

Growth, Structural, Optical, Spectral and Thermal analysis of L-Theronine Cadmium Iodide NLO single crystal

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Abstract

L-Theronine Cadmium Iodide (LTCI) semi organic single crystal was grown from slow evaporation technique. LTCI crystals have been grown by slow evaporation technique. The single crystal XRD analysis shows that the grown crystal has orthorhombic system with space group $P2_12_12_1$ and X-ray powder diffraction study indicates that the crystalline nature of the compound. UV optical studies show that the grown materials possess minimum absorption in the UV and visible region making it an efficient NLO material for device fabrication. The optical studies give the energy gap of ~ 5.26 eV from Tauc's plot. The FT-IR spectroscopic studies revealed the various functional groups of the sample. TG-DTA study gave that LTCI crystal can be stable up to 251°C have NLO effect. The second order NLO responses are tested and calculated by using a pulsed Nd: YAG laser.

Keywords: LTCI; orthorhombic; tauc's plot; endothermic; SHG;

1. Introduction

Nonlinear optics has emerged as one of the most attractive fields of current research in view of its vital applications like in some of the areas of optical switching, optical data storage for the developing technologies in telecommunications and signal processing [1-3]. Organic crystals exhibit second order optical nonlinearities are some of the key materials for their use in frequency doublers, electro-optic modulators, optical limiters, high speed optical gates and parametric amplifiers. These materials shown large second order nonlinear optical properties and short transparency cut-off wavelength [4]. Among the organic NLO crystals, both the simple and complex amino acid crystals dominate the revolutionary advancement in various aspects of science and technology. Amino acids possess many explicit inherent qualities, for instance (i) molecular chirality, which makes safe as acentric structure (an essential condition to exhibit second-order optical nonlinearity) (ii) lack of powerfully conjugated bonds, primary for broad transparency in the visible region and (iii) Zwitterionic character of the molecule, which helps to improve the high hardness of the crystal [5]. Inorganic materials are highly resistant owing to their ionic or covalent nature of their intermolecular bonding, while their figure of merit reaches a plateau exemplified by KTP which may well be a ceiling [6]. In this view, organic amino acids single crystals like L-arginine phosphate (LAP) [7], L-histidine tetrafluoroborate [8] and

L-threonine [9] have been extremely studied. In particular L-threonine ($C_4H_9O_3N$) is an uncharged neutral amino acid possessing two asymmetric carbon atoms [10]. The present investigation is to study the structural, optical, spectral and thermal analyses are carried out for the grown LTCI crystals.

2. Synthesis and growth

L-Theronine Cadmium Iodide is synthesized from equimolar solution of L- Theronine and Cadmium Iodide by slow evaporation. The solubility data was determined by dissolving the synthesized salt of LTCI in 100 ml of double distilled water at a constant temperature. The solubility of LTCI increases with the temperature and thus exhibit positive solubility coefficient. The solubility curve is as shown in fig. 1. Transparent colorless single crystals were obtained from the re-crystallization salt. Seed crystal is then placed in its supersaturated solution kept in a bath at ambient temperature. Seed crystals are grown to big crystals by slow evaporation to a size of The dimension of crystal size measured about to be $0.5 \times 0.2 \times 0.3 \text{ mm}^3$ with good transparency in a time of about twenty four days as grown LTCI crystal are shown in the photograph fig.2.

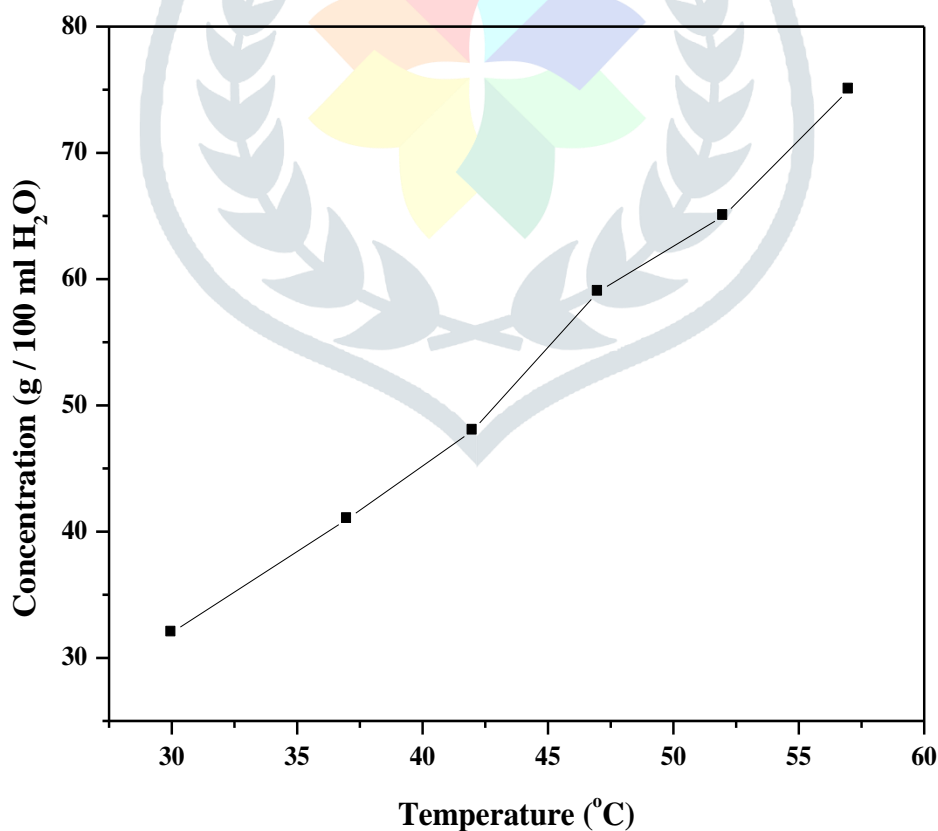


Fig. 1 Solubility curve of LTCI crystal

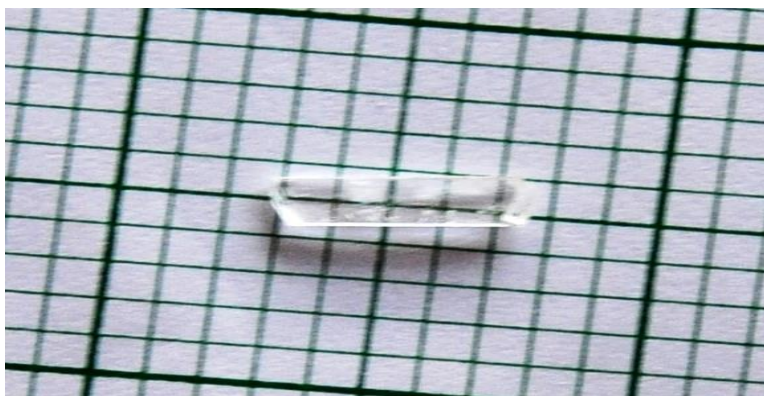


Fig.2. the photograph of grown LTCI crystal

3. Result and discussions

3.1 Single crystal XRD Analysis

The single crystal X-ray analysis of LTCI was recorded using ENRAF NONIUS CAD4 diffract meter. Single crystal X-ray data analysis was reveals that LTCI crystallizes in the orthorhombic system with space group $P2_12_12_1$. The crystallographic data was shown in table 1. The lattice parameters were found to be $a = 13.599 \text{ \AA}$, $b = 7.749 \text{ \AA}$, $c = 5.169 \text{ \AA}$, which are all in very well agreement with the reported values (Shoemaker et al 1950, Rajesh Kumar et al 2004).

Table 1. Lattice parameters values of LTCI crystal

Parameter	Single Crystal XRD
Crystal System	Orthorhombic
Space group	$P2_12_12_1$
a	$13.599 (\text{\AA})$
b	$7.749 (\text{\AA})$
c	$5.169 (\text{\AA})$
$\alpha = \beta = \gamma$	90°
Unit Cell Volume	$544.702(\text{\AA})^3$

3.2 Powder XRD Analysis

The Powder XRD spectrum of the crystals is recorded using PAN analytical Expert pro diffractometer with $\text{CuK}\alpha$ radiation $\lambda = 1.5418 \text{ \AA}$ to identify the compound. The recorded powder XRD pattern is given in Fig. 3. The powder pattern scanning variety of 10° - 80° at the rate of $2^\circ/\text{min}$. the 2θ values are transformed. The presence of sharp height confirms the good crystalline nature of the grown LTCI. From the XRD data, it is found

that L-Theronine Cadmium Iodide belongs to the Orthorhombic system which confirms the identity of the grown crystal the usage of the INDEXING software program package [11].

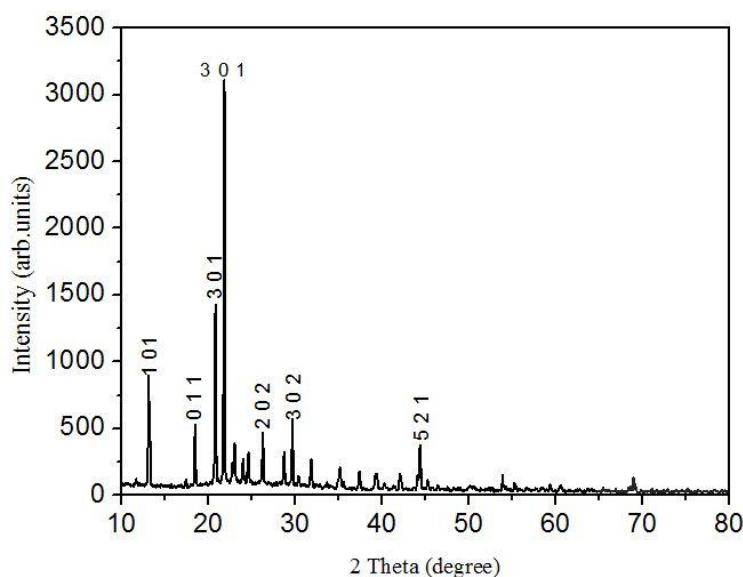


Fig.3. Powder X-ray diffraction pattern of LTCI crystal

3.3 FTIR Analysis

The characteristic vibrational frequencies of the functional groups in the crystal lattices of LTCI are identified FTIR technique and carried out at room temperature in the spectral range of 400–4000 cm^{-1} by using the FTIR spectrometer is Perkin-Elmer type and it has high resolution compared to ordinary infrared spectrometer of the sample mixed with KBr pellet method is shown in fig. 4. The band observed at 489.64 cm^{-1} is assigned to torsion mode of NH_3 . The rocking of CO_2 is assigned to the band observed at 560.19 cm^{-1} . The band at 701.52 cm^{-1} is assigned to the wagging vibration of CO_2 structure. Torsion of COH structure is observed around 750 cm^{-1} . The bending of CO_2 is observed at 767.90 cm^{-1} . The sharp band at 871.09 cm^{-1} is related to a stretching of CCN structure. Band at 931.50 cm^{-1} is associated with CC- stretching vibration. Due to the stretching vibration involving carbon and nitrogen of the amino group there exhibit a peak at 1040.52 cm^{-1} . The rocking of NH_3 structure is observed at wave numbers 1109.21 and 1184.12 cm^{-1} . Bending vibrations of the CH_3 group is assigned to the peak at 1457 cm^{-1} . The symmetric stretching of CO_2 structure is found at 1417 cm^{-1} in the IR spectrum. The symmetric bending of the NH_3 is observed at 1480.88 cm^{-1} . The band at 1625.99 cm^{-1} may be assigned to the asymmetric bending of NH_3 . The stretching vibrations also exist in both the NH_3 and CH structures. The NH_3 stretching vibrations are present in all amino acids. [12] The peaks corresponding to the wave numbers 2713 cm^{-1} corresponds to CH_2 symmetric stretching. The peak at 2049 cm^{-1} with strong intensity represents NH_3 asymmetric deformation [13], the peak against 930 cm^{-1} shows C- C stretching vibration [14].

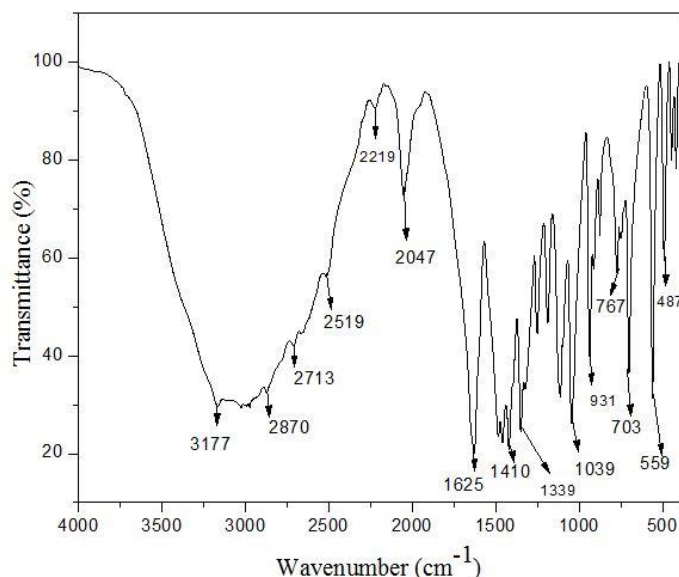


Fig.4 FT-IR spectrum of LTCl crystal

3.4 UV-Vis-NIR Studies and Band gap energy

3.4.1 UV-Vis-NIR Studies

Optical Transmittance spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. The optical absorption spectrum for the wavelengths between 200 and 1200 nm was recorded using a Varian carry 5E model dual beam spectrophotometer with an optically polished LTCl single crystal of thickness 1 mm. The recorded UV-Vis-NIR absorption spectrum is shown in Fig 4. From observation that very less absorption in the entire visible and near infrared region which exhibits the good quality of the crystal was conformed. Optical absorption coefficient α has been calculated using components, $\alpha = \frac{2.3026}{t} \log(1/T)$, in which t is the thickness crystal, T is the transmittance [15]. The optical band hole became evaluated from the transmission spectrum. The absorption is found to be minimum Value in the entire UV-visible region, and the UV - cutoff wavelength of LTCl is around 250 nm hence it can be used as a potential material for SHG.

3.4.2 Band gap energy

Optical absorption coefficient α close to the absorption edges is given through, $h\nu\alpha = A(h\nu - E_g)^{1/2}$, where E_g is the optically band gaps power, A is the consistent is the plank regular is incident photons frequency. The Tauc's plot drawn among $\alpha h\nu^2$ and photon energy $h\nu$ shown in fig.6. From the plot, the E_g energy of LTCl grown crystal is observed to be 5.26 eV. [16].

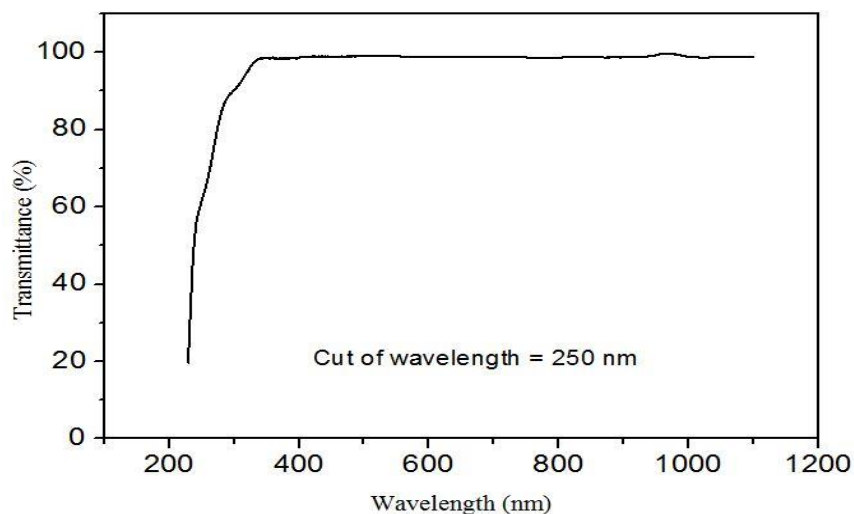


Fig.5 UV-Vis-NIR Transmittance Spectrum of LTCI crystal

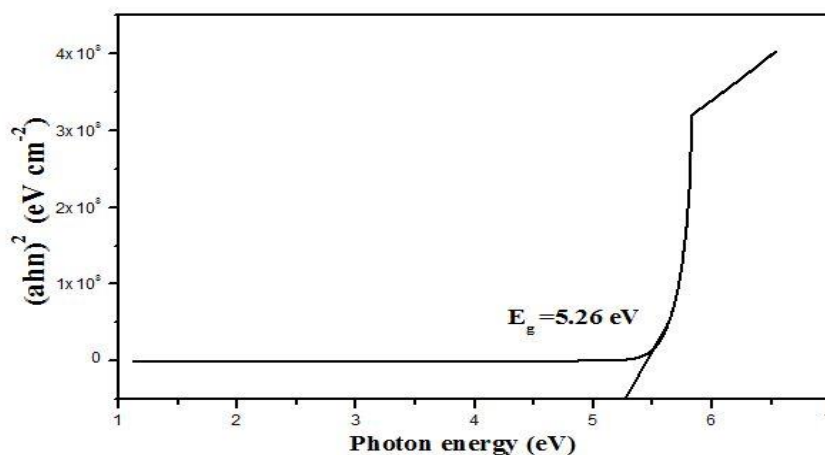


Fig.6. Tauc's plot of LTCI crystal

3.5 Thermal Analysis

The thermo gravimetric analysis of LTCI was carried out between 23 and 600°C in nitrogen atmosphere at a scanning rate of 10°C/min. The TGA and DTG traces are shown in Fig. 7. The DTA curve also shows a sharp endothermic peak at 251°C, which is assigned for decomposition point of the grown crystal. Before decomposition no characteristic endothermic or exothermic peaks were observed. It is observed that no phase transition occurs up to the decomposition point [17]. Thus from the thermal analysis, it is seen that LTCI crystal decomposes without melting and is stable up to 251°C. Hence it can be utilized for device application up to 251°C. There is a single stage of weight loss which establishes the quality of the grown crystals. The sharp peak in the DTA trace coincides with decomposition shown in the TGA trace.

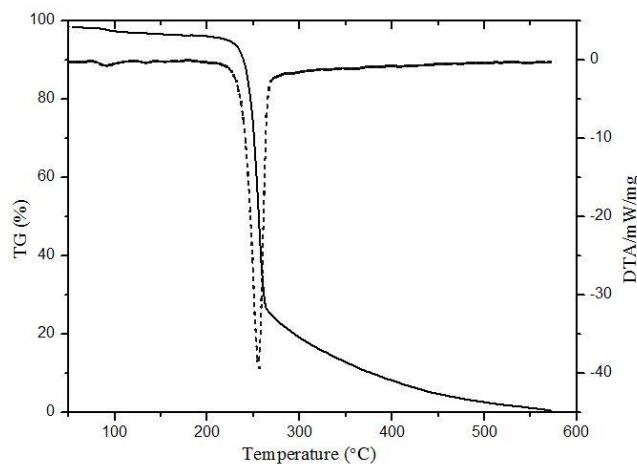


Fig.7 TG and DTA plot of LTCl

3.6 Dielectric Studies

The electric properties of dielectric substances are usually described in terms of the dielectric constant. For most materials, this quantity is independent of the strength of the electric field over a wide range of the latter, but in the case of alternating fields, it depends on the frequency. A study of dielectric response in crystals gives information about electric field distribution and charge transport mechanism. Hence the grown crystal was subjected to dielectric studies using HIOKI 3532-50 LCR HITESTER. Transparent polished crystals of rectangular dimension $1 \times 1 \text{ cm}^2$ was selected for dielectric studies. Graphite was applied on the surface of the sample in order to make firm electrical contact. The experiment was carried out for different frequencies starting from 50 Hz to 5 MHz. The dielectric constant was calculated using the relation

$$\epsilon = \frac{Cd}{\epsilon_0 A}$$

Where, C is the capacitance, d is the thickness of the crystal, ϵ_0 is the permittivity of free space and A is the area of the crystal. The variation of dielectric constant and dielectric loss for different frequencies are shown in figs. 8 and 9. From the curve, it is observed that the dielectric constant and dielectric loss decreases slowly with increasing frequency and attains saturation at higher frequencies. The low dielectric constant value of the grown crystals at high frequency is attributed to space charge polarization. It is observed that the low dielectric loss was consistent with nearly constant level of dielectric constant over the wide frequency range. The low values of dielectric loss indicate that the grown crystal contains minimum defects. The low values of dielectric loss suggest that the grown crystals are of good quality

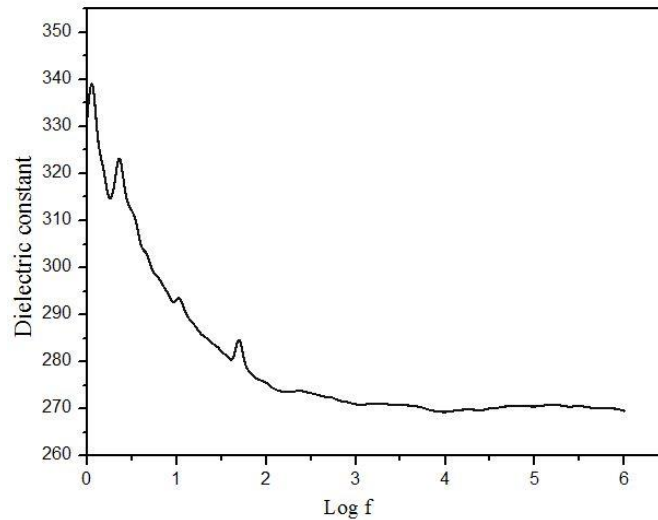


Fig.8. Log frequency vs dielectric constant for LTCI crystal

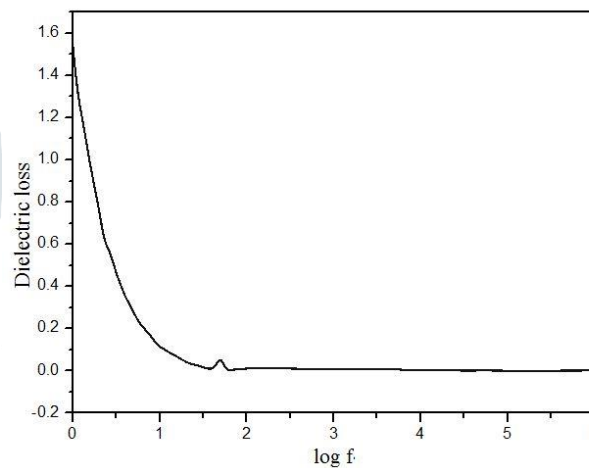


Fig.9. Log frequency vs dielectric loss for LTCI crystal

3.7 Nonlinear Optical Properties

The SHG efficiency of LTCI material was measured by the modified Kurtz and Perry powder technique in which the second harmonic output was generated by irradiating powder sample of randomly oriented crystallites of particle size in the range 100 – 150 μm . In this technique, the sample packed was as a polycrystalline powder in a cell sandwiched between two glass plates. The sample was then subjected to the output of a Q-switched Nd:YAG laser emitting a fundamental wavelength of 1064 nm, 8 ns pulse width, 10 Hz repetition rate and 2.75 mJ pul / energy. The SHG was confirmed by the emission of green radiation. The amplitude of the SHG output was measured using a photo multiplier tube (PMT) and box car averager. Pulse width 6ns and repetition rate 10HZ allowed commonly. The SHG incident wavelength light source became 1064 nm. The SHG output energy wavelength light emitted from the 532 nm bright green radiation. The second harmonic efficiency is due to powder pattern of LTCI crystal are 3.6 instances better than KDP crystal. [18].

4. Conclusion

L-Threonine cadmium iodide is an NLO material which can be used for second harmonic generation applications. LTCI crystals have been grown by slow evaporation technique. Single crystal X-ray analysis was used to find the lattice parameters and it is found that orthorhombic system with space group $P2_12_12_1$. UV optical studies show that the grown materials possess minimum absorption in the UV and visible region making it an efficient NLO material for device fabrication. The optical studies give the energy gap of ~ 5.26 eV from Tauc's plot. The FTIR Spectrum confirms the presence of functional groups of LTCI crystal. TG-DTA proves that LTCI crystal can be used up to 251°C have NLO effect. The second harmonic efficiency is due to powder pattern of LTCI crystal are 3.6 times better than KDP crystal.

Acknowledgments

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Reference

- [1] P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Organic Molecules and Polymers, Wiley, New York, 1991.
- [2] H.O. Marcy, L.F. Warren, M.S. Webb, C.A. Ebberts, S.P. Velsko, G.C. Kennedy, G.C. Catella, Appl. Opt. 31 (1992) 5051–5060.
- [3] X.Q. Wang, D. Xu, D.R. Yuan, Y.P. Tian, W.T. Yu, S.Y. Sun, Z.H. Yang, Q. Fang, M.K. Lu, Y.X. Yan, F.Q. Meng, S.Y. Guo, G.H. Zhang, M.G. Jiang, Mater. Res. Bull. 34 (1999) 2003.
- [4] M. Prakash, D. Geetha, M. Lydia Caroline, Materials and Manufacturing Processes, Taylor & Francis, 27 (2012) 519–522.
- [5] G.R. Desiraju, Crystal Engineering, the Design of Organic Solids Elsevier, New York (1989)
- [6] J.D. Bierlein, H. vanherzeele J. Opt. Soc. Am. B, 4 (6) (1989), pp. 622–633
- [7] D. Eimerl, S. Velsko, L. Davis, F. Wang, G. Loiacono, G. Denedt, IEEE J. Quantum Electron. QE 25 (1989) 179–193.
- [8] H.O. Marcy, M.J. Rosker, L.F. Warren, P.H. Cunningham, C.A. Thomas, L.A. Deloach, S.P. Velsko, L.A. Ebberts, J.H. Liao, M.G. Kanatzidis, Opt. Lett. 20 (1995) 252–254.
- [9] J.J. Rodrigues Jr., L. Misoguti, F.D. Nunes, C.R. Mendonça, S.C. Zilio, Opt. Mater. 22 (2003) 235–240.

- [10] K.E. Rieckhoff, W.L. Peticolas, *Science* 147 (1965) 610–611.
- [11] S.Venda, S.Gunasekaran, S.Srinivasan, *Optik* Volume 127, Issue 2, January 2016, Pages 848-851
- [12] R.Subaranjani, J.Madhavan, M.Victor Antony Raj, *Materials today proceedings*, Volume 8, Part 1, 2019, Pages 108-116.
- [13] E.Chinnasamy, S.Arulmani, K.Deepa, D.Suresh Kumar, J.Madhavan, S.Senthil, *Materials Today: Proceedings* 8 (2019) 264–270.
- [14] G. Ramesh Kumar, S. Gokul Raj, R. Mohan, R. Jayavel, J. Cryst. Growth 283 (2005) 193–197.
- [15] S.Manikandan, R.Mahalakshmi, P.Krishnan, F.Yogam, P.Rajesh, *Optik* Volume 127, Issue 13, July 2016, Pages 5316-5321.
- [16] D.Sankar, Vinay RajMenon, P.Sagayaraj, J.Madhavan, *Physica B: Condensed Matter*, Volume 405, Issue 1, 1 January 2010, Pages 192-197.
- [17] P. Kalaiselvi, S. Alfred Cecil Raj, K. Jagannathan, N. Vijayan, G. Bhagavannarayana, S. Kalainathan, *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* Volume 132, 11 November 2014, Pages 726-732
- [18] S.K. Kurtz, T. T Perry. *Apply phy*,39.3798.1968