



Growth, Mechanical, Electrical, Optical, and Thermal properties of γ - Glycine crystal Grown using the Aqueous Solution of α -Glycine and (P- Chlorobenzoic acid) 4-Chlorobenzoic acid

D.Arul Asir Abraham^{1*}, U.Sankar², S.Perumal³, P.Selvarajan⁴

¹ Department of Physics, St. John's College, Palayamkottai-627002, Tamil Nadu, India.

² Department of Physics, Sri K.G.S Arts College, Srivaikuntam-628601, Tamil Nadu, India.

³ Physics Research Centre , S.T.Hindu College , Nagercoil-629003, Tamil Nadu, India.

⁴ Department of Physics, Aditanar College of Arts and Science, Tiruchendur-628216, Tamil Nadu India.

Abstract: An organic nonlinear optical single crystal of gamma glycine (GGLY) has been grown by slow evaporation of the saturated solution at room temperature. Single crystal of gamma glycine (GGLY), an organic nonlinear optical (NLO) material, has been grown by slow solvent evaporation technique. Good optical quality single crystals with dimension up to $32 \times 31 \times 7 \text{ mm}^3$ are obtained. The crystals are characterized by optical absorption spectrum, FTIR and X-ray diffraction studies. The dielectric response of the sample is studied as a function of frequency and temperature. The mechanical, photoconductivity and ac/dc behavior and Differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) study of the grown crystals are also investigated.

Key words: NLO materials; Crystal growth; Dielectric measurement; Conductivity; Mechanical and thermal properties.

1. Introduction

In recent years NLO materials is always importance high due to its practical applications in optical modulation, switching and other signal processing devices etc. The research on organic and semi-organic crystals was started in 1980s. The Organic materials offer good optical response time, non-resonant susceptibility, second harmonic generation and high phase-conjugate reflectivity [1] materials.

Amino acids and their complexes belong to a family of organic materials that have been considered for photonic applications and the Amino acids are essential materials for NLO applications [2]. The importance of amino acids in NLO applications is due to the fact that all the amino acids have chiral symmetry and crystallize in non Centro-symmetric space groups. Out of 20 amino acids glycine is the simplest of all. The Glycine family crystals have been subjected to extensive research by several researches [3-6] for their efficient NLO properties. Glycine is the only protein forming amino acid and is optically inactive too. It exists as dipolar ions in which the carboxyl group is present as a carboxyl ate ion and the amino group as an ammonium ion. Its high melting point is due to its dipolar nature. Under different conditions, glycine crystallizes in 3 kinds of polymorphs with different thermal stabilities[7]. The phenomenon of polymorphism is well-known as the property of a solid with different arrangements of molecules or conformations in the crystal lattice [8]. The possibility of polymorphism may exist for any particular compounds, but the conditions and systematic methods required to prepare certain polymorphs are still challenges for many years [9]. The control and optimization of the polymorphic form play key roles in the crystallization process, especial in the pharmaceutical industry. Polymorphic crystallization is affected by various factors, such as cooling rate [10],

super saturation [11], agitation [12], solvent [13], pH values [14], additives [15], solution concentration [16], impurity [17], seeding [18]. Glycine ($\text{NH}_2\text{CH}_2\text{COOH}$) was chosen as the model compound in this study. In the gaseous phase, glycine can exist as a nonionic form, while exist as a zwitterions in solution and solid form [19]. Under different conditions, glycine crystallites exist in at least three kinds of polymorphs, α , β and γ , which have different relative stabilities [20], crystal shape [21], thermal, and physical properties [22]. The α - and γ -forms have quite different conformations [23]. The two polymorphs differ in the different hydrogen bond networks, which are formed between NH_3^+ groups and COO^- groups [24]. Accordingly, the α -form appears in centrosymmetric space group P21/n [25], while the γ -form crystallizes in noncentrosymmetric space group P31 [26]. Crystallization of glycine solutions in the water at isoelectric point always produced the α form [27] while the γ -form apparently appears when crystallization takes place from solution is acidified, made alkaline [28] or by the addition of compounds that inhibit the growth of α -form [29]. Also α , β and γ glycine exhibit different characteristics. Both α and β forms are crystalline in centrosymmetric space group P21/c that is not feasible for optical second harmonic generation [30-31]. But γ glycine crystallizes in non centrosymmetric space group P31 & P₃₂ enabling itself ideal for piezo electric and NLO applications. Due to the presence of chromophores namely amino groups, carboxyl group, γ glycine finds itself absolutely transparent in the U-V visible region. Many researchers reported that single crystals of GGLY (gamma glycine) can be grown from aqueous solutions of glycine which can be acidic as well as basic [32-33]. The growth of single crystals of Gamma glycine from aqueous solution incorporated with sodium chloride (NaCl) has been reported recently by Srinivasan and Arumugam employing slow solvent evaporation technique [34]. Ambujam et al [35] and Ramachandran et al [36] have successfully crystallized GGLY (Gamma glycine) via gel technique. A scaled quantum mechanical force field calculations on the Gamma Crystal polymorph have confirmed the effect of hydrogen bond stretching in vibrational analysis. Gamma Glycine is actually grown by many conventional methods like slow cooling, slow evaporation as well as gel method. Though there are numerous reports on this title compound wherein mixed solvents like water with sodium acetate, sodium hydroxide, ammonium sulphate, ammonium hydroxide, potassium chloride, lithium bromide, lithium acetate etc are used, still the indispensable characteristics of gamma glycine urges the researches to implant deeper studies on its properties. Bharaniraj et al have been reported the growth of gamma glycine from the aqueous solutions of alpha glycine and sodium acetate with de ionized water. The present article also addresses the growth of Gamma glycine crystals in the presence of the aqueous solution of α -Glycine and 4-Chlorobenzoic acid.

The crystals of Gamma glycine grown with 4-Chlorobenzoic acid are characterized by single crystal and powder XRD, FT-IR, NLO test, optical, micro hardness, dielectric, Electrical conductivity, photoconductivity study and thermo gravimetric analysis (TGA) studies.

Materials and Methods

2. Experimental procedure

2.1 Synthesis

The single crystals of Gamma Glycine (GGLY) crystals were grown by slow evaporation method at ambient room temperature. The commercially available annular grade Glycine (99.5%) was dissolved in de-ionized water and 4-Chlorobenzoic acid mixture was dissolved in the ethyl alcohol and the mixture of bi volume is taken in the 1:1 molar ratio and the mixture was stirred at 80 °C then the solution was filtered in room temperature (30 °C). The solvent of the supersaturated solution was allowed to evaporate through the perforated lid of the container. Due to spontaneous nucleation, optically clear tiny yellowish transparent crystals of the title compound were formed by slow evaporation technique after four to seven weeks. The defect free and well shaped ones were chosen and used as seed crystals for further growth experiments.

2.2 Solubility determination

The growth rate of a crystal depends on its solubility and growth temperature. Solubility of a material governs the amount of material, which is available for the growth and hence defines the total size limit. The solubility curve of Gamma Glycine (Glycine and 4-Chlorobenzoic acid) was determined by dissolving the synthesized product by water and ethyl alcohol in Millipore in an airtight container kept in a constant temperature bath, the content was continuously stirred for 1-2 hours. After attaining the saturation, the equilibrium

concentration of the solute was estimated gravimetrically. The same process was repeated for different temperatures (30, 35, 40, 45, 50 and 55 °C). The variation of solubility with temperature Fig. 1 indicates that γ -glycine with 4-Chlorobenzoic acid have high positive solubility-temperature co-efficient values.

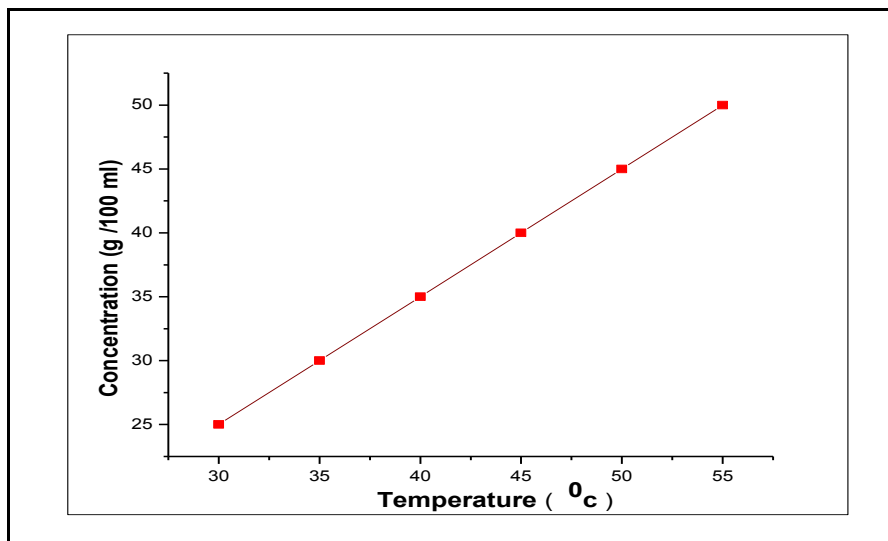


Fig. 1 Solubility curve of GGLY(Glycine with 4-Chlorobenzoic acid)

2.3 Crystal Growth

The synthesized salt of Gamma Glycine (GGLY) is purified by repeated crystallization and saturated solution is prepared in accordance with the solubility. The optimized pH is measured to be 5.5 respectively. Saturated aqueous solution of GGLY (Glycine and 4-Chlorobenzoic acid) 1:1 is taken in a crystallizing vessel with perforated covers and placed in a constant temperature bath. Seed crystals are harvested within few weeks. A suitable seed crystal is selected from the harvested crystals. A saturated solution is prepared and the seed crystal is hung inside the solution that is optimally closed for controlled evaporation. By slow evaporation of the solvent, Gamma Glycine (GGLY) single crystal of size 32 x 31 x 7 mm³ is grown in a period of 30-60 days. The resulting crystals are of slightly yellowish needles. The grown crystals are stable, do not decompose in air and non-hygroscopic in nature. Fig. 2 shows the photograph of the as grown crystals of Gamma Glycine (GGLY). An important observation during the growth of GGLY is the absence of any kind of microbial contamination during the growth period even when the solution was kept for nearly 1-2 months.



Fig. 2 Photograph of GGLY Crystal grown from α Glycine and 4-Chlorobenzoic acid

2.4 Characterization

The grown crystal of GGLY was confirmed by single crystal X-ray diffraction analysis. Single crystal XRD data was collected by ENRAF NONIUS CAD4-F single crystal X-ray diffractometer with MoK α ($\lambda=0.71073$ Å) radiation. The grown crystals of GGLY were confirmed by powder XRD analysis. In this system, a fine focus (0.4 x 8 mm; 2 kW Mo) X-ray source energized by a well-stabilized Philips X-ray generator (PW 1743) was employed. The FT-IR spectrum was recorded using BRUKER IFS-66V FT-IR

spectrometer with KBr pellet technique for the range 4000 – 400 cm⁻¹. The linear optical properties of the crystals were examined between 200 and 2000 nm using the VARIAN CARY 5E UV-Vis-NIR spectrophotometer. The powder SHG measurement was done using Nd:YAG laser fundamental ($\lambda = 1064$ nm) radiation. In this work, HMV SHIMADZU micro hardness tester, fitted with diamond Vickers pyramidal indenter was used. The static indentations were made at room temperature with a constant indentation time of 20 seconds for all indentations. Indentations were made by varying the loads from 10 to 50 g; above this load micro cracks are observed. Good quality single crystals of GGLY grown (Glycine added with 4-Chlorobenzoic acid) were selected for dielectric measurements. Silver paint was applied on opposite faces of planes of the crystal grown with 4-Chlorobenzoic acid respectively, to make a capacitor with the crystal medium. The dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of the samples were determined by measuring the capacitance and dissipation factor as a function of frequency (100 Hz-5 MHz) and temperature ($T = 308$ – 368 K). Using a HIOKI-3532 LCR HITESTER the ac conductivity study was taken.

Results and Discussion

3.1 Structural studies

3.1.1 Single crystal XRD analysis

The structure of GGLY (Gamma Glycine) was solved by the direct method and refined by the full matrix least-squares fit technique employing the SHELXL program. It is observed that GGLY crystal crystallizes in the Hexagonal system with space group P32. The lattice parameters are $a = 7.021$ Å, $b = 7.021$ Å, $c = 5.467$ Å with $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 120^\circ$ and volume $V = 233.23$ Å³. The single crystal XRD data is obtained in the present work coincides with the previously reported work.

3.1.2 Powder XRD analysis

The Powder XRD pattern of the grown crystals was recorded using D8 Advanced Bruker Powder Xray Diffractometer. The positions of the peaks are found to be matching with the literature . Fig. 3 depicts the powder XRD pattern of the γ glycine crystals.

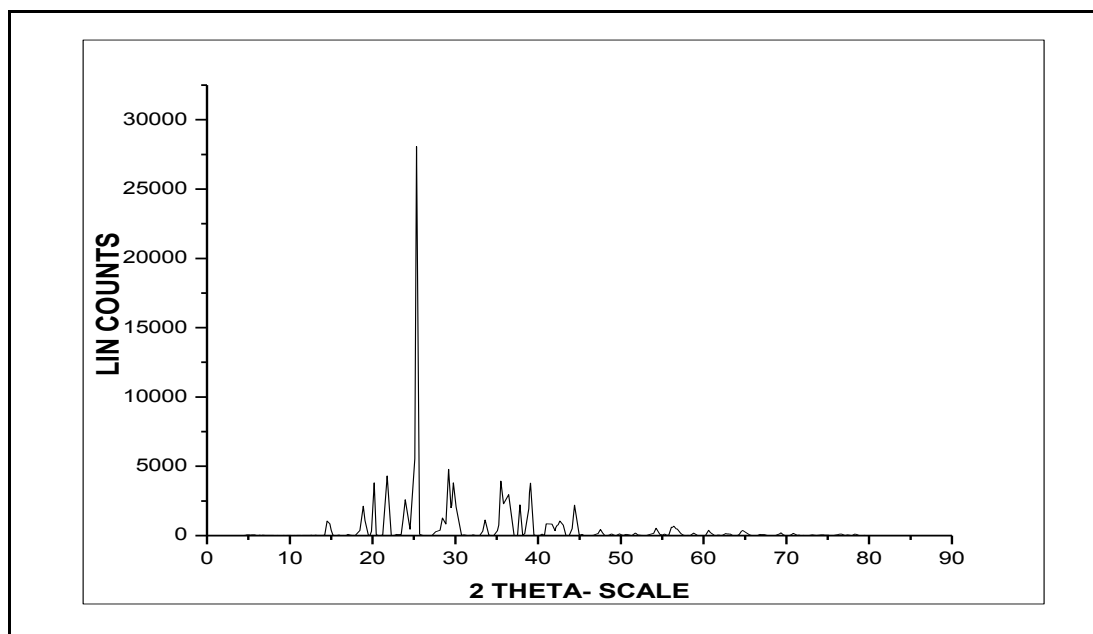


Fig. 3 Powder XRD data of GGLY grown from 4-Chlorobenzoic acid

3.1.3 FT-IR Spectroscopic Studies

This FTIR analysis was accomplished to identify the functional groups present in the grown crystal. For this, an Alpha-T/Bruker Spectrometer was used in the frequency range 400 – 4000 cm⁻¹. The sample used was in pellet form in KBr phase. The FT-IR spectrum is depicted in the Fig .4 which was found to be matching with the previous literature.

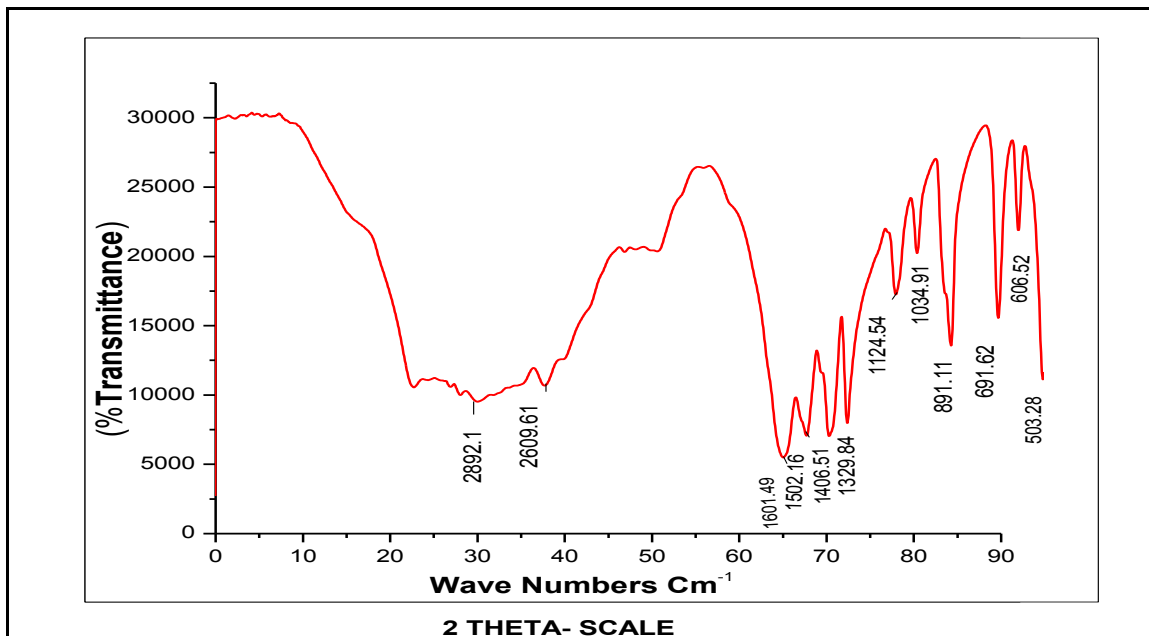


Fig. 4 FT-IR Spectrum for GGLY grown from 4-Chlorobenzoic acid

Table 1 FT-IR spectral assignments for GGLY

Wave number	Assignments
2892.81	N-H asymmetric stretch
2609.61	Combination and overtone bands
1601.49	-COO ⁻ asymmetric stretch
1502.16	NH ₃ ⁺ symmetric bending
1406.51	-CH ₂ bend
1329.84	-COO ⁻ symmetric stretch
1124.54	-CH ₂ wag
1034.91	NH ₃ ⁺ rock
891.11	-CH ₂ rock
691.62	-CCN symmetric stretching
606.52	-COO ⁻ bend
503.28	NH ₃ ⁺ torsion

3.2 Optical properties

3.2.1 UV-VIS Spectroscopy study

Nonlinear optical single crystals are mainly used in optical applications. The optical absorption range and the cut-off wavelength are the most important optical parameters for laser frequency applications. Fig.5 represents the optical Reflectance spectrum of GGLY. The UV cut-off wavelength of the sample is found to be at 200 nm and the absorption is very less in the entire visible region and part of IR region. Fig 6 represents the

optical absorbance spectrum of gamma glycine. The optical band gap is obtained by plotting the graph between $h\nu$ and $(\alpha h\nu)^2$ (Fig. 7). From the graph, the optical energy gap of GGLY is determined as 4.53 eV.

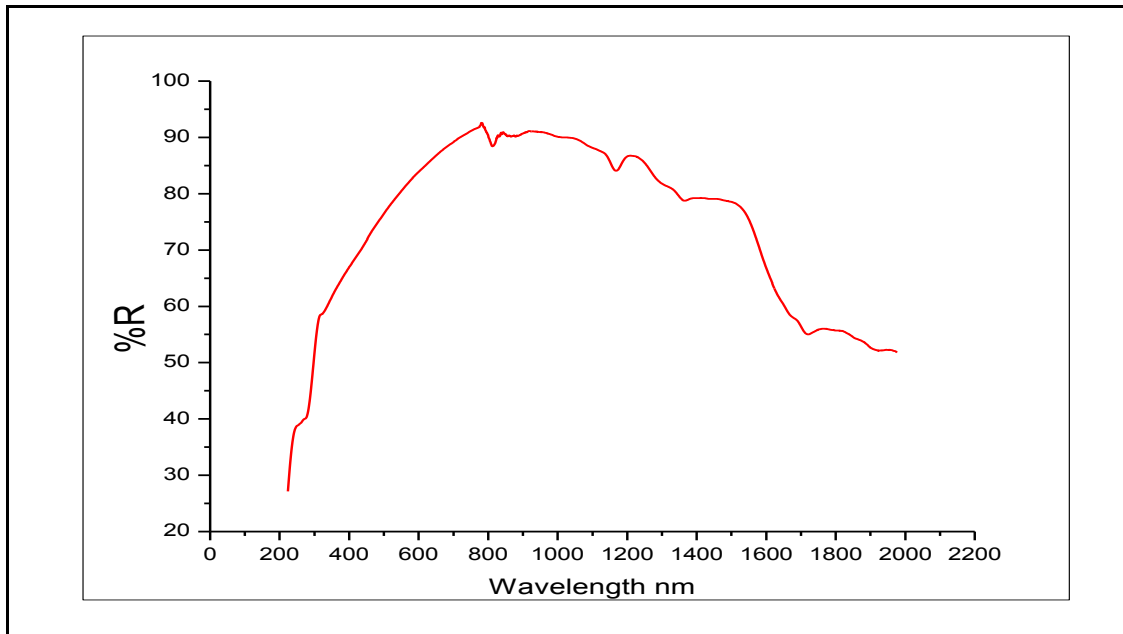


Fig. 5 Optical Reflectance spectrum of Gamma Glycine crystal

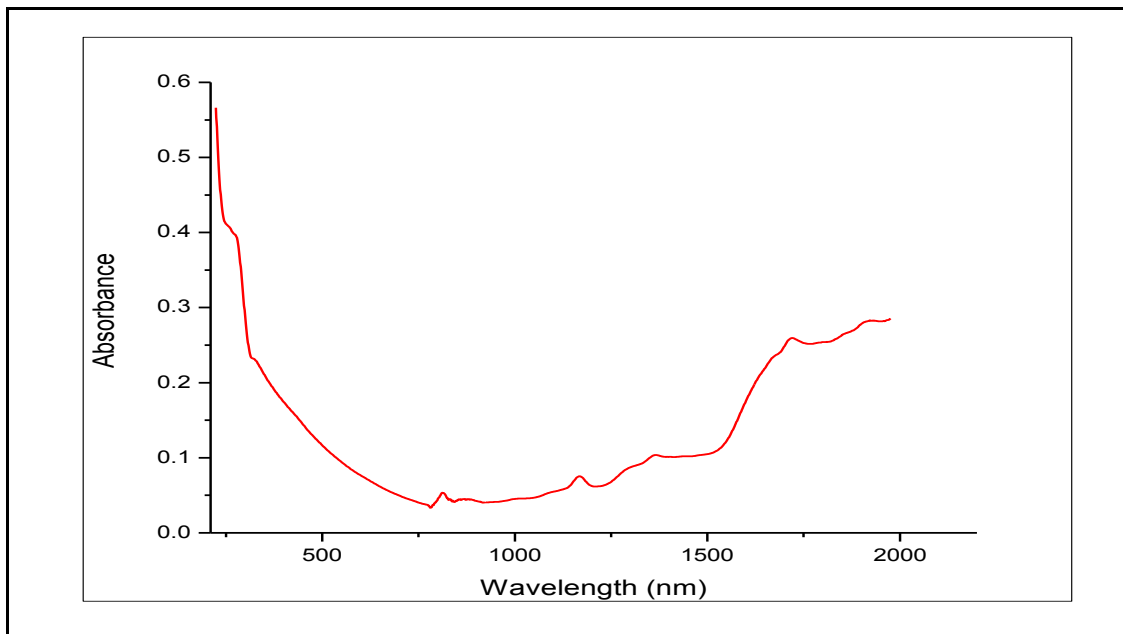


Fig. 6 Optical absorption spectrum of Gamma Glycine crystal

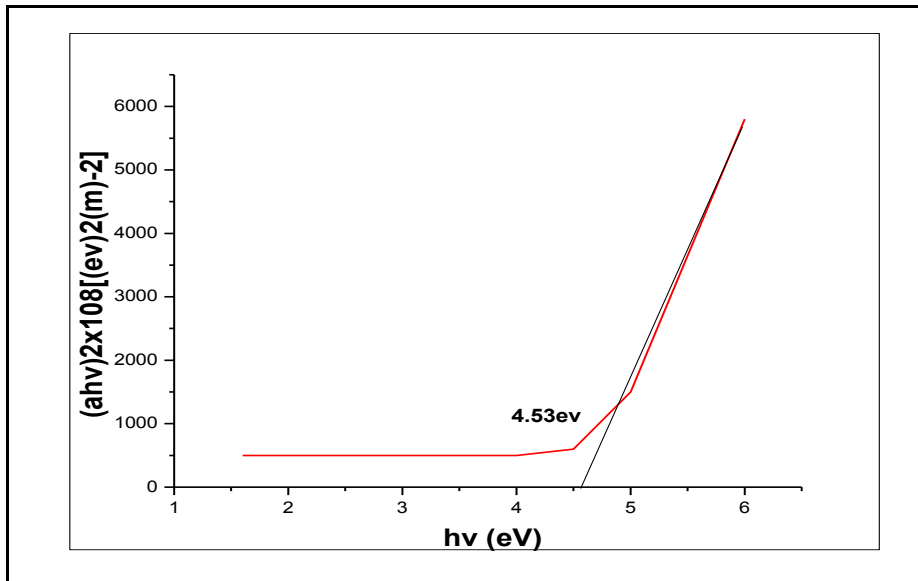


Fig. 7 Tauc's plot. of Gamma Glycine crystal

3.2.2 NLO studies

The SHG test was carried by Kurtz and Perry powder out on grown GGLY single crystals to study the NLO properties. The second harmonic generation (SHG) test on the GGLY crystal is performed by Kurtz powder SHG method [37]. The fundamental beam of Nd: YAG laser with 1064 nm wavelength, pulse duration of 8 ns and 10 Hz repetition rate is focused onto the powdered sample of GGLY and KDP. When the input pulse of .68 J is passed through the sample and KDP, output signals 6.3mj are obtained from GGLY and KDP respectively. It is observed that the NLO efficiency of GGLY is 1.2 times more that of KDP crystal

3.3 : Microhardness studies

A plot between the hardness number and the applied load is depicted in Fig. 8. It is evident from the figure that the Vickers Hardness number (Hv) decreases with applied load (p). This indicates that the crystal exhibits normal indentation size effect behavior (ISE). A plot drawn between $\log p$ and $\log d$ is shown in Fig. 9. it supports normal ISE behavior of GGLY single crystal [38]. From the graph the work hardening coefficient (n) is calculated using linear fit method and is found to be 1.21

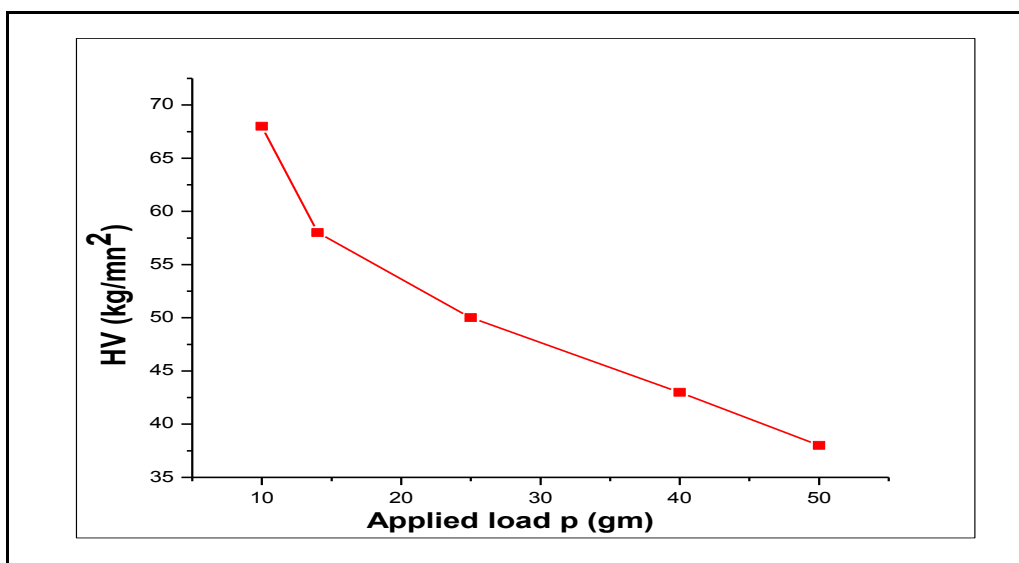


Fig. 8 Variation of Vickers Hardness Number with the applied load for GGLY

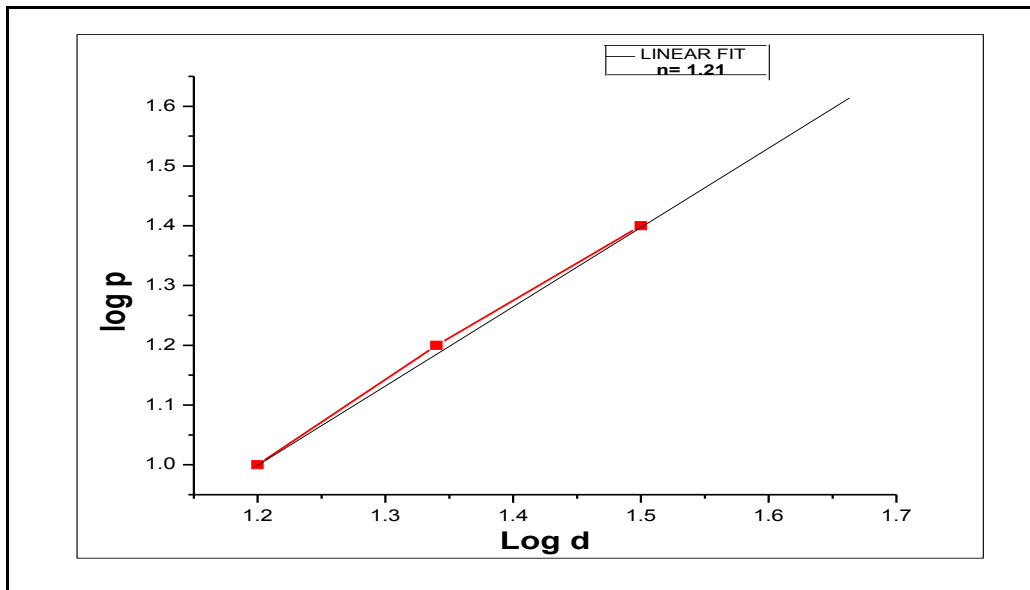


Fig. 9 Plot of log d versus log p for Gamma Glycine

3.4 Electrical properties

3.4.1 Dielectric studies

A graph is drawn between dielectric loss and for various temperatures (308, 324,334,344 and 355(K) and is shown in Fig. 10. The low value of dielectric loss at high frequency suggests that the GGLY crystals possess good optical quality [40]. This parameter is of vital importance for nonlinear optical materials in their applications. In Fig. 11 shows the plot of dielectric constant (ϵ_r) versus various temperatures for 308, 324, 334,344 and 354 K. It is seen that the value of dielectric constant is high in the lower frequency region for all the temperatures and then it decreases with increase in frequency up to 10 kHz. The high value of dielectric constant at low frequency is attributed to space charge polarization due to charged lattice defects Beyond 10 kHz, it is almost constant and is saturated at higher frequencies [41-46].

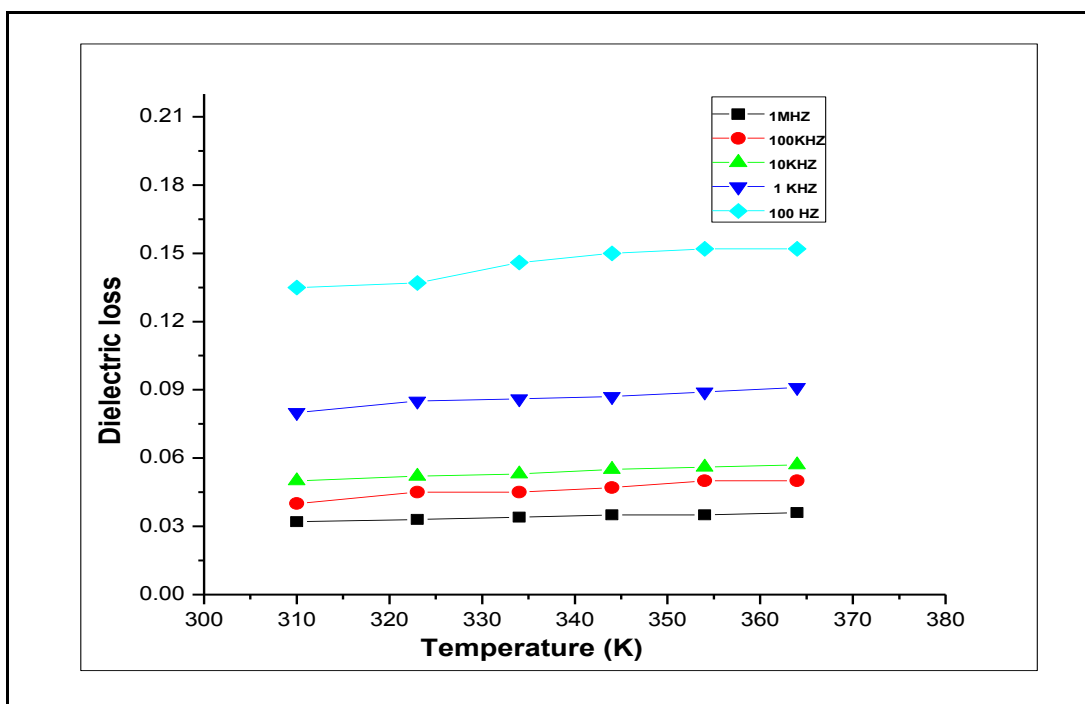


Fig. 10. Temperature dependence of dielectric loss for Gamma Glycine single crystal

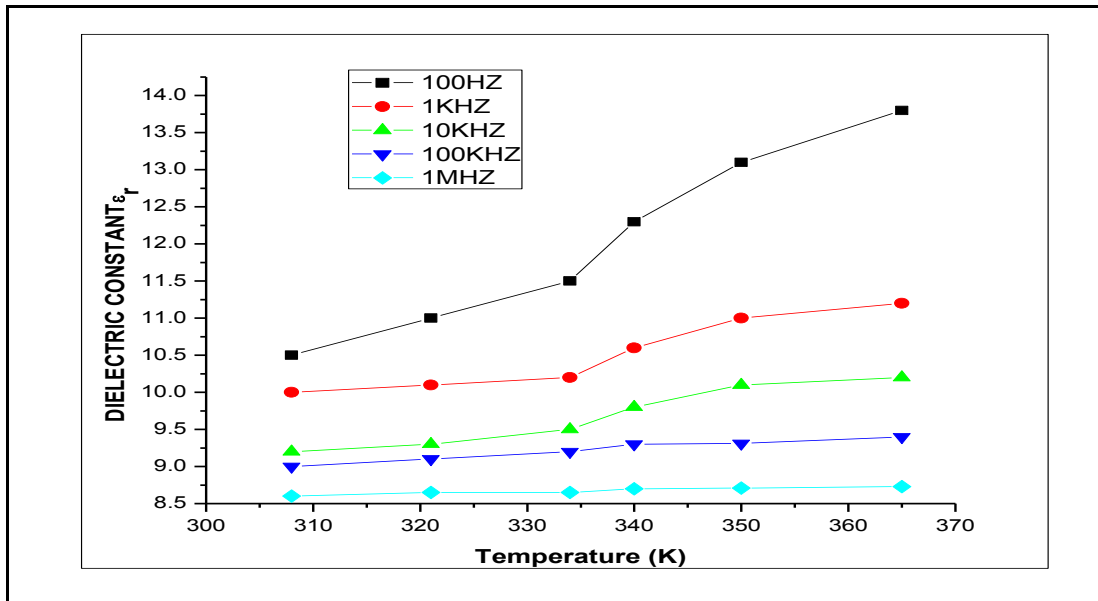


Fig. 11. Temperature dependence of dielectric constant for Gamma Glycine single crystal

3.6 Thermal characterization

The TG / DTA studies were carried out simultaneously on the sample in the temperature range 37 – 310°C and the recorded thermal curves are displayed in figure 12 and 13. From the TG curves, it is noticed that there is a slight weight loss up to 23°C [47] for the sample and there is a maximum weight loss in the temperature range 260-270°C. Hence the sample is found to be thermally stable and suitable for device applications. From DTA curves it is observed that the sample has an endothermic peak at 273.47°C which corresponds to the decomposition point of the sample. In TGA/DTA curve the transition temperature at 240 °C, the gamma Glycine samples are due conversion γ -glycine into α -glycine. The high melting point of the semi organic material when compared to the other crystals arises due to the strong bonding between the conjugation layers [48-49]. The sample crystal is thermally stable for designing the NLO applications.

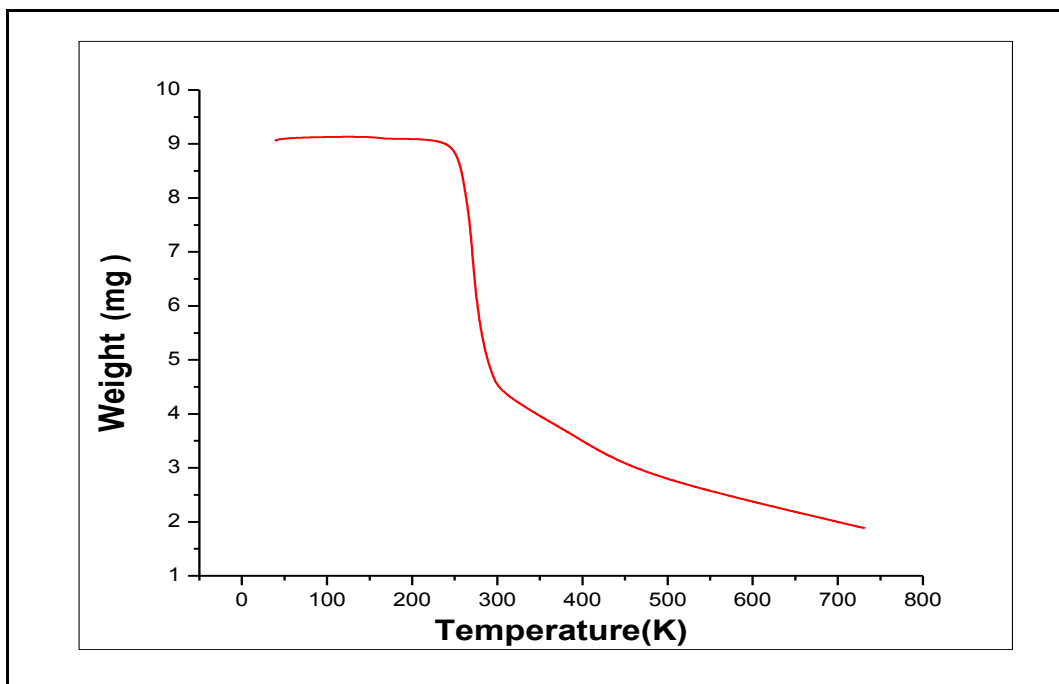


Fig 12. The DTA CURVE FOR GAMMA GLYCINE CRYSTAL

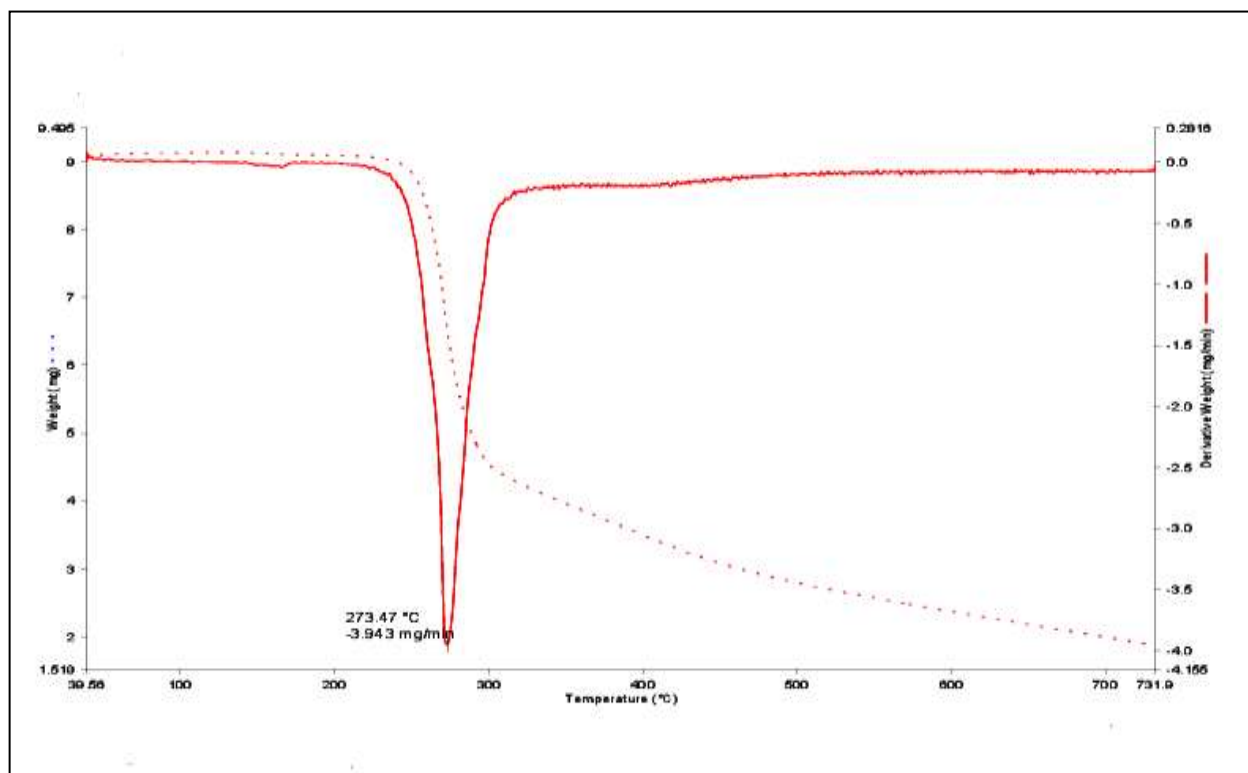


Fig 13: The DTG CURVE FOR GAMMA GLYCINE CRYSTAL

Conclusion

The Glycine and 4-Chlorobenzoic acid compound of GGLY was successfully synthesized and the single crystals have been grown by solution growth technique. Its cell parameters have been determined by the single crystal XRD and powder XRD analysis. The presence of functional groups in gamma glycine has been identified from the FTIR analysis. The second harmonic generation result confirm that the compound have good NLO property. Optical absorption study reveals the absorption edge at 230 nm. The phase matching natures of the grown crystals have been confirmed by Kurtz and Perry powder method. The micro hardness measurements prove that gamma glycine belongs to the soft category of materials. The activation energy is determined from the plots of ac/dc conductivity. The thermo characteristic study confirms the crystal is stable and is suitable for optical device applications.

Acknowledgement

The author thank to SAIF,IIT-Madras and St Josephs college,Trichy for their help and support of analysis tests. My sincere thank to Dr P.Selvarajan Associate professor of physics ,Aditanar college of arts and science,Tiruchendur.Also I extend my thank to Dr.U.Sankar (Guide) and Dr. Daniel sweetlylin ,Associate professor and head of the department of physics,St John's college Palayamkottai.

References:

1. Prasad PN, Williams DJ, Introduction to Nonlinear ical Effects in Molecules and Polymers, Wiley-InterScience, New York, 1991.
2. Narayana Moolya B, Jayarama A, Sureshkumar M.R, Dharmaprakash S.M, J. Cryst. Growth, 2005,280, 581.
3. Albert L. Lehninger, Principles of Biochemistry, CBS Publishers, New Delhi, 1984.
4. Marsh RE, Acta Crystallogr., 1958, 11, 654.
5. Iitaka Y, Acta. Crystallogr., 1960,13, 35.

6. Iitaka Y, Acta. Crystallogr., 1961,14, 1.
7. Xia Y, Jie L, Xiu-Juan W, Chi-Bun C (2008). Effect of sodium chloride on the nucleation and polymorphic transformation of glycine. *J. Cryst. Growth* 310:604-611.
8. Davey, R. J. Polymorphism in Molecular Crystals: Stabilization of a Metastable Form by Conformational Mimicry. *J. Am. Chem. Soc.* 1997, 119, 1767-1771
9. JOEL BERNSTEIN. Polymorphism in Molecular Crystals. Clarendon press. Oxford, 2002.
10. Madras, G., McCoy, B. J. Growth and ripening kinetics of crystalline polymorphs. *Cryst. Growth. Des.* 2003, 3, 981-990.
11. Datta, S.; Grant, D. J.W. Effect of supersaturation on the crystallization of phenylbutazone polymorphs. *Cryst. Res. Technol.* 2005, 40, 233-242.
12. Kishisihita, A., Hayashi, T., Kishimoto, S., Nagashima, N. Characterization of Aspartame Crystals. *Ind. Eng. Chem. Res.* 1999, 38, 2166-2170.
13. Threlfall, T. Crystallisation of Polymorphs: Thermodynamic Insight into the Role of Solvent. *Org. Proc. Res. Dev.* 2000, 4, 384-390.
14. Jones, H. P., Davey, R. J. Crystallization of a salt of a weak organic acid and base: Solubility relations, supersaturation control and polymorphic behavior. *J. Phys. Chem. B.* 2005, 109, 5273-5278.
15. Kitamura, M., Ishizu, T. Kinetic effect of L-phenylalanine on growth process of L-glutamic acid polymorph. *J. Cryst. Growth.* 1998, 192, 225-235.
16. Li, N., Shanks, R. A., Murphy, D. M. Microscopic study of polymorphism of a photographic coupler. *J. Cryst. Growth.* 2000, 220, 592-603.
17. Mukuta, T., Lee, A. Y., Kawakami, T., Myerson, A. S. Influence of Impurities on the Solution-Mediated Phase Transformation of an Active Pharmaceutical Ingredient. *Cryst. Growth. Des.* 2005, 5, 1429-1436.
18. Beckmann, W. Proceedings of the 15th International Symposium on Industrial Crystallization in Sorrento, 2002; Vol. 1, pp 1-12.
19. Chisholm, J. A., Motherwell, S., Tulip, P. R., Parsons, S, and Clark, S. J. An ab initio study of observed and hypothetical polymorphs of glycine. *Cryst. Growth. Des.* 2005, 5, 1437-1442.
20. Park, K., Evans, J. M. B., Myerson, A. S. Determination of solubility of polymorphs using differential scanning calorimetry. *Cryst. Growth. Des.* 2003, 3, 991-995.
21. Sakai, H., Hosogai, H., Kawakita, T. Transformation of α -glycine to γ -glycine. *J. Cryst. Growth.* 1992, 116, 421-426.
22. Mu, Y. D., Xiao, F., Zhang, R. J., Li, H. Y., Huang, W., Feng, X. S., Liu, H. G. Effects of pH and surface pressure on morphology of glycine crystals formed beneath the phospholipid Langmuir monolayers. *J. Cryst. Growth.* 2005, 284, 486-494.
23. Weissbuch, I., Leisorowitz, L., Lahav, M. "Tailor-Made" and Charge-Transfer Auxiliaries for the Control of the Crystal Polymorphism of Glycine. *Adv. Mater.* 1994, 6, 952-956.
24. Murli, C., Thomas, S., Venkateswaran, S., Sharma, S. M. Raman spectroscopic investigation of α -glycine at different temperatures. *Physica. B.* 2005, 364, 233-238.
25. Legros, J.-P. Kvick, A. *Acta. Crystallogr. B.* 1980, 36, 3052-3059.
26. Bhat, M. N., Dharmaprakash, S. M. Growth of nonlinear optical γ -glycine crystals. *J. Cryst. Growth.* 2002, 236, 3776-380.
27. Towler, C. S., Davey R. J., Lancaster R. W., Price C. J., Impact of Molecular Speciation on Crystal Nucleation in Polymorphic Systems: The Conundrum of γ Glycine and Molecular 'Self Poisoning', *J. Am. Chem. Soc.* 2004, 126, 13347-13353.
28. Yu, L., Ng, K. Glycine crystallization during spray drying: The pH effect on salt and polymorphic forms. *J. Pharm. Sci.* 2002, 91, 2367-2375.
29. Weissbuch, I.; Leisorowitz, L.; Lahav, M. *Adv. Mater.* 1994, 6, 953-966.
30. Akihiko Ito, Maiko Yamanobe-Hada, Hitoshi Shindo, *J. Crystal Growth*, 2005, 275, 1691.
31. Narayan Bhat MK, Dharmaprakash SM, *J. Crystal Growth*, 2002, 236, 376.
32. Narayan Bhat MK, Dharmaprakash SM, *J. Crystal Growth*, 2002, 242, 245.
33. Moolaya BN, Jayarama A, Sureshkumar MR, Dharmaprakash SM, *J. Crystal Growth*, 2005, 280, 581.
34. Jan Baran, Henryk Ratajczak, *Spectrochimica Acta Part A*, 2005 61, 1611
35. Srinivasan K, Arumugham J, *Optic. Materials*, 2007, 30, 40.
36. Ambujam. K, Selvakumar S, Prem Anand D, Mohamed G, Sagayaraj P, *Cryst. Res. Technol.*, 2006, 41,671.
37. Kurtz SK, Perry T.T, *J. Appl. Phys.*, 1968,39, 3798 3813.

38. Onitsch E.M., 'The present status of testing the hardness of materials', *Mikroskopie*, 1956, 95, 12-14.
39. Smyth CP, (1965) *Dielectric behavior and structure*, McGraw Hill, Newyork.
40. Balarew CP, Duhlew R, *J. Solid State Chem.*, 1984, 55, 1-10.
41. Vimalan M, Ramanand A, Sagayaraj P, *Crys. Res. Technol.*, 2007, 42, 1091- 1096.
42. Vimalan M, Cyrac Peter A, Rajesh Kumar T, Jayasekaran R, Packiam Julius J, Sagayaraj P, *Arch. Phy.Res.*, 2010, 1 (2): 94-102.
43. Vimalan M, Helan Flora X, Tamilselvan S, Jeyasekaran R, Sagayaraj P, MahadevanC.K, *Arch. Phy.Res.*, 2010, 1 (3):44-53 .
44. Mott BW, (1956) *Microindentation Hardness testing*, Butterworths, London.
45. Bube RH, (1981), *Photoconductivity of Solids*, Wiley Interscience, New York.
46. Joshi VN, (1990), 'Photoconductivity', Marcel Dekker, New York.
47. D.Arul Asir Abraham *et al*/Int.J.Chemtech Res.2015,8(1),pp 105-110.
48. G.L.Perlovich,L.K,Hansen,A.Baucer-Brand ,J.Therm. Anal.Calorimetry 66(2001) 699.
49. E.Ramachandran, K.Baskaran, S.Natarajan. *Crys.Technol.* 42(2007)73.
