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GROWTH AND CHARACTERIZATION OF PURE AND DOPING ADIPIC ACID CALCIUM NITRATE: SEMI ORGANIC NON LINEAR OPTICAL CRYSTALS

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ABSTRACT

New nonlinear optical crystals of Adipic acid doped Calcium Nitrate (AACN) was grown by slow evaporation solution growth technique. The UV-Vis-NIR spectrum of AACN showed a very good transparency in the visible region of 300nm to 1100nm. Fluorescence studies exhibited the spectral distribution of the emitted light from AACN crystal. The Peaks obtained in the PXRD gives the crystalline structure of AACN. The presence of various functional groups and purity of the grown crystals were confirmed by FT-IR and FT-Raman. The existence of nonlinear optical (NLO) property of AACN was confirmed by second harmonic generation test using Nd:YAG laser of fundamental wavelength of 1064 nm.

Keywords: Adipic acids Calcium nitrate, crystal growth, UV-Vis-NIR spectrum, Fluorescence studies, Powder X-ray diffraction analysis, FT-IR and FT-Raman spectra

INTRODUCTION

Non linear optics plays a major role in optical information, telecommunication, electronic optic switches, photonics etc. NLO acts as a polarizer so that it is made to get the quality control of beam for eye-protection. After the invention of fiber optics, there were limit in carrying information, for example input signal of light wave passing through the fibre optics, the output is set out without any frequency variation. In spite of using these but found the drawbacks in installing wide range on account of high cost and low flexibility. An alternative human search is to adopt diversified NLO materials where light conversion of different wavelengths or frequencies is made to progress. Modern NLOs imperative demand is to impart high-fidelity imaging signals, communication to be established over greater distance as using equipments, remote sensor in monitoring stealing, abduction and material movements by using spectroscopic of surfaces. Hence applicability of NLO in RADAR, Holography, military area particularly laser beam steering and diagnostic traces in medical field is being expected. It is ought to bestow the attention on generating semi organic crystals due to their much flexibility of ions, high non linearity and good transmittance in the visible region **[1]**. The non linear nature of the crystals is examined by laser source. The commercial machines require ultra short pulses of the order of femtosecond which has been fulfilled by femtosecond lasers **[2]**.

In order to manipulate multi disciplinary fields particularly in amplifying, modulating, polarizing and transforming signals, crucial demand is the blossom of NLO materials. Adipic acids has good optical and mechanical properties in most of the challenges in facing electronic telecommunication networks and integrated circuits and agricultural industries **[3]**. Adipic acid based crystals show the excellent nonlinear and electro optical properties and were grown by slow evaporation solution growth method **[4]**. The Re-search for generating newer types of NLO materials essentially satisfies the condition demanded for simple, compactness, adaptability in new trend of technology **[5]** based on its spectrum. In this paper, the effect of Adipic acid doped with Calcium nitrate on the structural, optical, spectral, purity and NLO properties were reported.

EXPERIMENTAL PROCEDURE

Single crystals of Adipic acid Calcium nitrate (AACN) were grown at room temperature by solution growth using slow evaporation method. The solution was

prepared by dissolving Adipic acid and Calcium nitrate in the stoichiometric ratio of 1:1 in deionized water. The solution is blended well with magnetic stirrer to have the homogeneous mixture and filtered, transferred in a glass vessel which has covered with small pin holes made in the tissue paper. Then the solution was allowed to evaporate in a clean place. The following reaction illustrates the compound.

$$(CH_2)_4(COOH)_2 + Ca(NO_3)_2 \rightarrow Ca[(CH_2)_4(COOH)_2]NO_3$$

Optically good quality of the crystals of the title compound was harvested in span of 45 days. The photograph of the AACN crystal is shown in **Figure 1**.

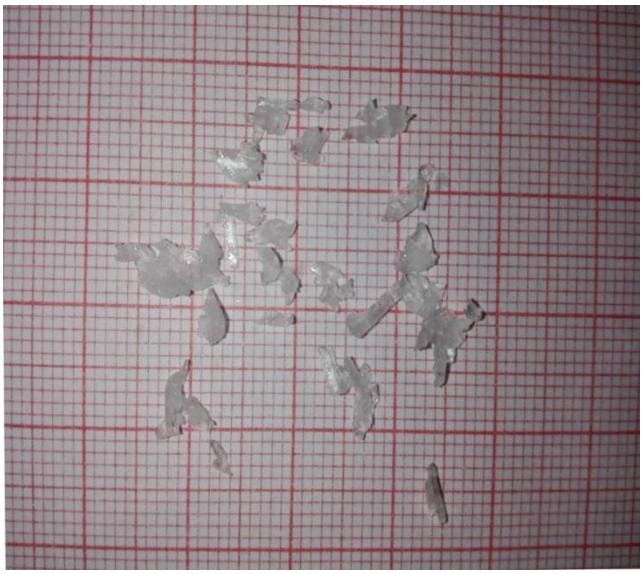

Figure 1: Photograph of Adipic acid with Calcium nitrate Crystals

RESULTS AND DISCUSSION

UV-Vis-NIR Absorption spectral analyses

The absorption spectrum of AACN was recorded using Perkin Elmer lambda 35 spectrophotometer in the wavelength range of 190 nm-1100 nm **[6]**. The absorption spectrum recorded is shown in **Figure 2**. The lower cut off wavelength occurs at 271nm and it is due to $\pi - \pi^*$ transition **[7]**. A little protuberance was recorded around 315 nm. It was due to optical plane transmission window of materials which are dielectric in nature. In the UV-Vis-NIR region the photons interact with materials start the transmitting from the cut off wavelength of 271 nm to 1100 nm **[8]** by this time photons have been absorbed the title material. The optical band gap was measured as 4.58 eV. The large transmission in the entire visible region of optical compound will

enable the production second and third harmonic generation.

UV-Vis-NIR Transmission spectral analysis

The UV transmittance spectrum for AACN crystal is indicated in **Figure 3**. The crystal was observed to be transparent with 99% of transmission.

Fluorescence spectral Analysis

AACN crystal was under investigation of fluorescence analysis by using Perkin Elmer LS 45 spectrofluorometer and the spectrum obtained is shown in **Figure 4**. The spectrum was measured in the range of 240 nm – 800 nm. Emission bands are due to interaction of radiation of compound between metal donor and acceptor **[9]**. A well defined peak of wavelength 455.37 nm represents the blue color along with four lesser peaks of wavelengths 394 nm(UV emission), 491 nm(cyan color emission) and 683 nm (Red color emission) were found. The highest peak refers indirectly the title compound can be used as a blue color light emitting diode lamps and optoelectronic laser device. The band gap is 2.7eV for the sharp peak of wavelength 455.37 nm.

Powder X-Ray Diffraction Analysis

The powder XRD analysis of AACN crystal was done by XPERT/PRO diffractometer with CuKα radiation at a wavelength of 1.5406 nm. The Bragg's diffraction obtained is shown in **Figure 5**. The powdered sample was scanned at the range of 10° to 80° with scan speed of 1°/min for $2\theta^{\circ}$ values from 10.133 to 57.123 are shown in **Figure 6**. **[10-12]**. A well defined sharp peak corresponding to an angle of θ=21.6 represents that the crystal has a good crystalline nature.

FT-IR AND FT -RAMAN Spectral Analysis

FT-IR and FT-Raman spectral analysis probed the information regarding the presence of fusion of amino acids with alkaline group in the grown material. The different vibrating segments obtained for both FT-IR **[13-14]** and FT-Raman were noted and verified with literature available and found to be in good agreement which are tabulated in **Table 1**. The spectral analysis of FT-IR and FT-Raman for AACN have been recorded in the range of 400-4000cm^{-1} using a Perkin Elmer spectrometer and recorded spectrum for FT-IR is evinced in figure-6 and FT-Raman is seen in figure-7. The bands at 2920 in FT-IR cm^{-1} 2936 cm^{-1} in FT-Raman corresponds to C-H stretching and 2755 cm^{-1} and 2428 cm^{-1} in FT-IR spectrum revealed the CH_2 asymmetric stretching **[15]** and C-H stretching. The bands at 1695 cm^{-1} in FT-IR and 1642 cm^{-1} in FT-Raman noticed C=O stretching. The peaks at 1463 cm^{-1} in FT-IR and 1444 cm^{-1}, 1410 cm^{-1} in the FT-Raman were identified by C-H deformation. The peak at 1368 cm^{-1} in FT-IR

specified the NO_3 stretching so that nitrate is confirmed. The peaks at 1279 cm^{-1}, 1193 cm^{-1} obtained only in FT-IR spectrum encountered the C=O stretching and CH_2 bending respectively. CH_2 bending is found to occur at the peaks at 1044 cm^{-1} in FT-IR and 1047 cm^{-1} in FT-Raman. The bands at 927 cm^{-1} in FT-IR and 908 cm^{-1} in FT-Raman confirmed the O-H out of plane bending. C-C stretching **[16-17]** only observed at the lowest wave number 735 cm^{-1} in FT-IR spectrum. C-O bending is found at 689 cm^{-1} in FT-IR and 658 cm^{-1} in FT-Raman spectra. Torsional oscillation of compound molecules noticed at 562 cm^{-1}, 514 cm^{-1} in FT-IR and 566 cm^{-1} in FT-Raman spectra which means vibration takes place between the molecules similar to oscillation of pendulum.

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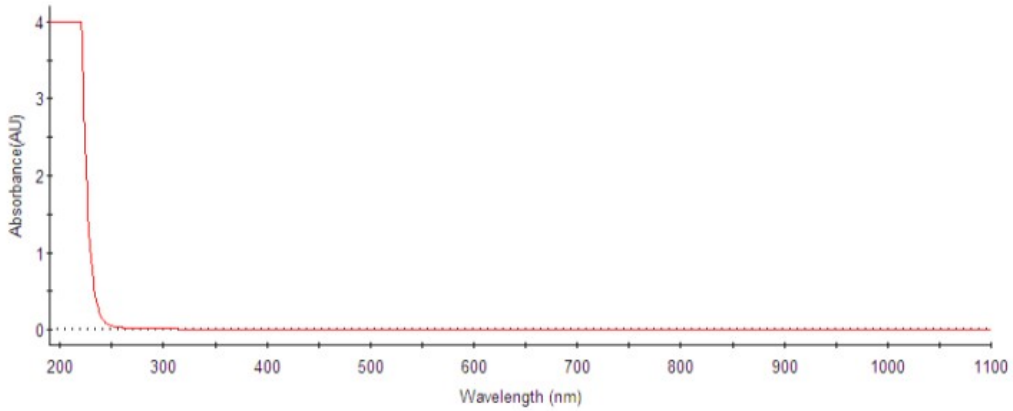

Figure 2: UV-Vis-NIR Absorption spectrum of AACN crystal

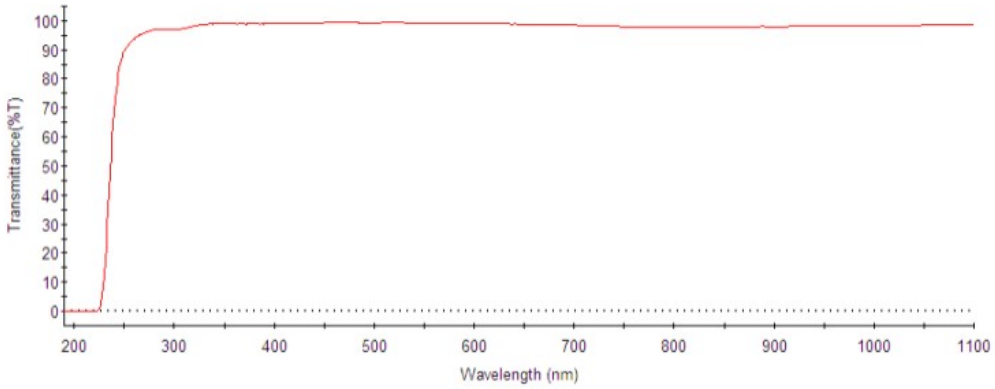

Figure 3: UV-Vis-NIR Transmission spectrum of AACN crystal

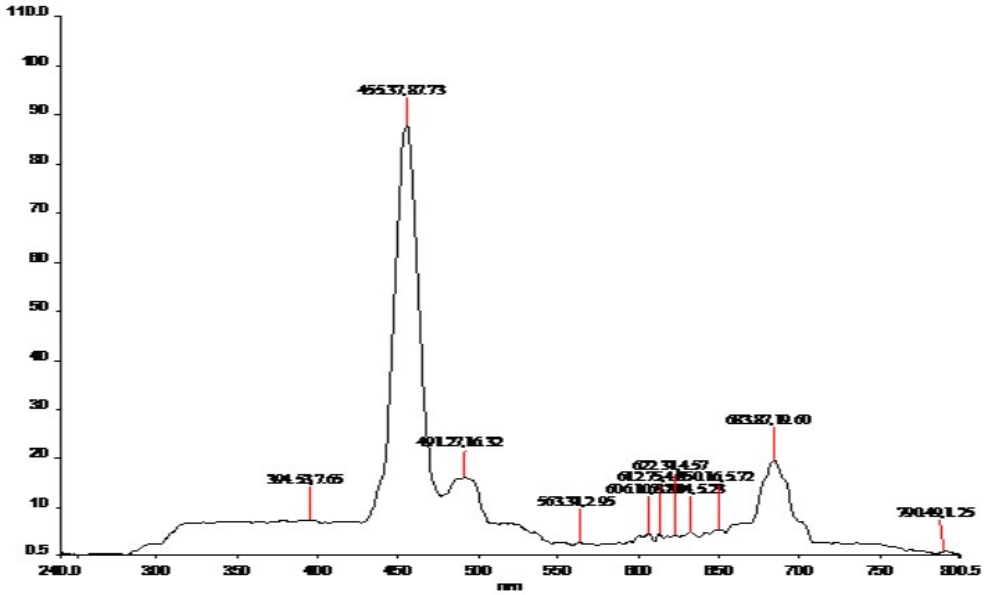

Figure 4: Fluorescence spectral Analysis of AACN crystal

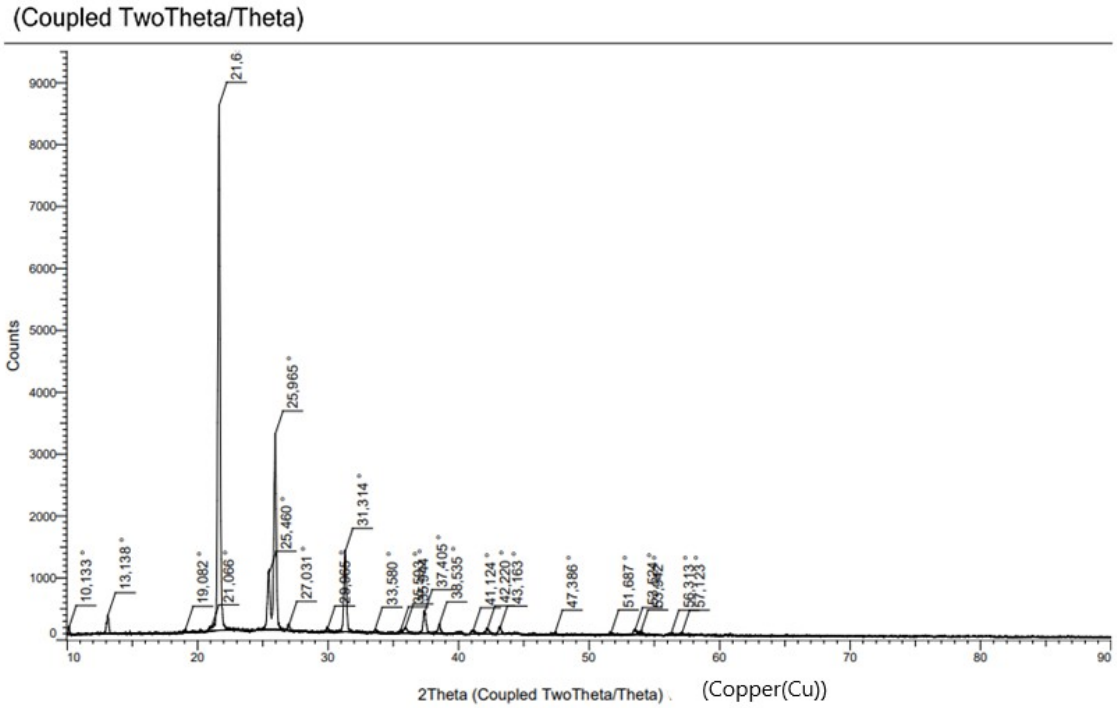

Figure 5: PXRD spectrum of AACN crystal

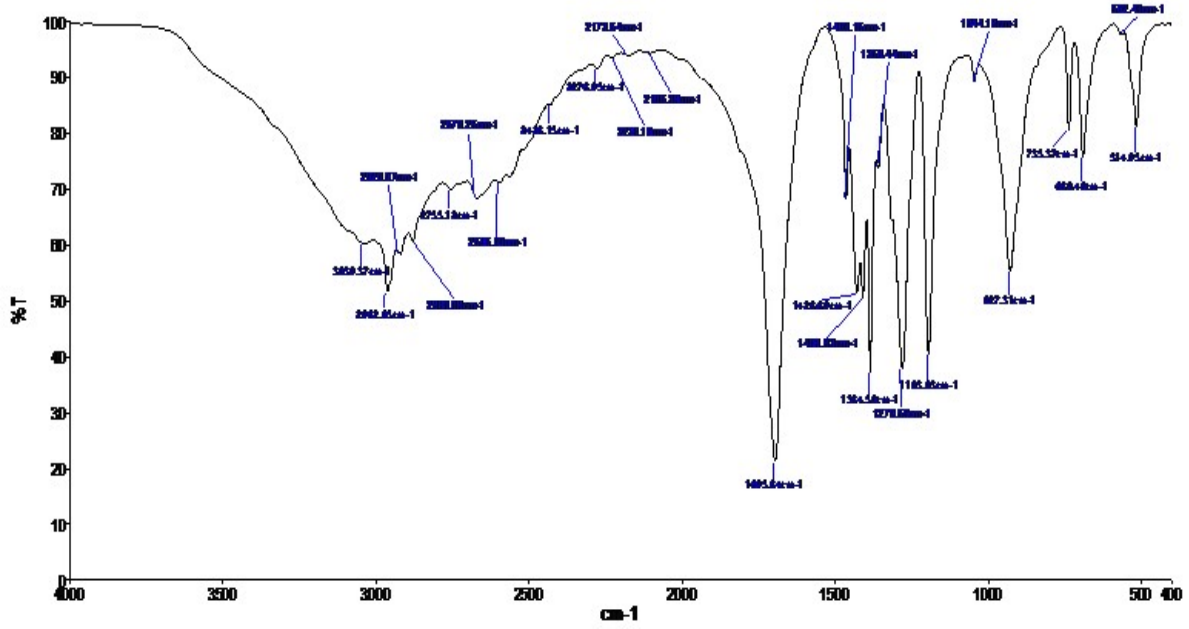

Figure 6: FT-IR spectum of AACN crystal

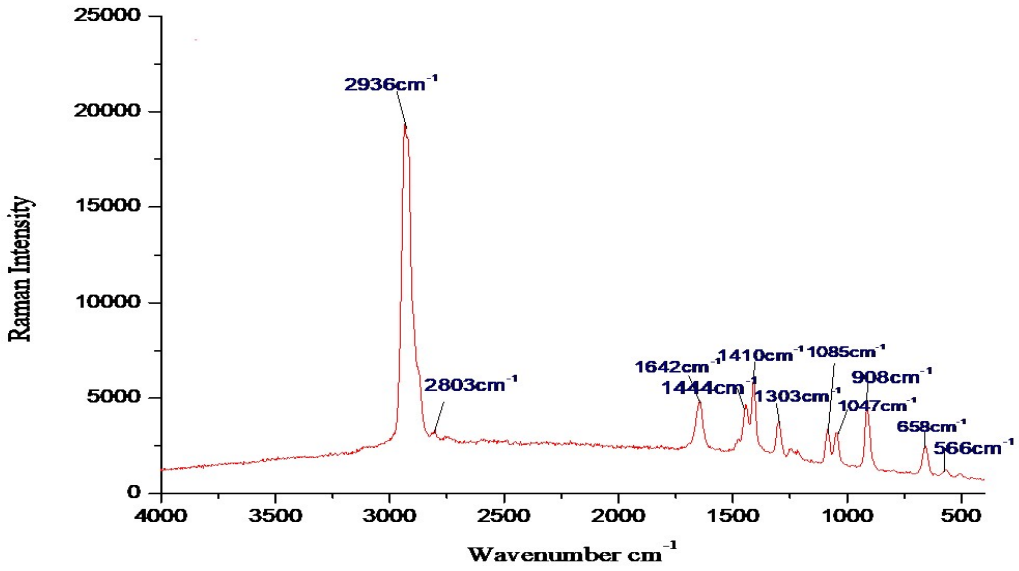

Figure 7: FT-Raman spectrum of AACN crystal

Table 1: FT-IR and FT-Raman analysis of AACN

Wave number cm^{-1} AAZN(FT-IR)	Wave number cm^{-1} AAZN (FT-Raman)	Vibrating Assignment
2920	2936	C-H stretching
2755	-	CH_2 stretching
2428	-	C-H stretching
1695	1642	C=O stretching
1463	1444, 1410	C-H deformation
1384	-	NO_3 stretching
1368	-	N=O asymmetrical stretching
1279	-	C=O stretching
1193	-	CH_2 bending
1044	1047	CH_2 bending
927	908	O-H out of plane bending
735	-	C-C stretching
689	658	C-O bending
562, 514	566	Torsion oscillation

SHG Efficiency

The NLO property of adipic acid doped with Cobalt nitrate was performed by Kurtz Perry powder technique **[18]**. The given crystal was grained into powder and densely packed in the microcapillary tube of uniform diameter. Quanta-Ray Spectra physics ND:YAG laser producing pulses with a width of 8ns and a repetition rate of 10Hz was used. The laser was focused on falling on the powder sample. SHG was confirmed by the emission of green radiation (532nm) when it was subjected to a wavelength of 6064nm and the optical signal was controlled by a photomultiplier tube (PMT) and converted into voltage output in CRO.

CONCLUSION

A new semi organic material of Adipic acid mixed with Calcium nitrate has been grown by slow evaporation technique from an aqueous solution. From the UV-Vis-NIR studies explore that transmittance of the AACN compound is about 99% in the entire visible region. Hence the grown crystal has a very good optical absorption and transmission in the entire visible region. FL studies suggested that the band gap of AACN crystal was estimated to 2.7 eV so it has a wide optical window and sharp peak obtained in the blue color of visible region which enables to use it as a blue light emitting diode. The powder XRD pattern reveals the purity and conformity of existence of expected atoms of the compound and various planes of reflection and good crystalline nature were noted. FT-IR analysis exhibits the characteristic of different functional groups. From the FT-Raman spectrum, the various intensity peaks corresponding to various frequencies obtained revealed the fact that the crystal has a good non linear in nature. FT-IR and FT-Raman comparative studies inferred that the grown crystal has pure in nature. SHG efficiency showed the NLO property of AACN crystal.

REFERENCES

[1] Chemla D.S., J. Zyss (Eds.), Nonlinear Optical Properties of Organic Molecules and Crystals, vols. 1 and 2, Academic Press, New York, 1987.

[2] Fundamentals of Non linear Optics, Peter.E.Powers, Joseph W.Haus II edition, CRC Press (Taylor and Francis Group).

[3] Ravi B., A. Jegatheesan, Neelakanda Prasad, C. Sadeesh Kumar, G. Rajarajan, "Optical and Conductivity Analysis of Thiourea Single Crystals", (2014) Rasayan J. chem. Vol. 7, No.3, (2005); 287-294.

[4] Sharada, G., Prabhu, P. and Mohan Rao. Growth and Characterisation of a New Promising NLO Mixed Borate Crystal. Journal of Optics, 29, (2000). 193-197.

[5] Julia M., Philips (Co-Chair), Sandia National Laboratories, Albuquerque, New Mexico, Meyya Meyappan (Co-Chair), NASA Ames research Centre, Moffett Field, California, Harold G. Craighead, Cornell University, Ithaca, New York, Narsingh B. Singh, (2011). 74.

[6] Northrop Gruman Corporation, Linthicum, Maryland, Ming C.W.U, University of California, Los Angeles, Edward Zellers, University of Michigan, Ann Arbor, "Material Research to Meet 21st century Defense

Needs: Chapter 5: Electronic and photonic materials", pp 95-100, The National Academics of Sciences and Engineering and Medicine, Washington D.C, The National Academic Press, https://doi.org/10.17226/10631.

[7] Anandan P., R. Jayavel, T. Saravanan, G. Parthipan, C.Vedhi, R. Mohan kumar, Crystal growth and Characterization of L-histidine hydrochloride monohydrate semiorganic non linear optical single crystals. (2012); 78

[8] Arthi D., D. Anbuselvi, D. Jayaraman, J. Arul Martin Mani and V. Joseph, "Nucleation, growth and characterization of semi-organic nonlinear optical crystal: L-Tyrosine Sodium Acetate (LTSA)", Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 136, 168-174. DOI:https://10.1016/j.saa.2014.08.117.

[9] William Kemp, "Organic Spectroscopy", Palgrave Macmillan, 1991.

[10] Goll N., N.Shinha and B.kumar, optical materials, 35,479-486 (2013).[adipic with

[11] Zulifiquar S. Ali Ahamed, G.R. Dilip, P. Ragavaiah, K.Mallikajuna, B.Deva Prasad Raju Arab. J Chem, 6, (2013); 429-434.

[12] Anbucheziyan M., S.Ponnusamy, S.P.Singh, P.K. Datta, (Muthami-zhchelvan, Cryst. Res, Technol, 45, (2012); 491-502.

[13] Balanagammal S., R. Mahalakshmi, Optic 126 (2015) 5294-5296.

[14] Sandhya Ravi, S. Chenthamarai, "Growth and Characterization of Single Crystals of Thiourea Based .Compounds", 2014, Indian J.Sci.Res. 9(1), (2014); 051-057.

[15] Masako Suzuki and Takehiko Shimanouchi, Infrared and Raman Spectra of Adipic acid Crystal, Journal of Molecular spectroscopy 29, (1969); 415-425.

[16] Shaikha R.N., Mohd, Anisa, M.D. Shirsath, S.S. Hussaini, study on optical properties of L-doped ADP crystal, spectracheimia Acta part a Molecular and Biomolecular spectroscopy, vol.81, (2011); pp, 270-275.

[17] Masamichi Tsuboi, Tadao Takenishi, Asao Nakamuba. Spectrochim Acta, 19 (1963); 271.

[18] Ramachadran E, Natarajan S. Crystal Research and Technology, 42, (2007); 617–20.

[19] Kurtz S.K, Perry TT. "A powder technique for the evaluation of nonlinear optical materials", Journal of Applied Physics, 39, (1968); pp 3798–3813.