CRYSTAL GROWTH AND STUDIES OF CRYSTALS OF UNDOPED AND IODIC ACID DOPED L-ASPARAGINE L-TARTARIC ACID

K.Jeyapappa[1], C.Krishnan[2], P.Selvarajan[3]
[1]Research Scholar, Reg.No. 10117, Department of Physics and Research Centre, S.T.Hindu College, Nagercoil-620003, Tamilnadu, India.
(Affiliated to Manonmaniam Sundaranar University, Abishekapatti-627012, Tirunelveli, Tamilnadu, India)
[2]HOD and Associate Professor of Physics, Arignar Anna College, Aralvoymozhi-629 301, Tamilnadu, India.
[3]Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628216, Tamilnadu, India.

Abstract **-** Salts of undoped and iodic acid doped L-asparagine L-tartaric acid were synthesized and single crystals were grown by solution method with slow evaporation technique. The grown crystals are observed to be stable, transparent and colourless. By XRD method, it is found that the crystal structure of the samples is found. The relative SHG efficiency of the sample was found by powder Kurtz-Perry technique. Mechanical parameters like hardness, work hardening coefficient, resistance pressure and corrected hardness of the samples were estimated. FTIR spectral studies were carried out to find the functional groups and EDAX studies were performed to identify the elements in samples. LDT values of the grown undoped and iodic acid doped LALTA crystals have been evaluated.

Index terms- **Single crystals; solution growth; doping; amino acid crystal; Spectroscopy; NLO; SHG; LDT; microhardness; XRD;EDAX**

I. INTRODUCTION

Nonlinear Optical (NLO) materials have attracted the attention in recent years owing to their potential applications in various photonic and optical technologies. Also they have a great impact on information technology and industrial applications. There are mainly three types of NLO materials viz., organic, inorganic and semiorganic NLO materials [1, 2]. The amino acid based NLO materials belong to organic and seminorganic NLO materials. An amino acid like L-asparagine has the proton donor carboxylic acid (COOH) group and the proton acceptor amine (NH_2) group. Asparagine is one of the 20 most common natural amino acids on earth. It has carboxamide as the side chain's functional group. It is a non-essential amino acid which means that it can be synthesized from central metabole pathway intermediates in humans and is not required in the diet. The precursor to asparagine is oxaloacetate. It is converted to aspartate using a transaminase enzyme. The enzyme transfers the amino group from glutamate to oxaloacetate producing alpha-ketoglutrate and aspartate. The enzyme asparagine synthetase produces asparagine, glutamate and pyrophospate from aspartate, glutmine [3,4]. Electron paramagnetic resonance (EPR) and optical absorption studies of VO^{2+} ions in LAM have been conducted at room temperature [5]. L-asparagine is having a tendency to form many stable organic and semiorganic compounds and their crystal structures have been solved [6-8]. Studies on various properties of L-asparagine with L-tartaric acid was reported [9]. The growth and characterization of the single crystals of the NLO material, viz., L-asparaginium picrate were reported by Srinivasan *et al.*[10]. In this work, the iodic acid was used as the dopant into L-asparagine L-tartric acid (LALTA) to modify the various properties of the host material. Iodic acid and lithium iodate crystals were discovered and efforts have been devoted to the explorations for new metal iodates with enhanced SHG performance and higher thermal stability [11,12]. The aim of the paper is to study various properties of undoped and iodic acid doped LALTA crystals and to report the results herein.

II.SYNTHESIS AND GROWTH CRYSTALS

Analar Reagent (AR) grade of L-asparagine and L-tartaric acid in the molar ratio of 1:1 were used for synthesis the salt of L-asparagine L-tartaric acid (LALTA).The calculated amounts of L-asparagine and L-tartaric acid were dissolved in double distilled water and stirred well using a magnetic stirrer for about 3 hours. The solution was heated until the synthesized salt of LALTA was obtained. To obtain iodic acid doped LALTA salt, 1 mole% of iodic acid was added to the aqueous solution of LALTA. Then, solution was stirred well and it was heated at 50 ^{o}C to obtain the salt of iodic acid doped LALTA. The

synthesized salts of undoped and iodic acid doped LALTA were re-crystallized twice to improve the purity of the samples. The single crystals of the samples were grown solution method with slow evaporation technique at room temperature. The aqueous saturated solutions of the synthesized salts were prepared separately and the solutions were constantly stirred for about 2 hours using a magnetic stirrer and were filtered using high quality Whatmann filter papers. Then the filtered solutions were taken in growth vessels covered with porous papers and these growth vessels were kept in a dust-free atmosphere. The single crystals were harvested after a period of about 35 days and the harvested crystals are shown in the **Fig.1.** There is a change of morphology of is noticed when LALTA crystals are doped with iodic acid. It seems that the transparency for iodic acid doped LALTA crystal is less than that of undoped LALTA crystal.

Fig.1. Harvested crystals of (a) undoped and (b) iodic acid doped LTLTA

III. RESULTS AND DISCUSSION

3.1 Lattice parameters and crystal structure

The lattice constants and crystal structure of the grown crystals were found by single crystal X-ray diffraction studies. The instrument used to carry out single crystal XRD studies was a single X-ray diffractometer Bruker-Nonius MACH3/CAD4) with MoK_{α} radiation (λ=0.71073 Å). The obtained lattice constants for both undoped and iodic acid doped LALTA crystals are given in the table 1. It is noticed that the lattice parameters of both the samples are slightly altered and this is due to incorporation of iodic acid in the host LALTA crystal. The crystal structure of both the samples is monoclinic and the space group of the samples is $P2_1$. This space group is a non-centrosymmetric space group and these undoped and iodic acid doped samples can emit SHG radiation and hence they are second harmonic generators. The crystallographic data obtained in this work are observed to be in good agreement with the data reported in connection with undoped LALTA crystal [13].

Table 1. Lattice parameters and crystal structure for undoped and iodic acid doped LALTA crystals

Sample	Unit cell parameters	Volume (Å)^3	Crystal structure
Undoped L-asparagine L-tartaric acid (LALTA) crystal	a = 5.092(2) Å b = 9.676(4) Å c = 11.841(2) Å α = 90°, β= 95.54(3)° γ=90°	580.67(5)	Monoclinic
Iodic acid doped LALTA crystal	a = 5.089(7) Å b = 9.668(4) Å c = 11.853(2) Å α = 90°, β= 96.02(5)° γ=90°	579.96(3)	Monoclinic

3.2 Identification of functional groups

The functional groups of crystalline samples could be identified by FTIR method and this method is an advanced infrared spectroscopic method with high resolution and accuracy. The FTIR spectrum of iodic acid doped LALTA crystal was recorded using an FTIR spectrometer in the wave number range 400-4000 cm^{-1} with KBr pellet technique and it is shown in the **Fig. 2**. The strong and broad band at 3323 cm−1 in the IR spectrum can be attributed to the O–H stretching vibration and NH_3^+ stretching vibration. The peak at 1729 cm^{-1} in the spectrum is corresponding to C=O stretching. The peak at 1414 cm^{-1} is associated with COO^- stretching. The complete FTIR spectral assignments for the spectrum are provided in the table 2. The assignments are given in accordance with the data reported in the literature [9].

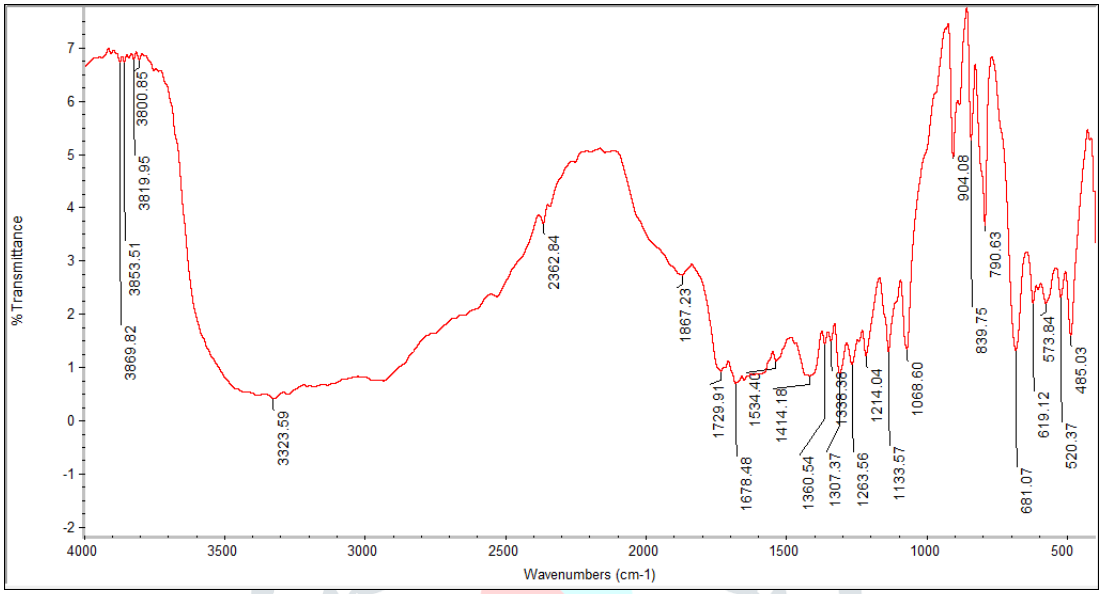

Fig.2. FTIR spectrum of iodic acid doped LALTA crystal

Table 2. FTIR assignments for iodic acid doped LALTA crystal

Bands/Peaks (cm^{-1})	FTIR assignments
3323	OH and NH_3^+ stretching
2362	CH_2 stretching
1867	CH stretching
1729	C=O stretching
1678	NH_3^+ assym. bending
1534	NH_3^+ sym. bending
1414	COO^- stretching
1307	CH_2 twisting
1263	C-C stretching
1214	CH_2 twisting
1133	CH_2 wagging
1068	C-C stretching
904	C-C stretching
839	C-N stretching
790	C-C stretching
681	COO^- scissoring
619	COO^- wagging
573	COO^- twisting
520	OH deformation
485	NH_3^+ torsion

3.3 EDAX spectrum

EDAX or EDS spectroscopy is used to find the elements present in a sample. In this method, electrons are used for the excitation process. When the sample is bombarded by the Scanning Electron Microscope's (SEM) electron beam, electrons are ejected from the atoms comprising the sample's surface. The resulting electron vacancies are filled by electrons from a higher state and an X-ray is emitted to balance the energy difference between the two electrons states. The spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sample. The recorded EDAX spectrum of iodic acid doped LALTA crystal is shown in the **Fig. 3.** The spectrum indicates that the elements such as C, N, I, O are in the doped sample. Since atomic mass of hydrogen is very low, hydrogen in iodic acid doped L-asparagine L-tartaric acid cannot be identified by EDAX analysis.

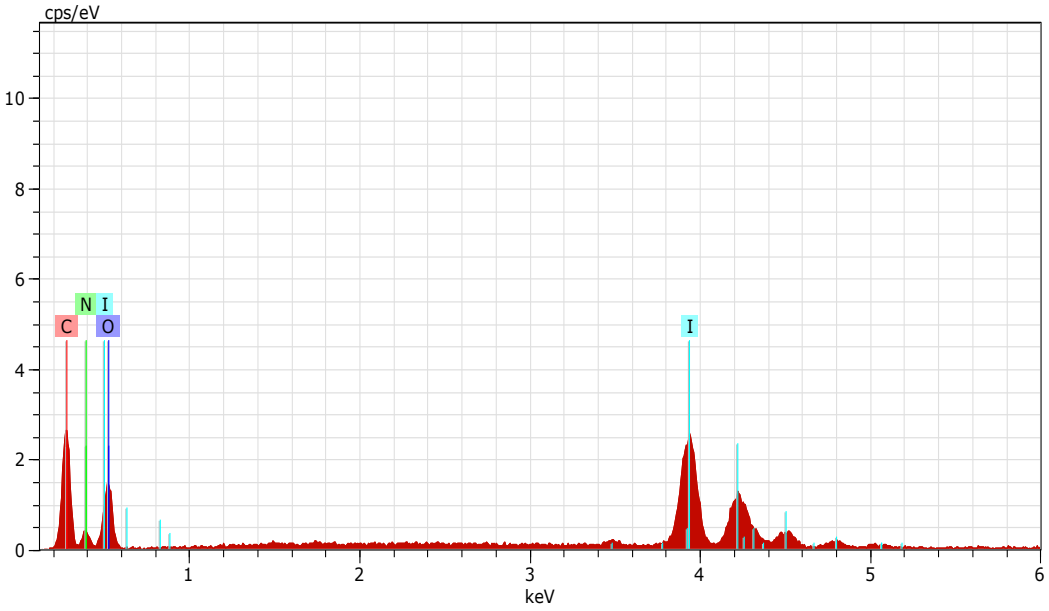

Fig.3. EDAX spectrum of iodic acid doped LALTA crystal

3.4 SHG analysis

Second harmonic generation (SHG) is a second order NLO process which can be seen from a non-centrosymmetric (NCS) crystal like L-asparagine L-tartaric acid (LALTA) crystal. When high intense laser light from Nd:YAG laser falls on the NCS crystal, green laser is emitted and frequency is doubled here. The emitted green laser is visible laser light and it can be used in the field like fibre optics and optical computing. The SHG generation from the undoped and iodic acid doped LALTA crystals has been checked by Kurtz-Perry technique [14] using a pulsed Nd:YAG laser (Model: YG501C, λ=1064 nm) and pulse width of 10 ns and repetition rate of 10 Hz were used. The second harmonic generation signal of 8.64 mJ/pulse was observed for iodic acid doped LALTA crystal for an input energy of 0.70 J/pulse and SHG signal of 7.57 mJ/pulse was noticed for undoped LALTA crystal. But the standard KDP sample gave an SHG signal of 8.91 mJ/pulse for the same input energy. Hence, relative SHG efficiency of iodic acid doped LALTA crystal is 0.97 times that of the referenc KDP sample and the SHG efficiency of unodoped LALTA crystal is 0.85 times that of KDP. All the data in connection with SHG studies of the samples are given in the table 3. Since the SHG efficiency of iodic acid doped LALTA sample is more than that of undoped LALTA crystal, iodic acid doped LALTA crystal is the better sample for NLO applications.

Table 3: Data of SHG experiment for undoped and iodic acid doped LALTA crystalline samples

S. No.	Sample name	Output Energy (milli joule/pulse)	Input Energy (joule/pulse)	Relative SHG efficiency
1	Undoped LALTA crystal	7.57	0.70	0.85
2	Iodic acid doped LALTA crystal	8.64	0.70	0.97

3.5 Mechanical characterization

(i) Hardness analysis

The hardness, yield strength, stiffness constant etc are the important mechanical parameters of crystalline samples. The hardness is defined as the resistance offered to plastic deformation and there are several contributions to the resistance offered to dislocation motion and they can be classified into two types: (i) the resistance which depends on structure insensitive physical parameters of the crystal; and (ii) a disorder parameter which depends on the concentration o the imperfections. The extent to which a material deforms plastically under an applied stress depends on the strength of intermolecular forces. The permanent deformation can be achieved by indentation, bending, scratching or cutting. The indentation hardness which relates to the various forms of the indenter is the ratio of the applied load to the surface area of indentation. The hardness of a material normally varies with applied load. Static indentation hardness tests such as Brinell, Rockwell, Vickers and Knoop are the frequently used methods for determining hardness. The basic concept utilized in all of these tests is that a set force is applied to an indenter in order to determine the resistance of the material to penetration. The hardness tests are often classified into two ways: either by the extent of the test force applied or the measurement method used. The macrohardness refers to a test where a load of more than 1 kg is applied but the microhardness refers to a test where a load of less than 1 kg is applied to the sample. The Vickers microhardness method is an important method and it is used here. The Vickers hardness can be calculated using the relation $H_v = 1.8544\ P/d^2$ where P is the applied load in kg and d is the average diagonal indentation length. Vickers microhardness indentations were carried out on the polished faces of the grown crystals room temperature with the load ranging from 25 g to 100 g using Vickers Leitz pyramidal hardness tester fitted with a diamond pyramidal indenter. Three trials were made for each indentation and average value was taken for each load. Time of indentation was kept as 10 seconds for all the trials. The obtained values of microhardness at different applied loads are put in the form of plots as shown in the **Fig.4**. The results show that the hardness increases with increase of the applied load for both the samples. The increasing trend of the plots is due to reverse indentation size effect. The hardness increases when LALTA is doped with iodic acid and this is due to increase of bond strength due to doping.

The values of work hardening coefficient of the samples were estimated by using Meyer's law and it is given by $P = a\ d^n$ where P is the load, n is the work hardening coefficient, a is a constant and d is the average indentation length. If logarithm is taken on both sides of Meyer's law, an equation of straight line is obtained and using this straight line equation, plots of log P versus log d are drawn (**Figs. 5 and 6**). The values of slope obtained from the plots are 3.0531 and 2.8356 respectively for undoped and iodic acid doped LALTA crystals.

(ii) Hays-Kendall's analysis

Since the variation of hardness with load (Fig.4) indicates that the plots are nonlinear, Hays-Kendall's approach [15] can be followed to evaluate the corrected hardness and the minimum load to initiate the plastic deformation. Hays-Kendall's relation is $P = W + Ad^2$ where P is the applied load, d is the average diagonal indentation length, W is the minimum load to initiate plastic deformation or resistance pressure, A is the load-independent constant. Using this relation, the values of W and A are evaluated. The plots of P versus d^2 are drawn and they are presented in the **Figs.7 and 8**. The obtained values of W are -31.6060 g and -24.7992 g respectively for undoped and iodic acid doped LALTA crystals. Since these values of resistance pressure are negative, both the samples show the behavior of reverse indentation size effect. The corrected size independent hardness (H_o) is determined using the relation $H_o = 1.8544 * A$. The calculated values of H_o for undoped and iodic acid doped LALTA crystals are 0.1158 g/μm^2 and 0.1217 g/μm^2 respectively.

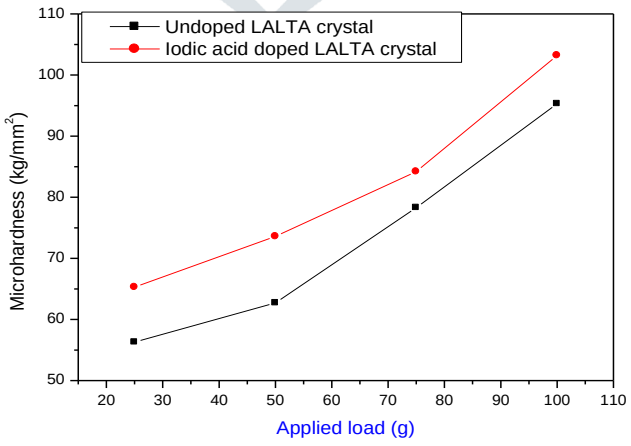

Fig.4. Plots of microhardness versus load for undoped and iodic acid doped LALTA crystal

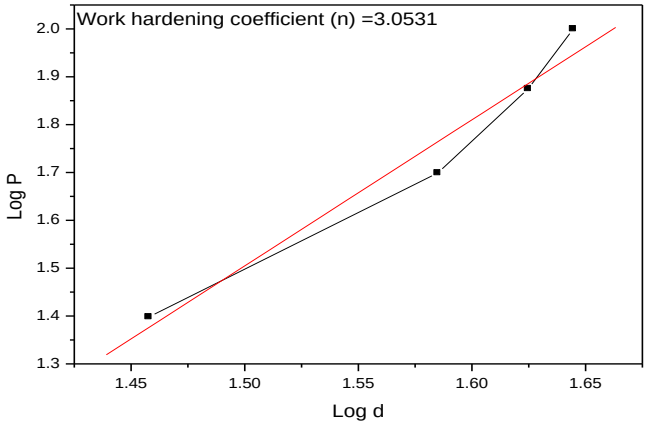

Fig.5. Plot of log P versus log d for undoped LALTA crystal

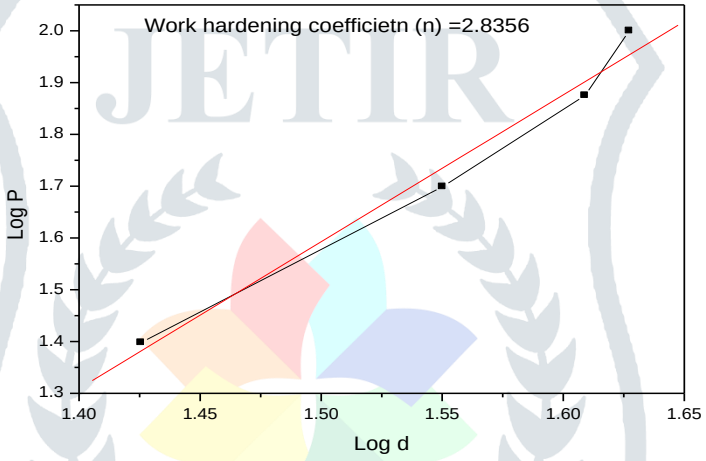

Fig.6. Plot of log P versus log d for iodic acid doped LALTA crystal

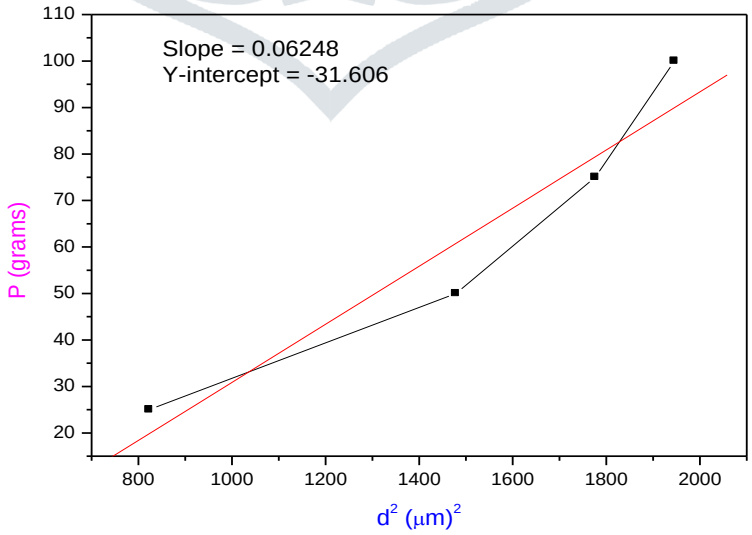

Fig.7. Plot of P versus d^2 for undoped LALTA crystal

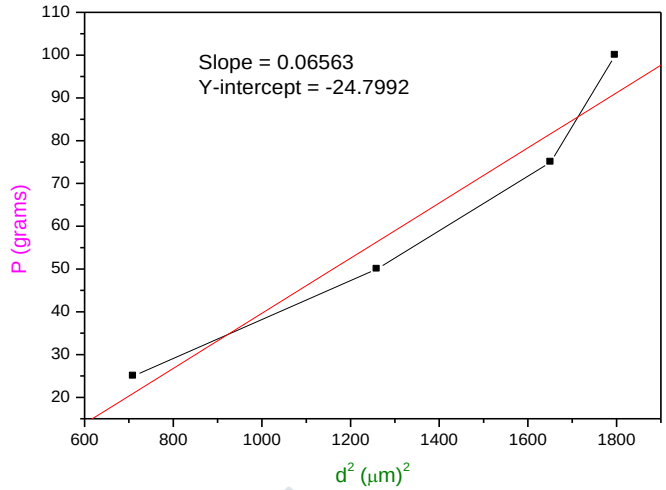

Fig.8. Plot of P versus d^2 for iodic acid doped LALTA crystal

3.6 Laser damage threshold (LDT) study

Laser damage threshold (LDT) is defined as the minimum value with which a material can withstand the laser intensity and it is a laser tolerance parameter for the device application. LDT value of grown crystal was measured using the Q-switched Nd-YAG laser and duration of the pulse is 10 ns. The laser beam is made to pass through the sample and the spot on the sample where the damage is affected. If damage is occurred, there is a sharp reduction in the intensity of the transmitted laser beam. The LDT value was calculated using the relation $P = E/\pi\tau r^2$ where E is the energy in mJ, τ is the pulse width in ns and r is radius of the spot in mm. The calculated values of LDT for undoped and iodic acid doped LALTA crystals are 0.621 GW/cm^2 and 0.748 GW/cm^2 respectively.

IV.CONCLUSIONS

The crystals of this work have been grown by solution method and the morphology and transparency of iodic acid doped LALTA crystal are different when it is compared with undoped LALTA crystal. Both the crystals are found to be crystallizing in monoclinic structure. The elements like C,N,O, I are identified in the iodic acid doped LALTA crystal. The relative SHG efficiency of the undoped and iodic acid doped LALTA crystals are 0.85 and 0.97 respectively times that of KDP. Vickers microhardness and other relevant mechanical parameters were calculated in order to understand the mechanical strength of the grown crystals. The molecular groups of the samples have been identified by FTIR spectroscopy. LDT values are found to be 0.621 GW/cm^2 and 0.748 GW/cm^2 respectively for undoped and iodic acid doped LALTA crystals.

ACKNOWLEDGEMENT

The authors like to acknowledge the research supports obtained from STIC, Cochin University, Crescent Engineering College, Chennai, St.Joseph's College, Trichy, VIT, Vellore to carry out this work.

REFERENCES

[1].D.S. Chemla and J. Zyss, Nonlinear optical properties of organic molecules and crystals, Vol. 1-2, Academic Press, Orlanto (1987).
[2]Sweta Moitra, Tanusree Kar, Optical Materials 30 (2007) 508.
[3]K. Syed Suresh Babu, M. Anbuchezhiyan, M. Gulam Mohamed,P. A. Abdullah Mahaboob and R. Mohan, Arch.Physics Research, 4 (2013)31.
[4]Grace Sahaya Sheba, P. Omegala Priyakumari, M. Gunasekaran Int.J. Chemical, Nuclear, Metallurgical and Materials Eng. 8 (2014)99.
[5]R.Kripal, Mishra, SK Gupta, M Arora, Spectrochim Acta A,71(2009) 1969.
[6]K. Anitha, S. Athimoolam, R.K. Rajaram, Acta Crystallogr. E 61 (2005)1463.
[7]N.M. Slimane, A. Cherouana, L. Bendjeddou, S. Dahaoui, C. Lecomte, Acta Crystallogr. E 65 (2009)2180.
[8]S. Natarajan, V. Hema, J.K. Sundar, J. Suresh, P.L.N. Lakshman, Acta Crystallogr. E 66 (2010) 2239.

[9]K. Moovendaran, Bikshandarkoil R. Srinivasan, J. Kalyana Sundar, S.A. Martin Britto Dhas, S. Natarajan, Spectrochim. Acta B 92 (2012) 388.
[10]P.Srinivasan, T.Kanagasekaran, R. Gopalakrishnan, G. Bhagavannarayana, P. Ramasamy, Cry. Growth Des. 6 (2006) 1663.
[11] D.W. Lee, S.B. Kim, K.M. Ok, Dalton Trans. 41 (2012) 8348.
[12] B. Bentria, D. Benbertal, M. Bagieu-Beucher, A. Mosset, J. Zaccaro, Solid State Sci. 5 (2003) 359.
[13] Mohd Shkir, Haider Abbas, Spectrochimica Acta Part A 118 (2014) 172–176.
[14]S.K. Kurtz, T.T. Perry, J. Appl. Phys. 39 (1968) 3798–3813.
[15]C. Hays, E.G. Kendall, Metallography 6 (1973) 275–282.