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Growth, Nucleation kinetics, Structural, Spectral and Mechanical studies of L-asparaginium nitrate single crystals

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Abstract: Nonlinear optical (NLO) crystals play vital roles in the emerging field of photonics and optoelectronics. L-asparaginium nitrate (LAN) is an NLO crystal and the single crystals were grown by solution method with slow evaporation technique. Crystals of size 14 x 8 x 7 mm^3 have been obtained in 25 days. The grown crystals were colorless and transparent. Solubility and nucleation kinetic parameters of the grown samples were found out. The lattice parameters of the grown crystals were determined by X-ray diffraction technique. UV-visible transmittance spectrum was recorded to study the optical transparency and band gap of LAN crystal. The nonlinear optical (NLO) property of the grown crystal was confirmed by Kurtz-Perry powder technique. The mechanical strength of the crystal was estimated by Vickers hardness test and the values of stiffness constant and yield strength have been evaluated.
Key words : Crystal Growth; Single crystal; Characterization; NLO; XRD; SHG; Microhardnes; Band gap.

1. Introduction

Amino acid family crystals have over the years been subjected to extensive investigation by several researchers for their nonlinear optical properties [1-4]. In the recent years, efforts have been made on the amino acid mixed organic-inorganic complex crystals, in order to improve the chemical stability, laser damage threshold and nonlinear optical properties [3-7]. L-asparagine is one of the fundamental natural amino acid residues in proteins and it has been believed that it plays an important role in the formation of the secondary structures in proteins due to the fact that the side chain can form efficient hydrogen bonds with the peptide backbone. It is an interesting material to investigate as it crystallizes in structures exhibiting a complex network of hydrogen bonds among asparagines and water molecules [8,9]. Some complexes of L-asparagine have been recently crystallized and various studies have been investigated [10-12]. In this work, an attempt has been made to synthesize and grow L- asparaginium nitrate crystal by solution method. We report here the investigations on growth and structural, spectral and mechanical studies of L- asparaginium nitrate (LAN) single crystals.

2. Experimental methods

2.1. Synthesis and solubility

L asparaginium nitrate (LAN) salt was synthesized by dissolving high purity L-asparagine and nitric acid in the ratio 2:1 in de-ionized water and salt was formed. Re-crystallization was carried out to improve the purity of the synthesized LAN salt. Solubility study was performed using a hot-plate magnetic stirrer and a digital thermometer and the solubility was determined by gravimetrical method [4]. The variation of solubility with temperature for LAN sample is shown in figure 1. From the graph, it is observed that the solubility of

LAN sample in water increases linearly with temperature, exhibiting a high solubility gradient and positive temperature coefficient, which reveals the fact that slow evaporation technique is the appropriate method to grow single crystal of LAN.

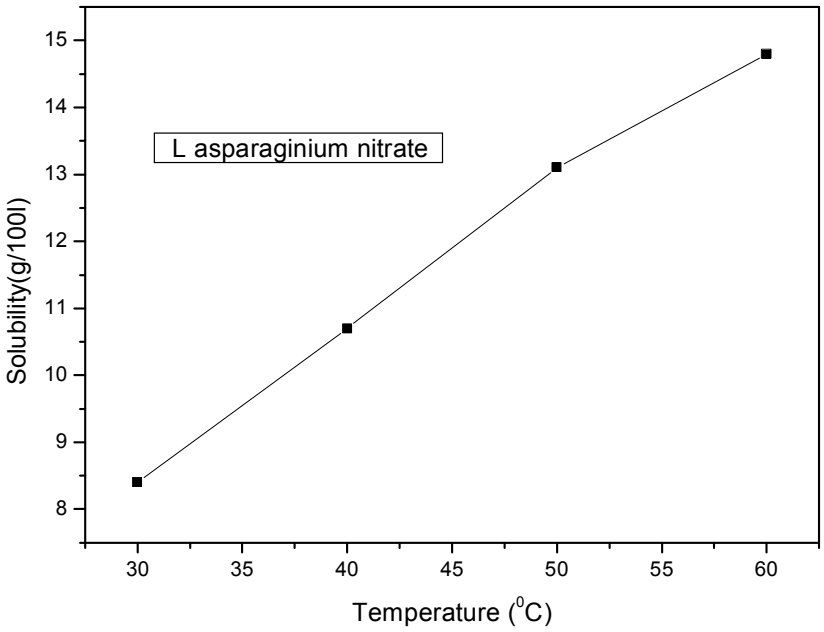

Fig.1: Solubility curve for L-asparaginium nitrate sample

2.2 Nucleation kinetics

To attain the crystal growth, nucleation is an important phenomenon. Crystallization starts with nucleation and control of nucleation is crucial for the control of the number, size, perfection, polymorphism and other characteristics of crystalline materials. When few atoms, ions or molecules join together in a supersaturated solution, a cluster or nucleus is formed and the overall excess free energy change (ΔG) between the nucleus and solute in the supersaturated solution is the Gibbs free energy change. Once the nucleation occurs in the supersaturated solution, the nucleus grows quickly and a bright sparkling particle is seen. The time interval in which the observation of the first sparkling particle in the undisturbed supersaturated solution is called the induction period (τ). The expression for the induction period in terms of Gibbs free energy is given by $ln\ \tau = -B + \Delta G / kT$ where B is a constant, k is the Boltzmann's constant and T is the absolute temperature. The Gibbs free energy will be maximum for a certain value of radius (r^*) of nucleus, which is known as critical radius. Supersaturation ratio S is given by $S = C/C_o$ where C is the supersaturated concentration and C_o is the saturated concentration. The induction period was measured at different supersaturation ratios viz. 1.4, 1.42, 1.44, 1.48 and 1.5 by isothermal method [13]. A plot of $1/ (\ln S)^2$ against $\ln \tau$ forms a straight line and the slope (m) is calculated. After finding the slope (m), the value of interfacial tension (σ) is calculated using the equation $\sigma = (RT/N) [3m/16\pi v^2]^{1/3}$ where R is the universal gas constant, v is the volume of a molecule (v = volume of unit cell / number of molecules per unit cell) and N is the Avogadro's number. The size of the critical nucleus (r^*) and critical Gibbs free energy change (ΔG^*) are given by $r^* = 2 \sigma v N / RT\ ln\ S$ and $\Delta G^* = mRT / [N (ln\ S)^2]$ respectively and the number of molecules in a critical nucleus is found using equation $n = (4/3) (\Delta/v) r^{*3}$. The number of crystals produced in the supersaturated solution is expressed as nucleation rate i.e. the number of crystals produced per unit volume per unit time. The nucleation rate (J) can be calculated using the equation $J = A \exp[-\Delta G^*/(kT)]$ where A is the pre-exponential factor [14]. From the obtained results, it is noticed that the plot of $\ln \tau$ against $1/(\ln S)^2$ is approximately linear (Fig.2) and this explains the classical theory of homogeneous nucleation**.** By linear fit method, the slope (m) is obtained from the figure 2 and using the relevant above equations, the critical nucleation parameters were determined and the values are provided in the table 1. From the results it is observed that the values of ΔG^*, n, r^* decrease with increase in supersaturation ratio (S) and also induction period decreases with increase of supersaturation ratio. The obtained data give idea for the growth of good quality LAN crystals.

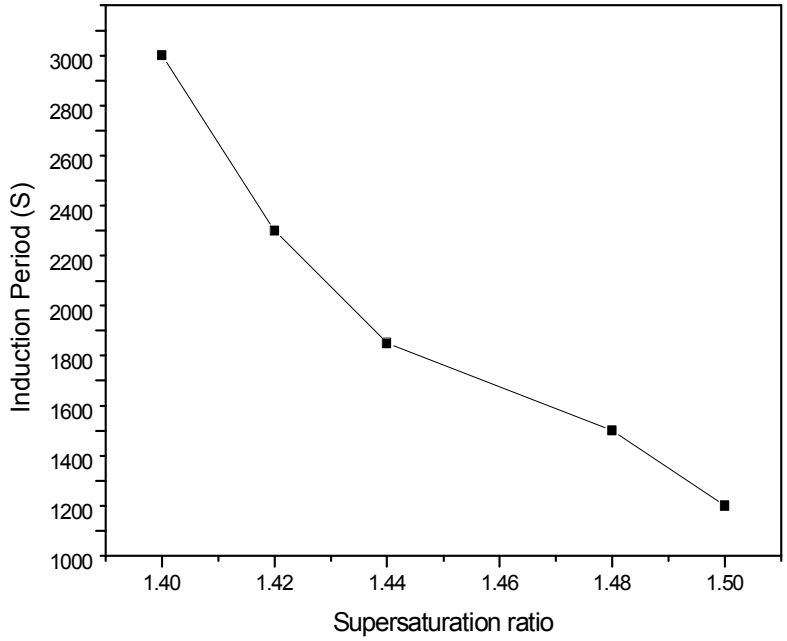

Fig.2: The plot of $1/(\ln S)^2$ versus $\ln \tau$ for LAN crystal

Table 1: Values of nucleation parameters for LAN crystal

Sample	S	σ x10^{-3} (J/m^2)	ΔG^*x10^{-21} J	r^* (nm)	N	J x 10^{23} (nuclei/sec/volume)
LAN crystal	1.4	1.890	13.103	1.210	16	4.35
	1.42		12.064	1.161	14	5.58
	1.44		11.157	1.116	12	6.93
	1.48		9.652	1.038	10	9.94
	1.5		9.023	1.004	9	11.5

2.3 Growth of LAN crystal

Single crystals of LAN were grown by solution method with slow solvent evaporation technique. In accordance with the solubility and the nucleation kinetic data, saturated solution of the re-crystallized salt of LAN was prepared by dissolving the salt in de-ionized water by continuous stirring of the solution using a magnetic stirrer and the saturated solution was filtered using 4 micro Whatmann filter paper. The seed crystals of LAN were obtained by spontaneous nucleation. The supersaturation of the solution was found by observing the first crystal formed at the bottom of the glass beaker due to slow evaporation of the solvent. The supersaturated solution of LAN was carefully transferred into another glass beaker and kept at 30 ^oC in the constant temperature bath. Two or three good quality seed crystals of LAN were placed in the supersaturated solution and the solution was allowed to evaporate the solvent slowly into atmosphere. A typical single crystal with size 14 x 8 x 7 mm^3 was obtained within a period of 20-25 days. Grown crystals are shown in the figure 3 and they are found to be non-hygroscopic at ambient temperature, transparent and colorless.

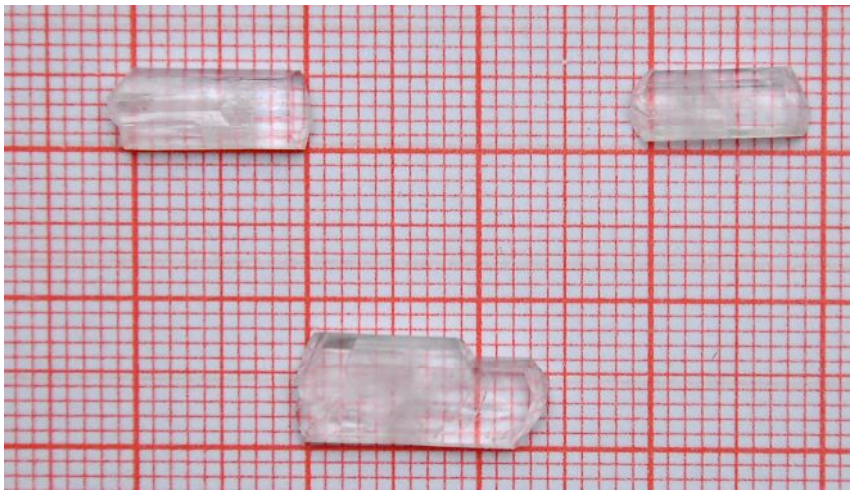

Fig. 3: Grown crystals of L-asparaginium nitrate

2.4. Instrumentation

The grown single crystal of LAN was subjected to single crystal X-ray diffraction studies using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK_{α} (λ=0.71069 Å) radiation to evaluate the lattice constants. The transmission properties of the crystals were examined using Lambda 35 model Perkin Elmer double beam UV-vis-NIR spectrometer in the range from 190 nm to 1100 nm. Optically polished single crystal of thickness 1.5 mm was used for this study. To confirm the nonlinear optical property, Kurtz and Perry powder SHG test was carried out for the grown crystal using Nd:YAG Q-switched laser which emits the first harmonic output of 1064 nm [15]. Microhardness analysis was carried out using Vickers microhardness tester fitted with a diamond indenter and two trials have been carried out to ascertain the correctness of the values.

3. Results and discussion

3.1. X-ray diffraction (XRD) analysis

The X-ray diffraction analysis on the grown LAN crystal was used to confirm the crystallinity and identification of the unit cell parameters. The grown LAN crystal has been subjected to single crystal X-ray diffraction study to obtain the crystallographic data which reveals that LAN crystal crystallizes in triclinic structure. The obtained single crystal XRD data for the grown crystal of this work are provided in the table 2 and these data are found to be good agreement with the reported literature [10].

Table 2: Crystallographic data for LAN crystal

Temperature	293(3) K
Symmetry	Triclinic
Space group	P1
a	5.371(2) Å
b	8.234(3) Å
c	10.185(1) Å
α	97.5°
β	88.4°
γ	101.35°
Volume	450.50 $Å^3$

3.2 Optical transmission spectral analysis

The UV-vis-NIR transmittance spectrum of LAN single crystal is shown in the figure 4. Low absorption in the entire visible and near infrared region with the low cut-off wavelength at 242 nm suggests that the material is quite suitable for SHG generation and other related optoelectronic applications.The optical absorption coefficient(α) was calculated from transmittance using the following relation [16]

$$\alpha = \frac{1}{d} log\left(\frac{1}{T}\right)$$

where T is the transmittance and d is the thickness of the crystal. The variation of optical absorption coefficient with wavelength for LAN crystal is shown in the figure 5. In addition to absorbance and transmittance, the crystal also reflects the light and the variation of reflectance with wavelength for LAN sample is shown in the figure 6.

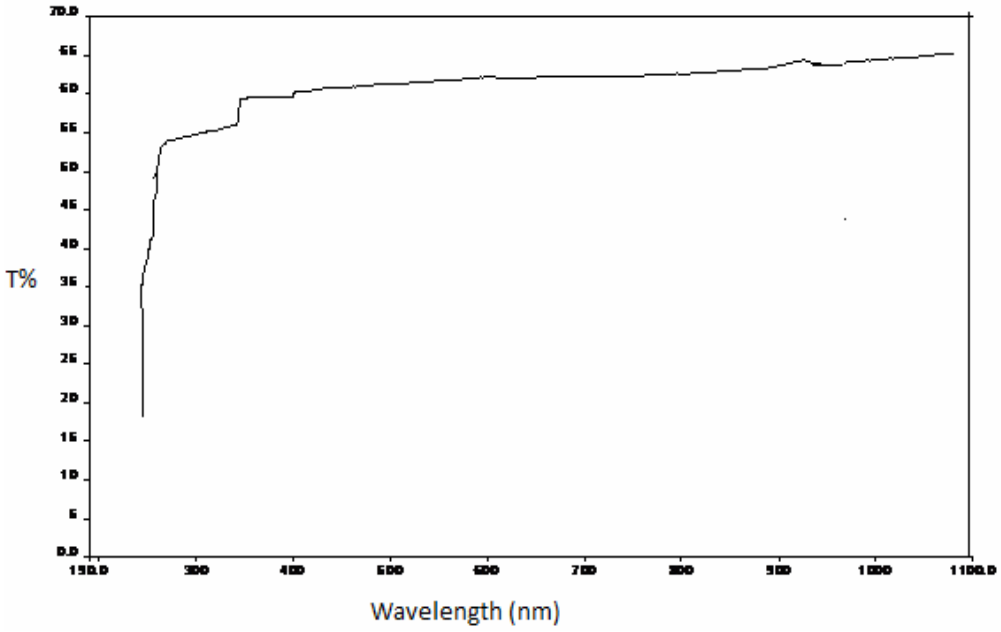

Fig.4:UV-visible transmittance spectrum of LAN crystal

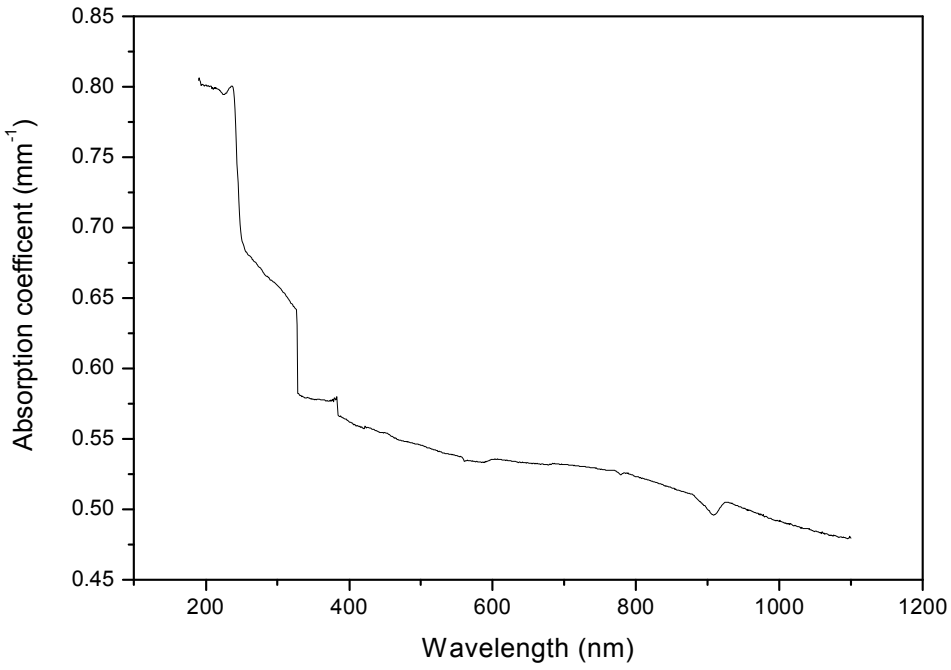

Fig.5: Variation of absorption coefficient with wavelength for LAN sample

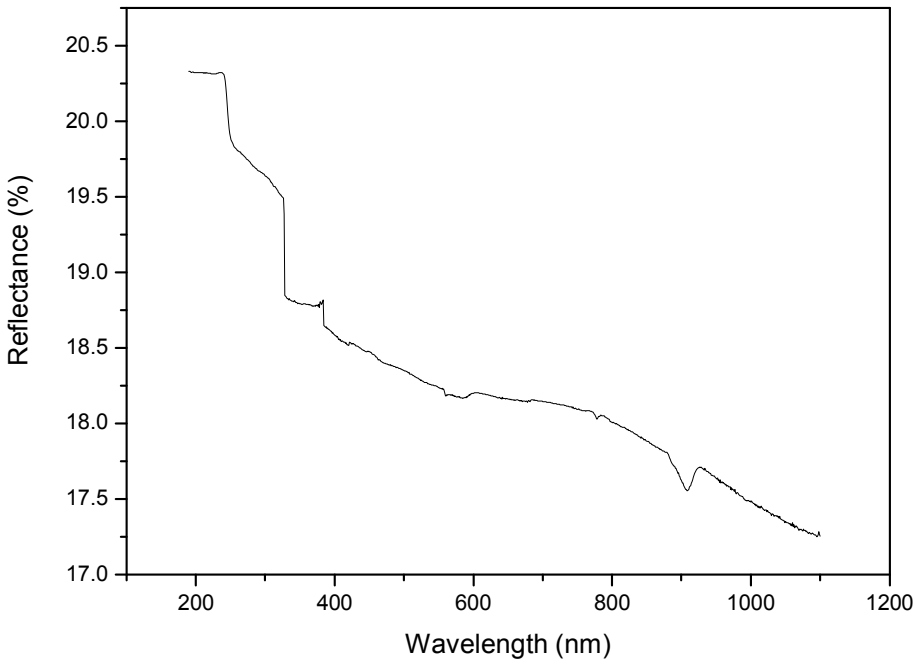

Fig. 6: Plot of reflectance versus wavelength for LAN crystal

3.3 Kurtz-Perry powder technique

The second harmonic generation (SHG) behaviour of the powdered material was tested using the Kurtz and Perry method. A high intensity Nd:YAG laser (λ=1064 nm) with a pulse duration of 6 ns was passed through the powdered sample. The SHG behaviour was confirmed from the output of the laser beam having the green emission (λ=532 nm) and thus it is a potential material for frequency conversion.

3.4 Vickers microhardness analysis

A well polished LAN crystal of 1.5 mm thick was placed on the platform on the Vickers microhardness tester and the loads of different magnitude were applied over a fixed interval of time. The hardness was calculated using the relation $H_v = 1.8544\ P/d^2\ kg/mm^2$, where P is the applied load in g and d is the diagonal length of the indentation impression in millimetre [17]. The variation of hardness number (H_v) with load (P) for LAN crystal is shown in the figure 7. The hardness increases gradually with the increase of load. The relation between load and size of the indentation is given by well known Mayer's law $P = ad^n$. Here a and n are constants depending upon the material. By plotting log(P) verses log(d), (Fig.8), the value of the work hardening coefficient n was found to be 1.75. As the value of n is more than 1.6, LAN crystal belongs to category of soft materials. Yield strength of the material can be found out using the relation, $\sigma_y = (H_v/3)$ where σ_y is the yield strength and H_v is the hardness of the material. A graph is drawn between yield strength and load as shown in the Fig. 9. It is observed that yield strength increases with increase of load and hence the grown LAN crystal has relatively high mechanical strength. The elastic stiffness constant (C_{11}) for different loads was calculated [18] using Wooster's empirical formula $C_{11} = H_v^{7/4}$ and variation of stiffness constant with the load is given in Fig.10 which gives an idea about the measure of resistance of plastic to bending and tightness of bonding between neighboring atoms.

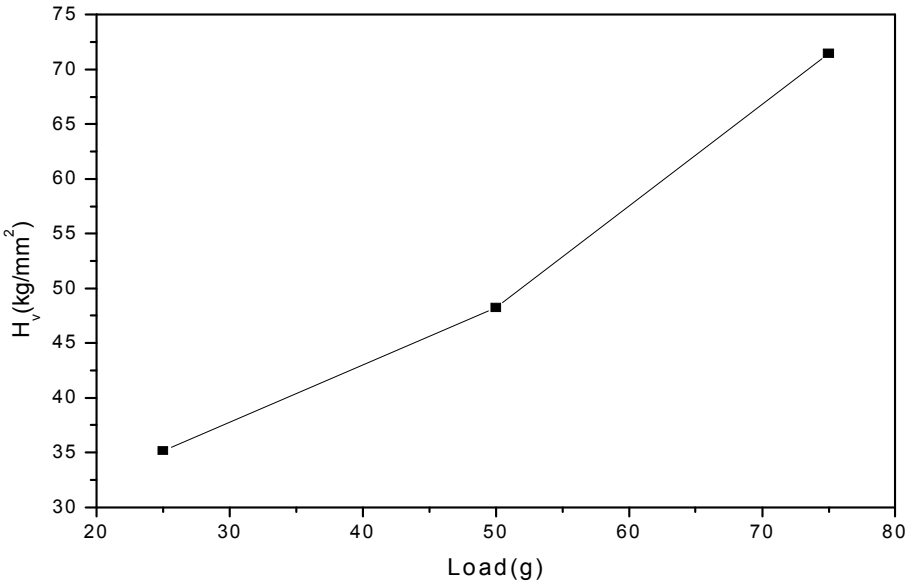

Fig.7: Variation of H_v with applied load for LAN crystal

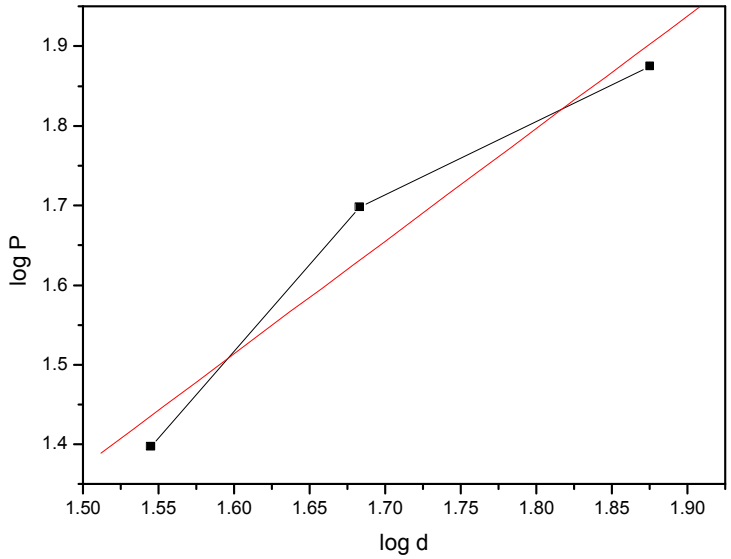

Fig.8: Variation of log P with log d for LAN crystal

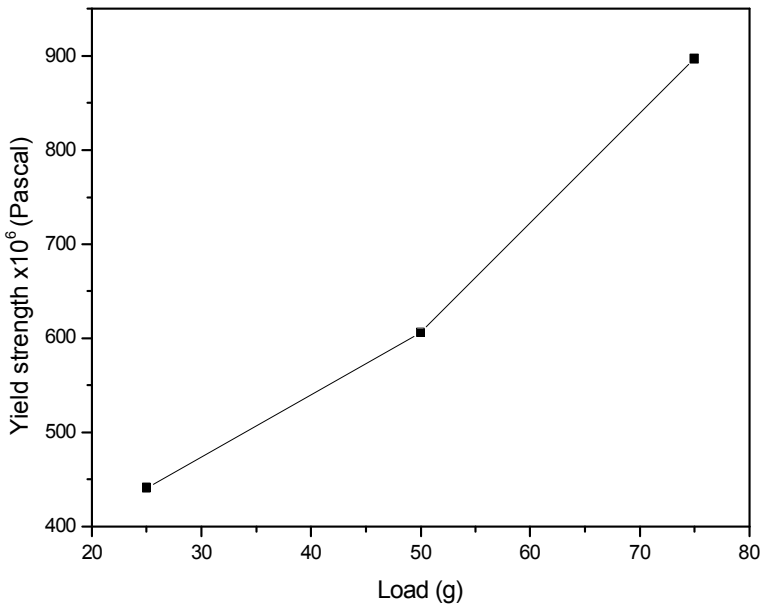

Fig.9: Variation of yield strength with the load for LAN crystal

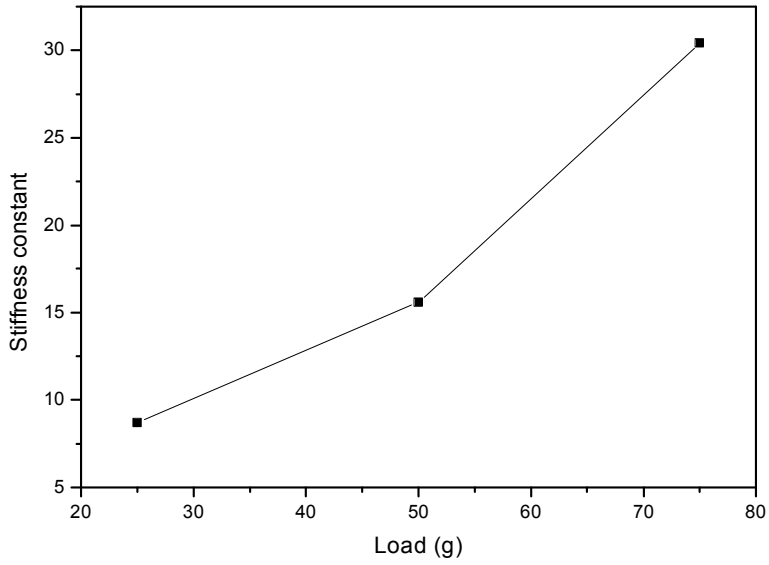

Fig.10: Plot of striffness constant versus load for LAN crystal

4. Conclusion

Good quality single crystals of L-asparanium nitrate (LAN) has been grown by slow evaporation technique and the solubility of LAN sample was estimated for water solvent at different temperatures. Critical nucleation parameters for the LAN sample were evaluated. The X-ray diffraction study confirms the triclinic structure of the grown LAN crystal. The optical studies reveal that LAN crystals possess about 63% of transmittance. SHG studies reveal that LAN crystal is a promising candidate for NLO applications. Vickers microhardness value was calculated in order to understand the mechanical strength and values of yield strength and stiffness constant were determined for LAN crystal at different loads.

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