

**Investigations on crystal growth and studies of L-lysine acetic acid crystals****C. Anbulakshmi<sup>1\*</sup>, P.Selvarajan<sup>2</sup>, S.Selvaraj<sup>3</sup>**

<sup>1</sup>Research Scholar, Reg. No. 12434, Department of Physics and Research Centre,  
MDT Hindu College, Tirunelveli-627010, Tamilnadu, India.

<sup>2</sup>Associate Professor of Physics, Aditanar College of Arts and Science,  
Tiruchendur - 628216, Tamilnadu, India.

<sup>3</sup>HOD and Associate Professor of Physics, MDT Hindu College,  
Tirunelveli-627010, Tamilnadu, India.

(Affiliated to Manonmaniam Sundaranar University, Abishekapatti-627012,  
Tirunelveli, Tamilnadu, India)

\*Corresponding author

**Abstract**

L-lysine and acetic acid were used as the reactants to grow the single crystals of L-lysine acetic acid (LLAA) and the crystals were grown by solution method at room temperature. The crystal structure was analysed by X-ray diffraction studies. Second order NLO studies were carried out for the grown LLAA crystal. Density of the sample was found by floatation method. The functional groups of the grown LLAA crystal were identified by FTIR analysis. The weight percentage of elements in the sample was determined by EDAX method. PL studies were carried out for the sample using the photoluminescence (PL) analyser and the obtained results were discussed.

**Key words:** Amino acid complex; single crystal; solution growth; XRD; FTIR; SHG; photoluminescence; EDAX

**1. Introduction**

Nonlinear optics is one of the branches of the optics and it has revealed many second order and third order optical phenomena such as second harmonic generation (SHG), third harmonic generation (THG), higher harmonic generations, optical rectification, stimulated Raman scattering etc. There are mainly three types of nonlinear optical (NLO) crystals viz., organic NLO, inorganic NLO and semiorganic NLO crystals. Organic NLO crystals have high SHG efficiency and high laser damage threshold and they can be easily fabricated [1-3]. Lysine is an  $\alpha$ -amino acid that is used in the biosynthesis of proteins. It contains an  $\alpha$ -amino group, an  $\alpha$ -carboxylic acid group and a side chain containing lysyl  $((\text{CH}_2)_4\text{NH}_2)$ . Like almost all other amino acids, the  $\alpha$ -carbon is chiral and lysine may refer to either enantiomer or a racemic mixture of both [4,5]. Here in this work, the biologically active enantiomer L-lysine has been considered for the crystal growth. Crystallographic data for L-lysine complexes exist in the literature. Carboxylic acids complexed with L-lysine have been studied by including formic, acetic, succinic, glycolic, oxalic, and maleic acids. The crystal structures of complexes of glutaric acid with D, L- and L-lysine were reported [6-10]. Krisnakumar *et al.* have reported the grown and characterization of L-lysine monohydrochloride crystals and here XRD studies, optical studies, FTIR, FT-Raman studies and NLO studies were discussed [11].

Vasudevan *et al.* have grown and studied the *L*-lysine *L*-lysinium dichloride nitrate [12]. In this work, an organic NLO crystal viz., *L*-lysine acetic acid was synthesized and crystals were grown by slow evaporation solution growth technique.

## 2. Synthesis and crystal growth

Analytical grade *L*-lysine and acetic acid were purchased commercially and they were mixed in stoichiometric ratio of 1:1 in double distilled water. The saturated solution was prepared and it was heated at 45 °C to synthesize the salt of *L*-lysine acetic acid (LLAA). The synthesized salt of LLAA was used for growth of single crystals. Using the synthesized salt and double distilled water, again the saturated solution was prepared and it was stirred well using a magnetic stirrer for about 3 hours. Then, the solution was filtered using Whatman filter paper and the filtered solution was taken in a growth vessel for slow evaporation at room temperature. Over a period of 35 days, the single crystals of LLAA was harvested. The good optical quality crystal of *L*-lysine acetic acid is shown in figure 1.



Fig.1. The harvested crystals of LLAA

## 3. Characterization techniques

Single crystal X - ray diffraction studies of the grown LLAA were carried out by Enraf Nonius CAD4-MV31 single crystal X-ray diffractometer. FTIR spectrum was recorded using Perkin Elmer spectrometer in the range of 4000-400  $\text{cm}^{-1}$  at a resolution of 4  $\text{cm}^{-1}$  by the KBr pellet technique. The composite elements of the title compound material were estimated by Energy Dispersive X-ray spectroscopy (EDAX). Second order NLO properties of LLAA were tested by Kurtz Perry Powder technique using a Q-switched high energy Nd: YAG laser (Quanta Ray model Lab-170-10) with  $\lambda = 1064 \text{ nm}$ . Using the photoluminescence spectrometer, the PL spectrum of the sample was recorded.

## 4. Result and discussions

### 4.1 Single crystal XRD studies

When X-rays fall on a crystalline material, they are diffracted. This is known as X-ray diffraction (XRD) and this will take place when Bragg's law is satisfied. A good quality crystal of LLAA of dimensions of 0.4 x 0.4 x 0.3 mm<sup>3</sup> was used for single crystal XRD study. To obtain the single crystal XRD data, the single crystal X-ray diffractometer with Mo K<sub>α</sub> radiation was used. The obtained crystallographic data for LLAA crystal are given in the table 1. From the results, it is noticed that the grown crystal of LLAA crystallizes in monoclinic structure with the space group of P2<sub>1</sub>. It is known that this space group is a non-centrosymmetric space group and hence it satisfies the condition for second order nonlinearity. Also, this crystal can give third order NLO and other higher order NLO properties.

Table 1: Single crystal XRD for L-lysine acetic acid (LLAA) crystal

X-ray radiation	Mo K <sub>α</sub> radiation
Wavelength	0.71073 Å
Temperature	293(3) K
Symmetry	Monoclinic
Space group	P2 <sub>1</sub>
a	7.539(4) Å
b	5.421(3) Å
c	12.658(2) Å
α	90°
β	92.11°
γ	90°
V	516.95(2) Å <sup>3</sup>
Z	2
Density	1.545 g/cc

### 4.2 Floatation method

Floatation method was adopted to find the density of the grown crystal of LLAA. In this method, a small piece of grown crystal is sufficient and xylene (density: 0.864g/cc) and carbontetrachloride (density: 1.602 g/cc) were used for the experiment. After mixing the xylene and carbon tetrachloride in a suitable proportion in a specific gravity bottle, the small piece of crystal was immersed in a mixture of the liquids. When the sample was attained in a state of mechanical equilibrium, the density of the crystal would be equal to the density of mixture of liquids.

The density was calculated using the relation  $\rho = \frac{w_3 - w_1}{w_2 - w_1}$  where  $w_1$  is the weight of empty specific gravity bottle,  $w_2$  is the weight of the specific gravity bottle with full of water and  $w_3$  is the weight of the specific gravity bottle full of the mixture of xylene and carbon tetrachloride. By this method, the density of LLAA crystal was found to be 1.552 g/cc and this value is observed to be in good agreement with the density value of LLAA crystal obtained by XRD method.

**4.3. EDAX studies for identifying elements**

EDAX means energy dispersive analysis by X-rays and it is a technique used for identifying the elemental composition of the sample. Usually, EDAX analysis system works as an integrated feature of a scanning electron microscope. In this technique, the sample is hit by electrons coming from the electron gun of the scanning electron microscope and the electrons in the atoms of the sample are knocked off. In this process X-rays are generated and the EDAX spectrum is recorded between the intensity and energy of the emitted X-rays. In the EDAX spectrum, there are many peaks and each peak corresponds to the element of the sample [13]. The EDAX spectrum was recorded using an EDAX analyser fitted with SEM and it is given in the figure 2. From the EDAX spectrum, it is ascertained that the elements like carbon, oxygen and nitrogen are in the grown L-lysine acetic acid crystal. The weight percentage and atomic weight percentage of the elements in the sample are given in the table 2.

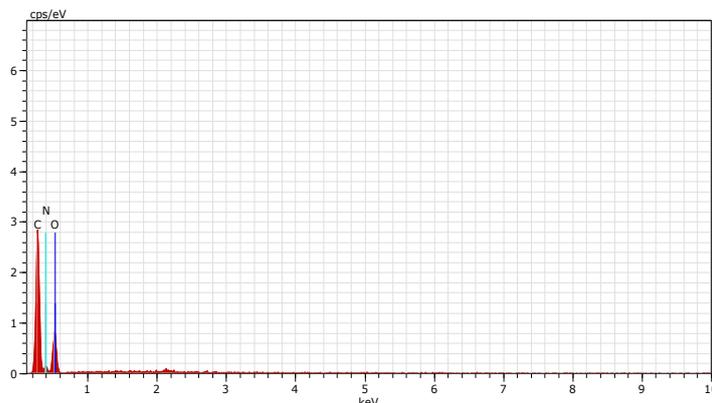


Fig.2. EDAX spectrum of the grown LLAA crystal

Table 2: Data obtained from EDAX spectrum for LLAA crystal

Element	Atomic number	Series	weight %	Atom%
C	6	K-series	54.67	60.79
O	8	K-series	33.70	28.13
N	7	K-series	11.63	11.08

#### 4.4 Identification of chemical groups by FTIR

Fourier transform infrared spectroscopy is an advanced technique useful for characterization of samples and it gives information about the composition and the structure of molecules. The advantages of FTIR technique are high sensitivity, high resolution, high precision, quickness of measurement, non-destructiveness, measurement under ambient atmosphere and the capability of providing detailed structural information. If a molecule has permanent dipole moment, it usually gives infrared absorption bands. The change in the dipole moment of the molecule during the vibration is responsible for producing infrared bands and the infrared spectrum is recorded using an FTIR spectrometer. The recorded FTIR spectrum of LLAA crystal is presented in the figure 3. The results indicate that broad band around  $3200\text{-}3000\text{ cm}^{-1}$  corresponds to  $\text{NH}_3^+$  stretching and the peaks at  $2993\text{ cm}^{-1}$  and  $2132\text{ cm}^{-1}$  are due to asymmetric and symmetric CH stretching modes. The absorption peak at  $1548\text{ cm}^{-1}$  is related to  $\text{NH}_3^+$  deformation and  $\text{COO}^-$  stretching. The  $\text{COO}^-$  deformation mode is noticed to be at the absorption peak at  $1397\text{ cm}^{-1}$ . The absorption peaks at  $1285$  and  $1091\text{ cm}^{-1}$  are corresponding to CH vibrational modes. The peaks at  $711$  and  $649\text{ cm}^{-1}$  are due to  $\text{COO}^-$  deformation modes. The spectral assignments to the absorption peaks in the FTIR spectrum of LLAA crystal are provided in accordance with the data reported in the literature [14,15]. The complete spectral assignments for the sample are given in the table 3.

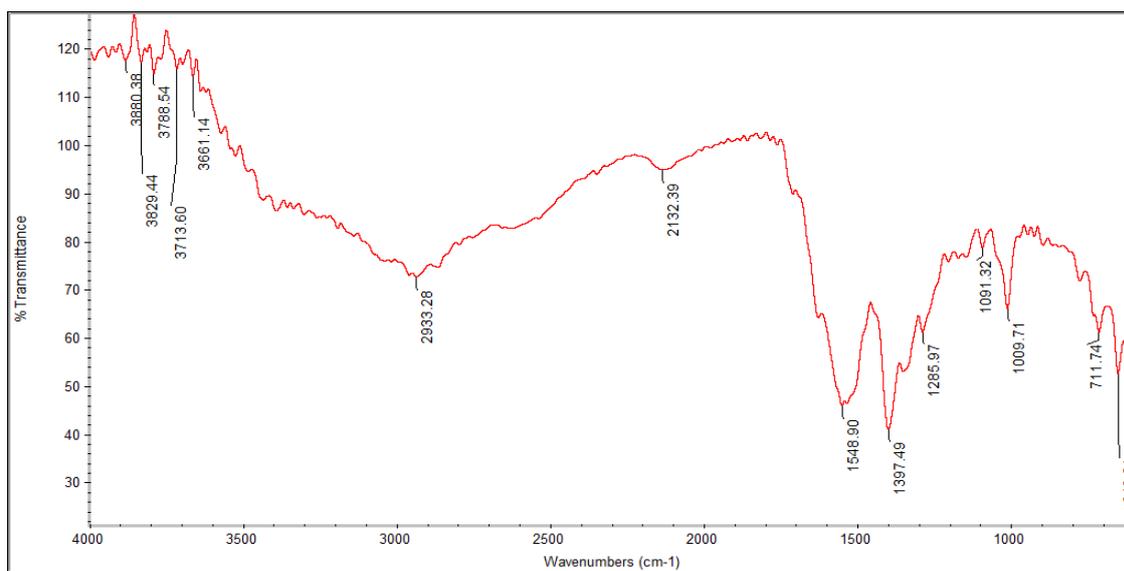


Fig.3: FTIR spectrum of LLAA crystal

Table 3: FTIR spectral peaks and their assignments for LLAA crystal

FTIR peaks/bands (cm <sup>-1</sup> )	FTIR assignments
3661	OH stretching
3200-3000	NH <sub>3</sub> <sup>+</sup> stretching
2933	CH asymmetric stretching
2132	CH symmetric stretching
1548	COO <sup>-</sup> stretching and NH <sub>3</sub> <sup>+</sup> deformation
1397	COO <sup>-</sup> deformation
1285	CH twist
1091	CH rocking
1009	C-C stretching
711	COO <sup>-</sup> scissoring
649	COO <sup>-</sup> wagging

#### 4.5 PL studies

In photoluminescence (PL) spectroscopy, the absorbed light has shorter wavelength and emitted light from the sample has longer wavelength and this kind of luminescence is the spontaneous emission of light radiation during the transition of the system from the higher excited state to the ground state. The PL spectrum of L-lysine acetic acid crystal was recorded using the photoluminescence spectrometer and it is shown in the figure 4. Here excitation wavelength used was 240 nm and the emission spectrum of the sample consists of four luminescence peaks and they are observed in the spectrum at 407 nm, 489 nm, 537 nm and 740 nm. When the grown LLAA crystal is excited at 240 nm, UV light is absorbed and the emitted radiations noticed are UV light, visible light and near infrared radiations.

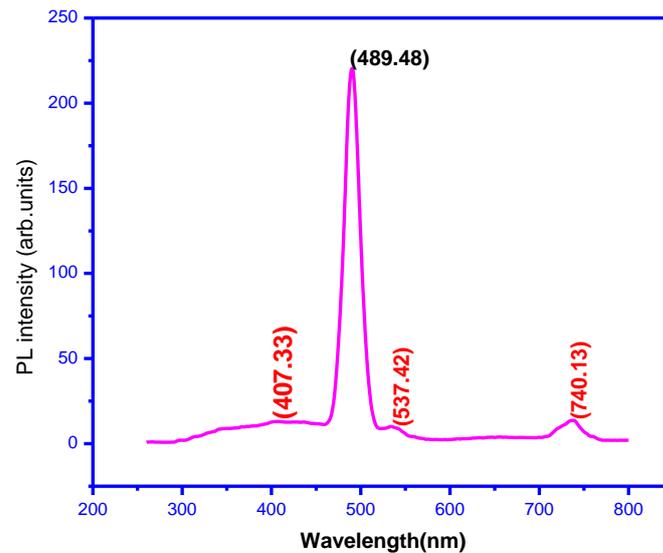


Fig.4: PL spectrum of LLAA crystal

#### 4.6 Mechanical studies

The mechanical properties of the crystals are controlled by various defects like vacancies, interstitials, dislocations and interfaces and these properties can be analysed by measuring microhardness at various applied loads. The microhardness of the sample was measured by using the Vickers microhardness tester. In this experiment, a pyramidal indenter was used. By applying loads, the average diagonal indentation was measured and using these values, the microhardness number was determined. The obtained values of average diagonal indentation are given in the figure 5. The results indicate that the average diagonal indentation value increases with increase of the applied load on the surface of the sample. Using the values of average diagonal indentation, the microhardness number ( $H_v$ ) of the grown LLAA crystal was calculated using the formula  $H_v = 1.8544 \times P / d^2$  where,  $P$  is the applied load and  $d$  is the diagonal length of indentation [16]. The plot of microhardness versus applied load for LLAA crystal is shown in the figure 6. It is observed that the hardness increases with increase of the applied load and this is due to reverse indentation size effect. Mayer's law relates the applied load ( $P$ ) and the diagonal length ( $d$ ) as  $P = a d^n$  where 'a' is an arbitrary constant and 'n' is work hardening coefficient of the sample material. The graph of  $\log(d)$  versus  $\log(P)$  in figure 7 shows a straight line and the slope gives the value of work hardening coefficient and value found is to be 3.1057. As this value is more than 1.6, the grown crystal of LLAA is a soft material. Some other mechanical parameters like plastic deformation or resistance pressure and the corrected indentation size independent hardness can be obtained by using the Hays-Kendall's method. The relation used in Hays-Kendall's method is  $P = W + A d^2$  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. The values of  $W$  and  $A$  are obtained from the plot drawn between  $P$  versus  $d^2$  as shown in the figure 8.

The value of  $W$  is obtained to be  $-25.668$  g and this value is observed to be negative and hence LLAA crystal exhibits the behaviour of the reverse indentation size effect. From the graph, the slope value obtained is  $A = 0.0585$   $\text{g}/\mu\text{m}^2$  and the corrected indentation size independent hardness ( $H_0$ ) is calculated using the relation  $H_0 = 1.8544 A$ . The calculated value of  $H_0$  for LLAA crystal is  $0.1084$   $\text{g}/\mu\text{m}^2$  for LLAA crystal [17].

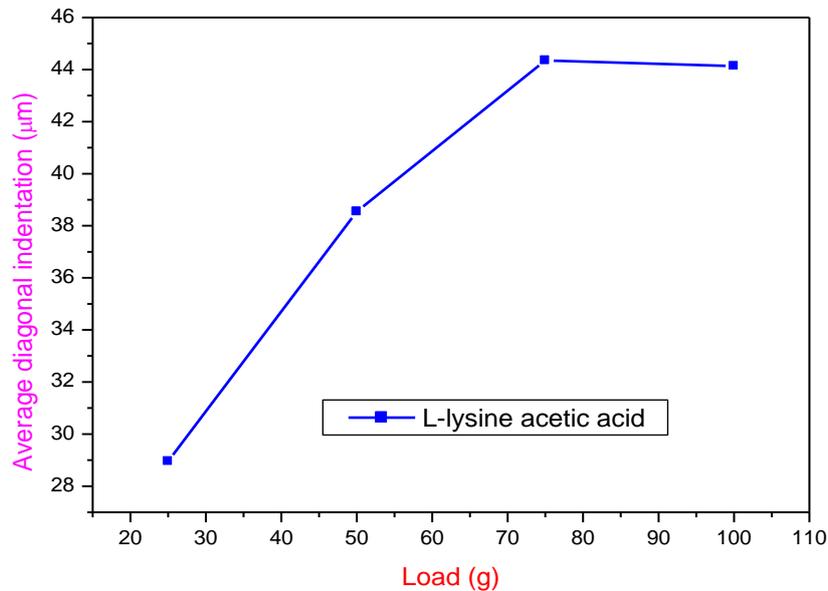


Fig.5: Plot of average indentation diagonal length versus applied load for LLAA crystal

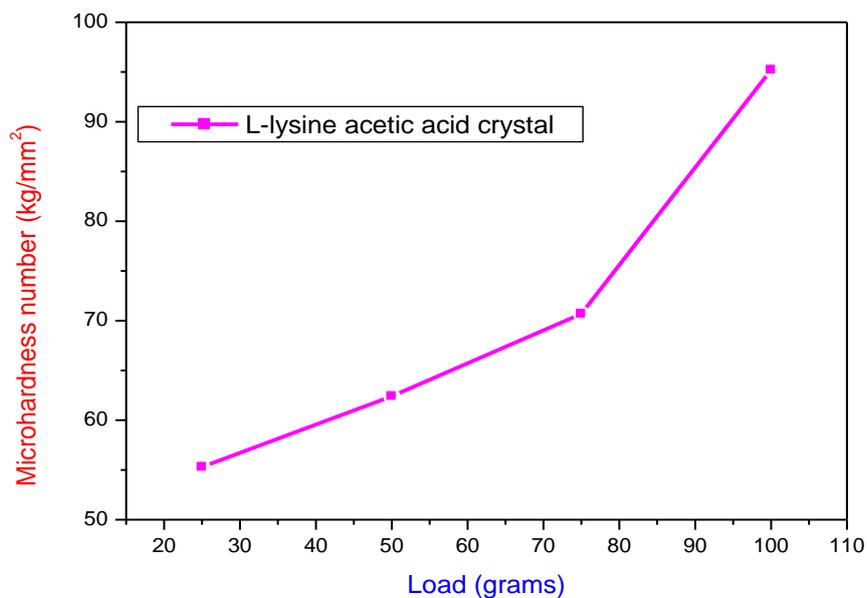


Fig.6: Plot of microhardness versus applied load for LLAA crystal

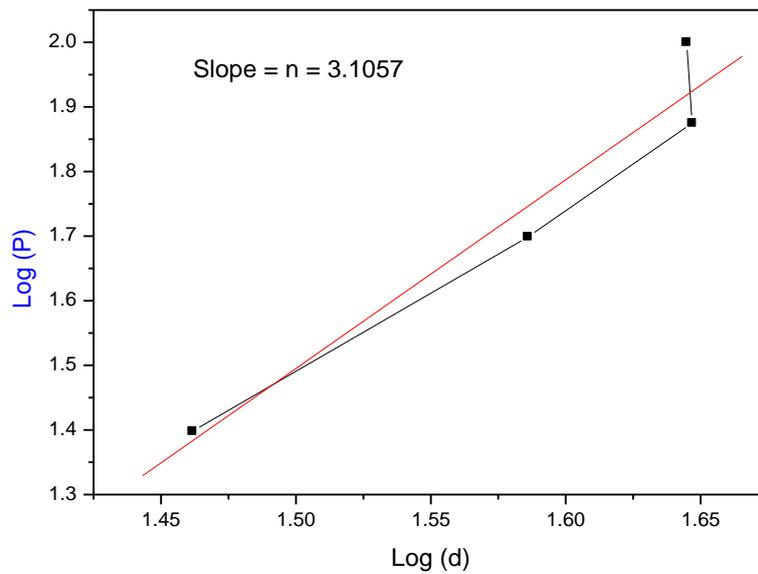


Fig.7: Plot of log (P) versus log (d) for LLAA crystal

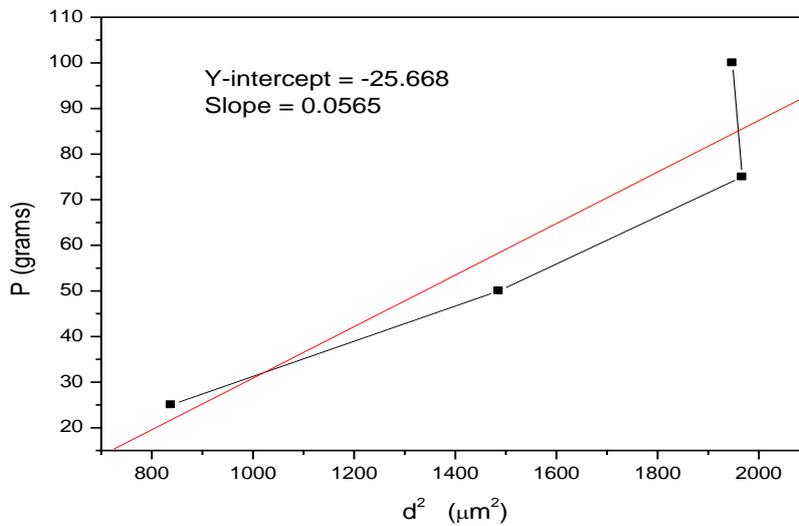


Fig.8: Plot of P versus d<sup>2</sup> for LLAA crystal

Yield strength is defined as the maximum stress that can be developed in a material without causing plastic deformation and it is also called as the yield stress. It is related to the yield point and it is the point on the stress-strain curve that indicates the limit of elastic behavior and the beginning of plastic behavior. Prior to the yield point the material will deform elastically and will return to its original shape when the applied stress is removed. Once the yield point is passed, some fraction of the deformation will be permanent and non-reversible. Yield strength increases with strain rate and decreases with temperature.

Yield strength depends on microhardness ( $H_v$ ) and work hardening coefficient ( $n$ ) and the relation connecting these parameters is yield strength ( $\sigma_y$ ) =  $(H_v/3)(0.1)^{n-2}$ . Here it is reminded that this relation is applicable when the value of 'n' is greater than 2. Another mechanical property viz., stiffness constant ( $C_{11}$ ) is determined using the relation  $C_{11} = H_v^{7/4}$  where  $H_v$  is the microhardness of the sample. The load dependence yield strength and stiffness constant for L-lysine acetic acid (LLAA) crystal is presented in the figure 9. The results show that the yield strength and stiffness constant of LLAA crystal increase with increase of applied load. It is observed that hardness, yield strength and stiffness constant of LLAA crystal are high and hence LLAA crystal has high mechanical strength and this indicates that there is the tightness of bonding between neighbouring atoms in LLAA crystal [18,19].

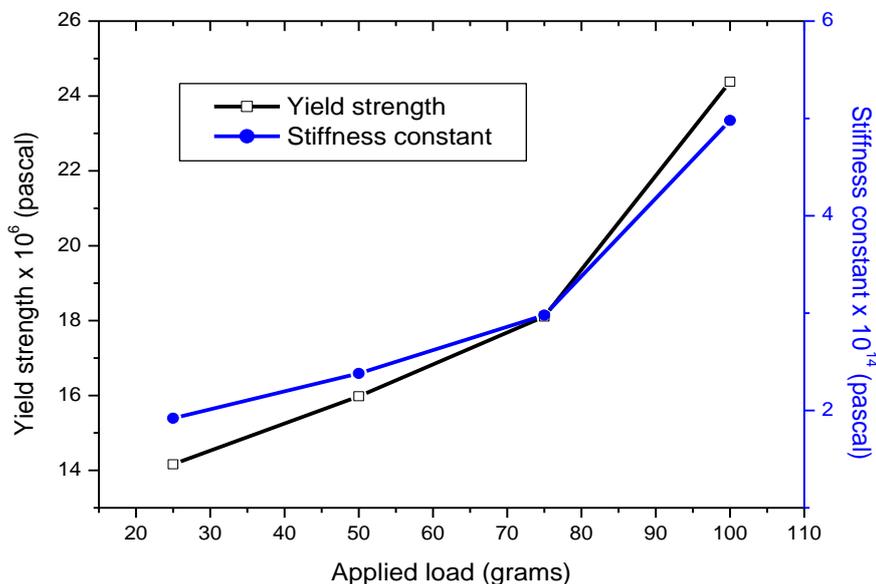


Fig.9: Variations of yield strength and stiffness constant with load for LLAA crystal

#### 4.7 Finding SHG efficiency

The second harmonic generation (SHG) efficiency of the grown LLAA crystal was carried out by Kurtz and Perry powder technique [20]. In SHG, photons are interacted with a nonlinear optical (NLO) material and are effectively combined to produce new photons of twice the energy and hence twice the frequency and half the wave length of the incident photons. The powdered sample of LLAA crystal was subjected to Nd: YAG laser of wavelength of 1064 nm and the emission of green laser light from LLAA crystal indicates that there is SHG process taking place in the sample. The second harmonic emission of 10.15 mJ/pulse for LLAA crystal for an input energy of 0.70 mJ/pulse was obtained.

It is to be mentioned here that SHG emission of 8.90 mJ/pulse from the KDP sample is obtained for the same input energy. Therefore, the relative SHG efficiency of LLAA crystal is 1.14 times more than that of the KDP crystal. Since the relative SHG efficiency is more than 1, LLAA crystal is a good candidate for NLO applications.

## 5. Conclusions

Bulk single crystals of L-lysine acetic acid (LLAA) were grown by solution method. XRD studies indicate that LLAA crystal has monoclinic structure. The density of the grown crystal was found to be 1.552 g/cc. The elements like C, N and O were identified in the sample and weight percentage was calculated. FTIR and PL studies of the sample were carried out. The mechanical properties like hardness, work hardening coefficient, corrected hardness, yield strength and stiffness constant of LLAA crystal were determined by Vickers microhardness analysis. The relative SHG efficiency of LLAA crystal was found to be 1.14 times that of KDP sample.

## Acknowledgment

The authors like to thank the staff members of IIT Madras, Chennai, STIC, Cochin University, Kerala, St. Joseph's College, Trichy, Crescent Engineering College, Chennai and M.S. University, Tirunelveli for the research supports to carry out this work.

## References

1. M.H.Jiang, Q.Fang, 1999, advanced materials, vol. 11, pp.1147 - 1151.
2. A.Chandramohan, R.Bharathikannan, J.Chandrasekaran, P.Maadeswaran, R.Renganathan V.Kandavelu, 2008, J. Crystal Growth, vol. 310, pp. 409-5415.
3. G.Bhagavannarayana, B.Riscob, Mohd.Shakir, 2011, Materials Chemistry and Physics, vol.126, pp. 20-23.
4. Marchewka M K, Debrus S and Ratajczak H, 2003, Crystal Growth Des. vol.3, pp .587.
5. Srinivasan N, Sridhar B and Rajaram R K 2001 Acta Crystallogr, vol.57, pp.888.
6. Suresh, S, Prasad, G. S Vijayan, M, 1994, Int J. Pept. Protein Res. vol. 43, pp.139.
7. Suresh, S. Vijayan, M. 1995, J. Biosci, vol.20, pp. 225.
8. Chandra, N. R Prabu, M. M. Venkataraman, M. M. Suresh, S. Vijayan, M, 1998,Acta Crystallogr. vol.54, pp.257.
9. Pratap, J. V Ravishankar, R. Vijayan, M. 2000, Acta Crystallogr, vol.56, pp. 690.
10. Saraswathi, N. T Manoj, N. Vijayan, M. 2001, Acta Crystallogr,vol.57, pp.366.
11. V. Krishnakumar, R. Nagalakshmi, S. Manohar, L. Kocsis, 2008, Spectrochimica Acta Part A,vol. 71,pp. 471- 479.

12. V.Vasudevan, R.Ramesh babu, A.Reicher nelcy, G.Bhagavannarayana, and K.Ramamurthi, 2011, Bull. Mater. Sci., Vol. 34, pp. 469-475.
13. <http://en.wikipedia.org/wiki/EDAX>
14. G.Socrates, 1980, in infrared characteristic group frequencies, wiley-Interscience, chichester.
15. K.Nakamoto, 1978, Infrared and raman spectra of inorganic and coordination compounds, John wiley and Sons, New York.
16. K.Russel Raj, P.Murugakoothan, 2013, Optik, vol. 124, pp. 2696 - 2700.
17. C. Hays, E.G. Kendall, 1973, An analysis of Knoop microhardness, Metallography, vol.7, pp. 275-282.
18. W.A. Wooster, 1953, Physical properties and atomic arrangements in crystals, Rep. Prog. Phys. vol.16, pp. 62-82.
19. A.A. El-Fadl, A.S. Soltan, N.M. Shaalan, 2007, Cryst. Res. Technol. vol.42, pp 364-377.
20. S.K.Kurtz, T.T.Perry, 1968, J.Appl.Phys.vol.39,pp.3798-3814.