GROWTH AND CHARACTERIZATION OF A NON-LINEAR OPTICAL CRYSTAL: THIOUREA ADDED L-HISTIDINE CRYSTALS

S. Nalini Jayanthi [a,b], A. R. Prabhakaran[c], D. Subashini[d], K. Thamizharasan[e]

[a] Research Scholar, Department of Physics, Pachaiyappa's College, Chennai, India.
[b] Assistant Professor, Department of Physics, AIHT, Kazhipattur, Chennai, India.
[c] Associate Professor, Department of Physics, Pachaiyappa's College, Chennai, India.
[d] Asst. Prof., Department of Physics, Dr. Ambedkar Govt. Arts College, Chennai, India.
[e] Associate Professor and Head, Dept. of Physics, Sir Theagaraya College, Chennai, India.

ABSTRACT

Single crystal of Thiourea added L-Histidine (TULH) have been grown by slow evaporation solution growth technique. Good optical quality single crystal of dimension up to 34x5x8mm^3 *have been obtained. To identify the morphology and structure, the as grown crystals were subjected to single crystal and powder x-ray diffraction analysis. The different mode of vibrations present in the crystal was identified with FT-IR spectra. The optical transmission spectrum and Second Harmonic Generation (SHG) have been studied to find its linear and Non-linear properties. It is observed that the crystal has transparency window from 350nm to 1100nm and its energy gap (*E_g*) found to be is 3.9eV. Second Harmonic Generation studies reveal that the crystal is suitable for frequency conversion application. The thermal stability of the grown crystal was found by thermo-gravimetric (TG) and differential thermal analysis (DTA). Mechanical property of the crystal carried out by Vicker's Micro hardness tests shows that TULH crystal is soft in nature. Photoconducting measurement reveals the positive Photoconducting nature of the as grown crystal.*

KEYWORDS: *Solution Growth, Characterization, Organic Crystal, Non Linear Optical material.*

I. INTRODUCTION

Non Linear Optical (NLO) materials play a vital role in the fields of optical data storage, image processing, electro-optical switching devices, optical information processing and telecommunication. Organic NLO materials have high non linearity and rapid response as compared to inorganic compounds but they have poor physiochemical and thermal stability [1]. L-Histidine is one of the optically active amino acid having an imiadazole side chain with pKa near neutrality [2]. It acts both as a proton donor and proton acceptor. It also acts as a nucleophilic agent [3].

In this paper, the growth aspects of TULH have been studied and the bulk crystals were grown by slow evaporation technique. The grown crystals were characterized by single crystal, powder XRD, FTIR, UV-Vis-NIR, TG-DTA analysis, Micro hardness and Photoconductivity measurements. The NLO property of the crystal has also been studied and reported. However, to the author's best knowledge, there is no existing report about structural parameters of TULH crystals. Therefore, for the first time in this paper, particle size (D), Dislocation density (δ) and Strain values (ε) for corresponding Full Width Half Maximum values (FWHM) are fully reported.

II. RELATED WORKS

L-Histidine possess imiadazole side chain and shows good SHG efficiency. This was first reported by Marcy et al. [4]. V.Kannan et al. reported single crystals of L-Histidine mono hydrochloride (LHMHCl) and L-Histidine dihydrochloride (LHDHCl) [5]. LHMHCl crystallizes in orthorhombic form with space group $P2_12_12_1$. While LHDHCl crystallizes in monoclinic form with space group $P2_1$.

Both crystals have excellent optical transmission but only LHDHCl exhibit strong second harmonic generation. Subramanian Natarajan et al. [6] reported a new organic compound L-Histidinium 2-nitrobenzoate. This compound has twice the SHG efficiency of standard KDP. Pandurangan Anandan et al.[7] identified L-Histidine monohydrate and tartaric acid mixed L-Histidine hydrochloride monohydrate crystals. It was found that, both crystals have wide transparency window in UV-Vis-NIR region and have good SHG efficiency. Ram Kripal et al. [8] reported Cr^{3+} doped L-Histidine hydrochloride monohydrate crystal. They studied the EPR and optical absorption of the crystal and obtained hyperfine structure of Cr^{53} isotope. Optical absorption spectrum shows Cr^{3+} doped L-Histidine hydrochloride monohydrate single crystal is transparent in UV-Vis-NIR region. G.P.De Sousa et al. [9] discussed the effect of changing pressure on the vibration raman spectra of L-Histidine hydrochloride monohydrate crystal. C. Alosious Gonsago et al. [10] for the first time reported about L-Histidinium maleate 1.5 hydrate (LHM). The crystal belongs to monoclinic system with space group $P2_1$. In the crystal, molecules are linked through inter and intramolecular N-H…O and O-H… hydrogen bonds, generate edge fused ring motif.

III. EXPERIMENTAL PROCEDURES

3.1. Experimental setup and crystal growth

Equimolar ratio of L-Histidine and Thiourea were dissolved in double distilled water and stirred well using a temperature controlled magnetic stirrer at 40 °C to get a homogeneous mixture of solution. Saturated TULH solution was prepared finally and this fully reacted solution was allowed for slow evaporation to get crystalline salt. Highly purified crystalline salt was obtained by repeating recrystallization process. The supersaturated solution of synthesized Thiourea added L-Histidine (TULH) was kept undisturbed at room temperature. Optically good quality seed crystals were grown from this solution. Transparent TULH crystals with well defined morphology were obtained by spontaneous crystallization. TULH crystals of size 34x5x8 mm^3 were obtained in a period of about a week [Fig.1].

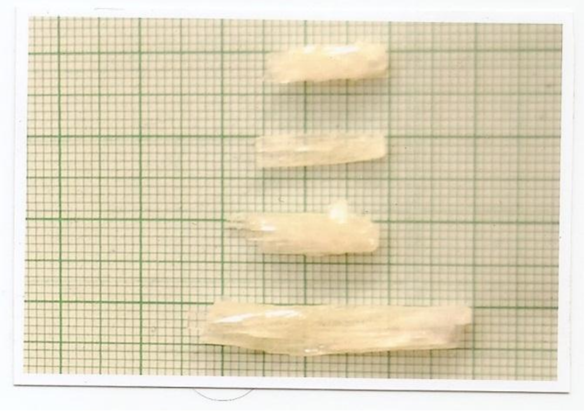

Fig.1 Photograph of as grown TULH Crystal

3.2. Characterization analysis

The crystalline perfection was examined using ENRAF NONIUS CAD4 single crystal X-ray diffractometer with MoKα (λ=0.71073Å) radiation. The grown TULH crystals were crushed into uniform fine powder and subjected to X-ray powder diffraction analysis using monochromated CuKα radiation source (λ=1.540598Å). The sample was then scanned for a 2θ range 10-70° at a scan rate of 1°/min. The Fourier Transform Infrared [11] was carried out between 450 Cm^{-1} and 4000 cm^{-1} using Perkin Elmer Spectrum-1. The UV-VIS-NIR spectrum was recorded in the wavelength range 200 to 1100nm using VARIAN CARY 5E UV-VIS-NIR Spectrophotometer. The NLO efficiency of the crystal was examined by Kurtz and Perry Powder Technique using Quanta ray series Nd: YAG laser emitting first harmonics output of 1064 nm with a pulse width of 8ns. The thermo gravimetric analysis of TULH crystals has been carried out between 35℃ to 808℃ at a heating rate of 10℃/min. The experiment has been performed in nitrogen atmosphere using Netzsch STA 409 TGA/DTA .

Microhardness studies have been carried out using Leitz Wetzlar Vickers microhardness tester fitted with a Vickers diamond pyramidal indentor attached to an incident light microscope. Photoconductivity study of the crystal was carried out using a KEITHLEY Picoammeter at room temperature.

IV. RESULTS AND DISCUSSIONS

4.1. Single Crystal X-ray diffraction analysis

The single crystal analysis data indicates that the TULH crystal belongs to orthorhombic crystal system with space group $P2_12_12_1$. Lattice parameters were found to be a=5.14 Å, b=7.33 Å, c=18.61Å, $\alpha= \beta= \nu =90^\circ$, Z=4 with cell volume as 701 Å. TULH values were compared with the crystallographic data of pure L-Histidine crystals [2]. It was found that there was a slight change in the lattice parameters and the cell volume of the crystals. This change may be due to the presence of thiourea in the L-Histidine crystal.

4.2. Powder X-ray diffraction analysis

The powder form of TULH crystal was subjected to powder X-ray diffraction analysis and the recorded spectrum is shown in Fig.2. Miller indices of the planes have been calculated and Bragg's peaks have been indexed. The sharp and well defined peaks confirm the good crystallinity of the grown crystals. Particle size (D), Dislocation density (δ) and Strain values (ε) for corresponding full width half maximum (FWHM) were calculated and listed in the Table 1.

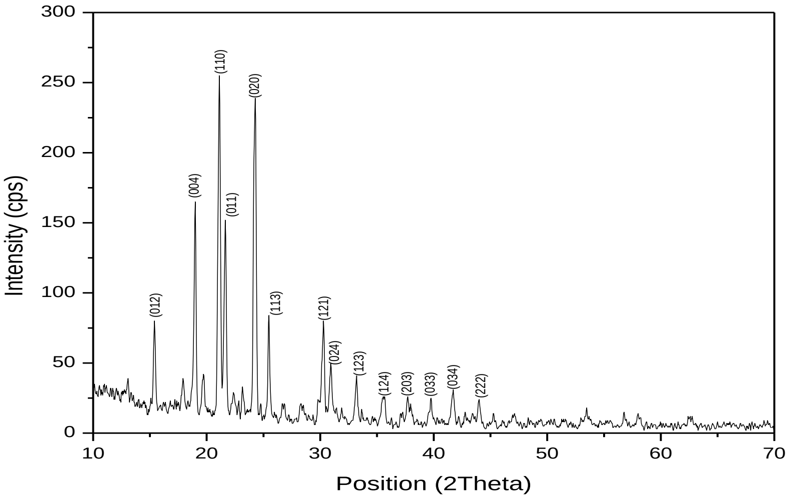

Fig.2 Powder XRD of TULH crystal

Table 1-Structural Parameters

FWHM deg	Particle size(D) nm	Dislocation density(δ) Kg/m^3	Strain(ε) lin^{-2}m^{-4}
0.1867	0.78926x10^{-9}	1.6053x10^{18}	0.04592
0.1400	1.04981x10^{-9}	0.9080x10^{18}	0.034495
0.28	0.542485x10^{-9}	3.3998x10^{18}	1.06675
0.933	1.7189x10^{-9}	3.3885x10^{17}	0.021075

4.3. FT-IR spectral analysis

FTIR spectrum of TULH crystal is shown in Fig.3. In the spectrum, the sharp peak at 3451cm^{-1} [12] is the clinching evidence for the protonated form of the Histidine ring nitrogen and NH_2 group. C-H asymmetric stretching occurs at 2933 cm^{-1}. Symmetric bending vibrations of NH_3^+ are seen at 1490 cm^{-1} [13]. It also identifies the symmetric stretching of nitro group [14]. The band at 1064 cm^{-1} is due to the presence of antisymmetric stretching vibration in five membered imiadazole ring $(C_3H_4N_2)^+$. The C-C-O stretching and in plane bend gives a peak at 860 cm^{-1}[15]. The stretching mode of C=S gives a peak at 706 cm^{-1} which corresponds to the absorption of thiourea [16-18, 14]. The peak at 598 cm^{-1} is due to the ring in-plane deformation [7].

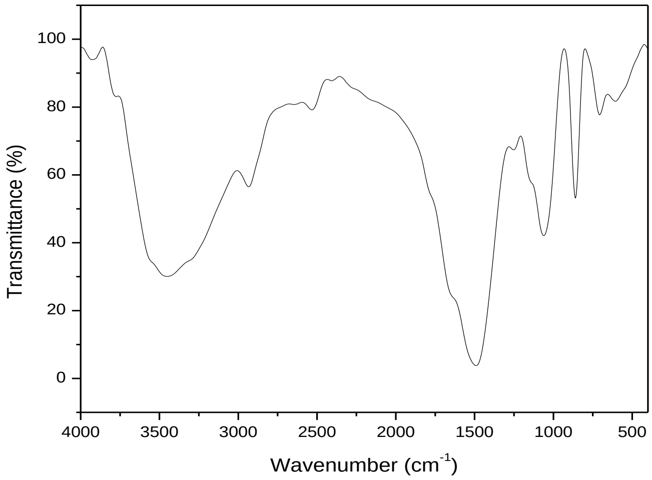

Fig.3 FTIR Spectrum of TULH crystal

4.4 UV-Vis-NIR

The UV-Vis-NIR spectrum of TULH crystal is shown in Fig.4. It is observed that for an entire visible region absorbance is less than 1.5 units and the as grown crystal is transparent in the UV and visible regions of the spectrum. This is a constructive nature of a NLO material [19]. The lower cutoff wavelength was around 310nm and there was no absorption from 350nm to 1100nm which clearly shows that the crystal possess good optical transparency for the second harmonic generation of Nd:YAG laser radiation at 1064nm[20].

The optical band gap of the crystal is determined from Tauc relation [21]. According to this relation a direct band gap material obeys the following relation for high photon energies (hυ)

$$\alpha = \{A(h\upsilon - E_g)^n\}/h\upsilon \quad \text{.........(i)}$$

where A is a constant. E_g is the band gap of the material and n is an index which can have values 1/2, 3/2, 2 (or) 3 depending on the nature of the electron transition.

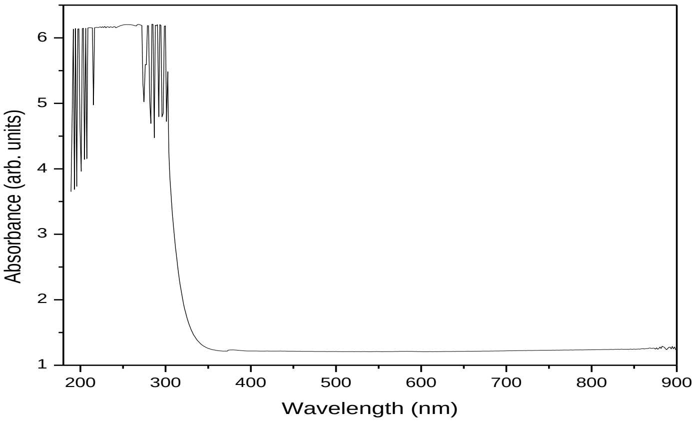

Fig.4. UV-Vis-Absorption spectrum of TULH crystal

A plot of variation of $(\alpha h\upsilon)^2$ versus hυ is shown in Fig.5 . E_g can be calculated by extrapolating the linear part [22]. The energy gap is of direct type and band gap energy is found to be 3.9eV. The grown crystal is very useful for analyzing the induced polarization due to a wide band gap.

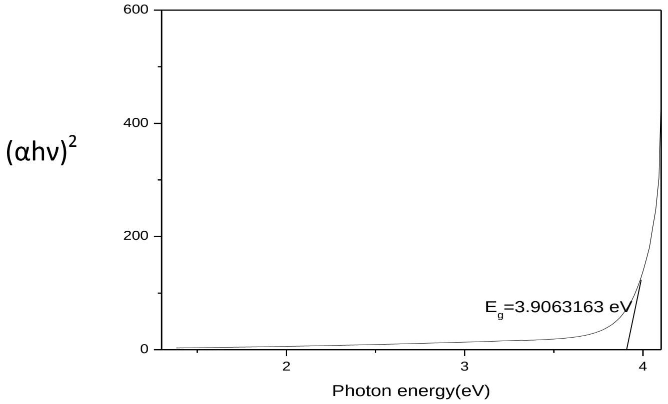

Fig.5 Tauc's plot of TULH crystal

4.5. NLO property

Kurtz SHG test [23] was performed to find the Nonlinear Optical Property (NLO) of TULH crystal. As grown TULH crystals were grounded into microcrystalline size and the powder was tightly packed between two glass slides. It was then introduced to the light path. The conversion efficiency of TULH crystal was compared with Microcrystalline KDP. The second harmonic signal generated by the crystal was confirmed from the emission of green radiation and it was found to be 4.1 times of KDP. SHG efficiency of TULH crystal was compared with SHG efficiency of Pure L-Histidine crystals [24]. It was found that TULH crystals had high SHG efficiency as compared with Pure L-Histidine crystals.

4.6. Thermal analysis

Thermal analysis provides information about the thermal stability of the as grown crystals. This is very important point when viewed in the perspective of fabrication techniques. TG, DTA plots of TULH crystals are shown in Fig.6. TG curve shows a weight loss starting at about 80℃. The weight loss in this state is 3.32%. It is followed by two more stages of weight loss between 100℃ and 280℃. This is due to the loss of (-CS-NH) unit of Thiourea [25]. A major weight loss is present in the range 280 to 380℃. The weight loss in this stage corresponds to 20.82%. There is a gradual increase in weight loss if the temperature is increased beyond 380℃. The total weight loss is about 39.69% and shows that the stability of the crystal is about 80℃.

DTA curve shows sharp peak around 84.67℃ which is due to water of crystallization [26]. It is followed by two more peaks at 119.94℃ and 204.93℃ which are due to volatization of the compound. The title compound loses its texture at around 80℃ due to the presence of water molecules. It is closely matching with TGA trace.

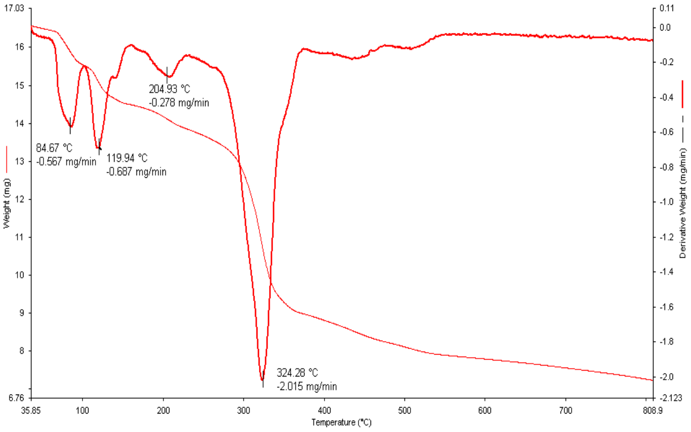

Fig.6. TG-DTA traces of TULH crystal

4.7. Micro Hardness Measurement

It is used to find the resistance of the material against plastic deformation. Vicker's micro hardness study for TULH crystal is performed on polished smooth surface of the crystal with different loads like 25g, 50g, 100g, and 200g. The maximum load is restricted to 200g as micro cracks were developed at higher loads. Fig.7 shows the variation of Vicker's hardness number against applied load. The plot indicates that the hardness number of the crystal increases with increase in load and it is in agreement with Reverse Indentation Size Effect (RISE) [27-30].

The relation between load (P) and diagonal length of indentation (d) is given by Mayer's law [31] which is given below

$$P = a\, d^{n} \ldots(ii)$$

Where 'a' and 'n' are constant for a particular material. Fig.8 shows the variation of log P with log d. Slope of the straight line can be obtained and it is known as Mayer's index number (or) work hardening coefficient (n). The value of "n" for a TULH crystal is 3.12684 as shown in the graph. According to Onitsch, if n > 1.6 then those materials are soft materials [32]. Hence, it is concluded that TULH crystal is a soft material.

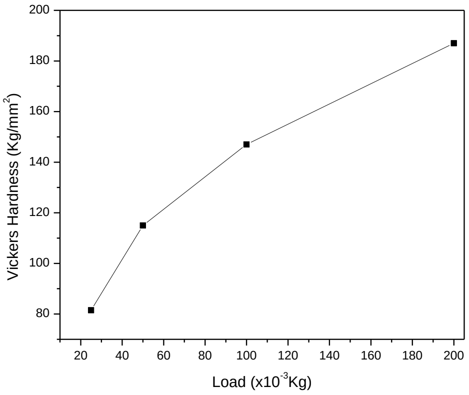

Fig.7 Variation of H_v with P of TULH crystal

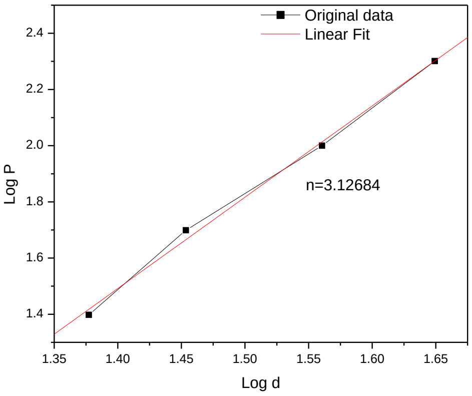

Fig.8 Plot of log P vs. Log d of TULH crystal

4.8. Photoconductivity studies

Initially the sample is covered with black paper to avoid external light radiation and the dark current (I_d) was measured for different applied field. The sample is then exposed to 100W halogen lamp containing Iodine vapour and Tungston filament. The corresponding photocurrent (I_p) is measured for same values of applied field. The field dependent photo conductivity of TULH crystal is shown in Fig.9. Dark current of TULH crystal is found to be less than that of Photo current and shows positive photo conductivity. This may be due to large number of mobile charge carriers generated by absorption of photons [33].

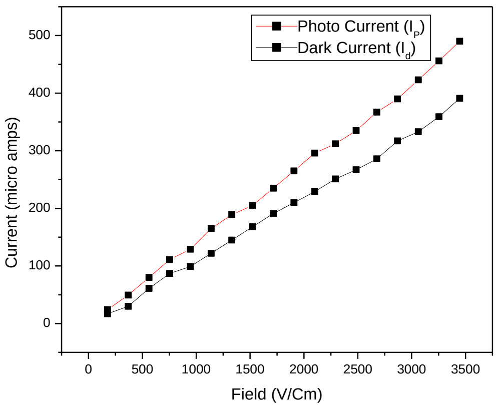

Fig.9 Variation of Dark and Photo current with applied field of TULH crystal

V. CONCLUSIONS AND FUTURE WORK

A Non Linear Optical single crystal, TULH (dimension34x5x8 mm^3) was successfully grown by slow evaporation method. Single crystal XRD method reveals the crystalline nature of the as grown crystal and the structure is observed to be orthorhombic. FTIR analysis confirms the presence of various functional groups in the crystal. Optical transparency of the crystal is analyzed from UV-Vis-NIR spectrum. It is observed that the absorbance is less than 1.5 units in the region 350-1100nm. Optical band gap energy of the crystal is found to be 3.9eV. NLO property is confirmed by Kurtz powder SHG test. The NLO efficiency is 4.1 times of KDP. TG/DTA confirms that the crystal is stable up to 80°C and indicates its thermal stability and suitability in the field of laser application. Micro hardness test shows the soft nature of the crystal and its Mayer index number is 3.1268. Positive photo conducting nature of the crystal is found using Photoconductivity studies. Thus Preliminary studies suggest TULH crystal is a Non Linear Optical crystal and it can be used for Photonics device fabrication.

Further studies on structural analysis, Photo Luminescence analysis, DC conductivity and dielectric measurements can lead to some concrete conclusion regarding the use of this crystal in NLO devices.

REFERENCES

[1] A.S. Gill and S. Kalainathan, Journal of Physics and Chemistry of Solids, 72(2011) 1002-1007.
[2] V.G. Dmitriev, G.G. Gurzadyan, D.N.Nikogosyan, Hand book of Nonlinear Optical Crystals, 2nd ed., Springer, New York, 1997.
[3] J.J. Madden, E.L.Cgandy, N.C. Seeman, Acta Crystallogr.B 28(1972)2377.
[4] H.O. Marcy, M.J. Rusker, L.F. Warren, P.H. Cunningham, C.A. Thomas, L.A. Deloach, S.P. Velsko, C.A.Ebbers, J.H. Liao, M.G. Kanatzidis, Opt. Letters, 20(1995) 252-254.
[5] V. Kannan, R. Bairava Ganesh, and P. Ramasamy, Crrystal growth and design 6(8)(2006) 1876-1880.
[6] Subramanian Natarajan, Kalimuthu Moovendran, Journal of Amino Acids, 2012, Article id 463183, doi:10.1155/2012/463183.
[7] Pandurangan Anandan, Ramasamy Jayavel, Journal of crystal growth, 322(2011) 69-73.
[8] Ram Kripal, Sangita Pandy, Journal of physics and chemistry of solids, 72 (2011) 67-72.
[9] G.P.De Sousa, P.T.C, Freire, J.A. Lima Jr., J. Mendes Filho, F.E.A. Melo, Vibrational Spectroscopy, 57(2011)102-107.
[10] C. Alosious Gonsago, Helen Merina Albert, J. Karthikeyan, P. Sagayaraj, A. Joseph Arul Pragasam, Materials Research Bulletin, 47(2012) 1648-1652.
[11] R.M. Silverstein, F.X. Webster, Spectroscopic Identification of organic compounds, 6th Edition, Wiley, Inc., New York, 1998.
[12] J. Madhavan.S, Aruna, K.Prabha, J.Packium Julius Ginson, P.Joseph, S.Selvakumar, P. Sagayaraj, Journal of crystal growh 293(2006) 409-414.
[13] B. Dhanalakshmi, S. Ponnusamy, C. Muthamizhchelvan, Journal of Crystal growth, 313(2010)30-36.
[14] N.P. Rajesh, V. Kannan, M. Ashok, K. Sivaji, P.Santhana Raghavan, P. Ramasamy, Journal of Crystal Growth, 262 (2004) 561-566.
[15] G.H. Sun, X.T. Sun, Z.H. Sun, X.Q. Wang, X.J. Liu, G.H. Zhang, D. Xu, Journal of crystal growth 311(2009) 3904-3910.
[16] K. Nakamoto. In: IR spectra of inorganic and coordination compounds II EDn., Wiley & Sons, NY, 1978.
[17] M. Oussaid, M. Kemiche, P. Becker, C.C. Nedelec, O. Watanabe, Phys. Status solidi(b) 1(96)(1999)487.
[18] J.P. Yurkanis Bruice, Organic chemistry III edn. Parson Edision Asia, 2002.
[19] S.K. Kurtz, T.T. Perry, J. Appl. Phy. 39(1968)3798.
[20] M. Senthil Pandian, P. Ramasamy, Journal of crystal grown, 312(2010) 413-419.
[21] N. Vijayan, G. Bhagavannarayana, K. Nagaraj, V. Upadhyaya, Mater. Chem. Phys, 115(2009)656.
[22] J. Tauc(1974) Amorphous and liquid semiconductors, Plenum press, New York.
[23] C.A. Kumar, D. Kaur and R. Chandra, Opt. mater, 29, 995-998(2007)
[24] C. Alosious Gonsago, Helen Merina Albert, R. Umamaheswari and A. Joseph Arul Pragasam, Indian Journal of Science and Technology, 5(2012)2369-2373.
[25] R. Umamaheswari, S. Nirmala, P. Sagayaraj, A. Joseph Arul Pragasam, J Therm Anal Calorim, 110 (2012)891–895.
[26] C. Alosious Gonsago, S. Pandi, Helen Merina Albert and A. Joseph Arul Pragasam, International Journal of Applied Physics and Mathematics, 2(2012) 54-57.
[27] B. Venkatesan, N. Kanniah, P. Ramaswamy, Journal of Materrial Science Letters 5 (1986) 987.
[28] K.Sangwal, Mater. Chem. Phys. 63(2000)145.

[29] B.W, Mott, Microindentation Hardness Testing, Butterworths, London, 1956.
[30] D.Tabor, The Hardness of materials, Oxford University Press, pxford, 1951.
[31] E. Mayer, Z. Phys. 9(1908)66.
[32] E.M. Onitsch, Mikroskopie, 95(1950)12.
[33] V.N. Joshi, Photoconductivity, Marcel Dekkar, New York, 1990.

AUTHORS

S. Nalini Jayanthi received her B.Sc., Degree in Physics(2000), M.Sc., Degree in Physics(2002), M.Phil., Degree in Physics(2003) from Bharathidasan University and Ph.D., Degree at Pachaiyappas College, Chennai-25 (Affiliated to Madras University). She is currently working as Assistant Professor in Anand Institute of Higher Technology, Chennai-603 103. She has published more than 6 research papers in various National and International Conferences. Her research interest includes Ultrasonics and Spectroscopy.

A. R. Prabhakaran received his M.Sc., Degree in Physics (1984) from Madras University, M.Phil., in Physics(1989) from Anna University and Ph.D., from (1991) from Pondicherry University. Now he is working as an Associate Professor in Physics at Pachaiyappas college. He has 21 years of teaching experience. He published more than 15 papers in National and International Journals.

D. Subashini received her B.Sc., Degree In Physics, M.Sc., Degree in Physics and M.Phil. Degree in Physics from Madras University. She is currently working as Assistant Professor in Dr. Ambedkar Govt. Arts College, Chennai-39. She has published more than 6 research papers in the National and International Conferences.

K. Thamizharasan received his Ph.D., degree from Madras University(2000). He has 30 years of teaching experience. Now, he is working as Associate professor and Head of Physics department in Sir Theagaraya College, Chennai-21. He published more than 20 papers in Nation/International conferences. He published nearly 25 papers in international Journals. He guided nearly 15 M. Phil., students and guiding 5 Ph.D., scholars. His area of Interest is Crystal growth.