters of solution grown benzophenone. *J Therm Anal Calorim.* 2007;90:673–9.
- Mojumdar SC. Thermoanalytical and IR-spectral investigation of Mg(II) complexes with heterocyclic ligands. *J Therm Anal Calorim.* 2001;64:629–36.
- Pragasam AJA, Selvakumar S, Thamizharasan K, Anand DP, Sagayaraj P. Growth and optical characterization of Cu<sup>+</sup> and Mg<sup>+</sup> substituted L-arginine di phosphate single crystals. *J Cryst Growth.* 2005;280:271–8.
- Rao CNR. *Chemical application of infrared spectroscopy.* 2nd ed. New York: Academic Press; 1963.
- Bellamy LJ. *The infrared spectra of complex molecules.* 3rd ed. New York: Wiley; 1975.
- Herzberg G. *Infrared and Raman spectra of polyatomic molecules.* 1st ed. New York: Van Nostrand Reinhold; 1945.
- Krishnakumar V, Sivakumar S, Nagalakshmi R, Bhuvanewari S, Rajaboopathi M. Effect of doping an organic molecule ligand on TGS single crystals. *Spectrochim Acta A.* 2008;71:480–5.
- Fochs PD. The measurement of the energy gap of semiconductors from their diffuse reflection spectra. *Proc Phys Soc London.* 1956;B69:70–5.
- Aneesh PM, Krishna KM, Jayaraj MK. Hydrothermal synthesis and characterization of undoped and Eu doped ZnGa<sub>2</sub>O<sub>4</sub> nanoparticles. *J Electrochem Soc.* 2009;156:33–6.
- Meenakshisundaram SP, Parthiban S, Kalavathy R, Madhurambal G, Bhagavannarayana G, Mojumdar SC. Thermal and optical properties of ZTS single crystals in the presence of 1,10-phenanthroline (Phen). *J Therm Anal Calorim.* 2010;100:831–7.
- Kurtz SK, Perry TT. A powder technique for the evaluation of non-linear optical materials. *J Appl Phys.* 1968;39:3798–813.