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Physical and chemical properties of L-alanine potassium nitrate single crystal

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Abstract
L-alanine potassium nitrate (LAPN) single crystal was grown by slow evaporation solution growth technique. The lattice parameters of the grown crystals were determined by X-ray diffraction technique. Fourier transform infrared (FT-IR) study reveals that the functional groups present in the crystal. The UV-Vis-NIR studies were carried out to find the transmittance and other optical parameters. The Vicker's microhardness test was carried out to estimate the mechanical strength of the grown crystals. Further elastic stiffness constant (C_{11}), yield strength (σ_y) and the Vicker's parameter such as work hardening coefficient (n) were estimated using microhardness studies. Thermal stability of the grown crystals was confirmed by Thermogravimetric Analysis (TGA).

Keywords: Lattice parameters X-ray diffraction, UV-Vis-NIR, TGA, yield strength

Introductions

Recently, the growing of single crystals has helped advance modern technology. Nonlinear optical (NLO) materials have been studied extensively for their possible applications and are expected to play a major role in photonic technology such as telecommunication, optical computing, optical data storage and optical information processing [1-3]. Amino acid family crystals are playing an important role in the field of non-linear optical organic molecular crystal. They are interesting materials for non-linear optical application as they contain proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH_2) group in them [4]. Some amino acids like L-arginine, L-lysine, L-alanine and γ-glycine are evidently showing non-linear optical activity because they have a donor NH_2 group and acceptor COOH group and also intermediate charge transfer is possible [5]. L-alanine (LA) is the smallest, naturally occurring chiral amino acid with a nonreactive hydrophobic methyl group (-CH_3) as a side chain. L-alanine has the zwitterionic form (+NH_3-C_2H_4-COO–) both in crystal and in aqueous solution over a wide range of pH, which favours crystal hardness for device application [6, 7]. Among various organic materials, amino acids exhibit specific features of interest like (i) molecular chirality, (ii) lack of strongly conjugated bonds (leads to wide transparency in the entire visible range), (iii) high hardness (due to zwitterionic nature) that makes it a potential candidate for various NLO applications [8]. Interests have been shown in growing semi-organic NLO crystals due to the combination of excellent mechanical and thermal properties with high optical nonlinear efficiency [9].

In the present work, we report the growth of single crystal of L-alanine potassium nitrate (LAPN) by slow evaporation solution growth technique. The material (LAPN) was synthesized by taking L-alanine and potassium nitrate in the ratio 1:1. The starting materials were dissolved in double distilled water and stirred well for about 5 hrs at 40℃. Prepared solution was filtered using Whatmann filter paper, then the solution was transferred to a petridish and allowed to undergo slow evaporation. The photograph of the grown LAPN crystal is shown in the Fig 1.

Fig 1: Photograph of L-alanine potassium nitrate

Result and Discussion

In the present study, the powdered samples were analyzed by employing CuKα (λ=1.5405 Å) radiation of X-ray. The standard unit cell parameter of LAPN was given as reference and the unit cell parameters were calculated by the software with assignment of different planes to Bragg reflections. The powder X-ray diffraction pattern of the grown LAPN crystal is shown in Fig 2. Powder X-ray diffraction study confirms that grown crystal crystallizes into the orthorhombic crystal system with lattice parameters a = 4.78 Å, b = 5.25 Å, c = 11.42 Å and the volume V = 467 $Å^3$. The crystalline size (Listed in Table 1) of the crystal was determined by Debbie Scherer formula and using the following relation:

$$D = k\lambda/\beta\cos\theta \quad (1)$$

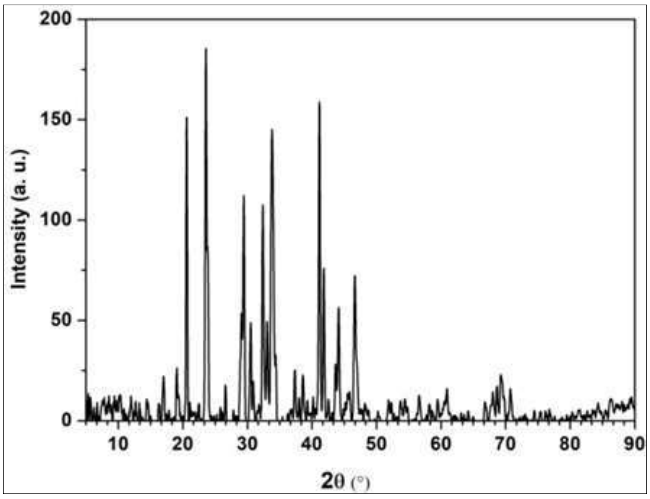


Fig 2: PXRD pattern of L-alanine potassium nitrate

Table 1: Crystalline size of the crystal

2θ	FWHM	Crystalline size D (nm)	D (nm) Average
41.15991	0.26314	32.24835853	
20.60103	0.21416	37.70275018	
23.61873	0.39015	20.80244583	
29.36876	0.47167	17.41161389	
32.40433	0.27748	29.81426068	26.16838849
33.85062	0.48354	17.17329501	
41.83027	0.25069	33.92500398	
44.1162	0.33848	25.32411935	
46.67555	0.40979	21.11364896	

In order to analyze the presence of functional groups, the Fourier Transform Infrared (FTIR) spectrum of the grown crystal has been recorded in the range of 400-4000 cm^{-1} using a Perkin Elmer FTIR spectrometer by KBr pellet technique and is shown in Fig 3. The presence of O-H stretching vibration is indicated due to the peak at 3309.02 cm^{-1}. The band observed at 1013.63 and 918.43 cm^{-1} is due to Overtone of torsional oscillation of NH_3^+. The peaks in the range 1013-1100 cm^{-1} are due to the addition of nitrate in the grown material. Hence, the presence of COO^- and NH_3^+ indicates the characteristics of amino acid group material. The peak observed at 465.17 cm^{-1} is corresponds to NH_3^+ in plane rocking. The band assignments and the corresponding wavenumbers of the FTIR spectrum of LAPN Crystal are given in the Table 2.

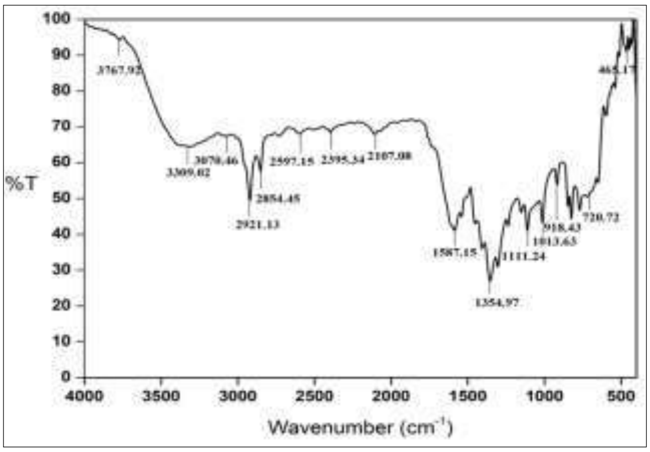
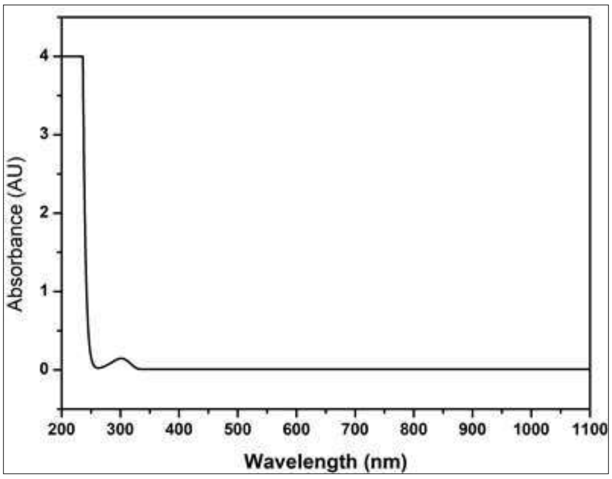


Fig 3: FTIR spectrum of L-alanine potassium nitrate

Table 2: Band assignments of LAPN crystal

Wavenumber (cm^{-1})	Band Assignments
3309.02	O-H stretching
3070.46	NH_3^+ stretching
2921.13	C-H stretching
2854.13	NH_3^+ asymmetric stretching
2597.15	NH_3^+ symmetric stretching
1587.15	NH_3^+ bending
1354.97	NO_3 stretching
1111.24	NH_3^+ asymmetric stretching
1013.63	Overtone of torsional oscillation of NH_3^+
918.43	Overtone of torsional oscillation of NH_3^+
770.49	NO_3 stretching
650.58	COO^- in plane deformation
539.87	Torsional oscillation of NH_3^+
465.17	NH_3^+ in plane rocking

The UV-Vis analysis gives the valuable information about molecules absorption and transmission which involves the promotion of σ and π electron from ground state to higher energy state. Optical absorbance and transmittance are most important properties for scintillator detectors. Perkin-Elmer lambda-35 spectrometer was used to measure the absorbance spectrum of the LAPN single crystal with the wavelength ranging from 200 to 1100 nm. UV analysis reveals that there is no transmittance up to 301 nm, and the optical band gap was estimated to be 4.1eV. The crystal absorbs the entire portion of UV region which explains the transition of an electron from π-$\pi*$ energy levels. The cut-off wavelength is around 301 nm, and the crystal can transmit in the entire visible and NIR regions.



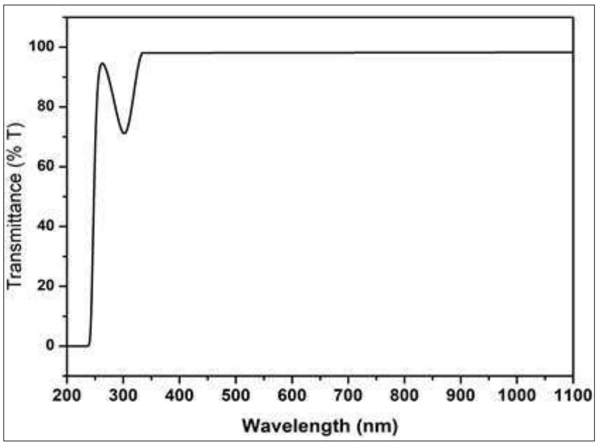


Fig 4: UV-VIS-NIR spectra of L-alanine potassium nitrate

Thermogravimetric analysis (TGA) of LAPN crystals were carried out in the temperature range of 24–800 °C in inert nitrogen atmosphere at a heating rate of 10 C/min. The TGA curve of LAPN is shown in Fig 5, In TG curve, it is shown that there is no weight loss and phase change in between 24 °C and 211.76 °C. It starts to decompose in two stages: during the first stage, there is little weight loss 0.2% of the initial mass between 211.76 °C and 513.24 °C, which is due to the evaporation of the solvent and volatile substances. In the second stage, 1.6% weight loss occurs in between the 513.24 °C-800 °C.

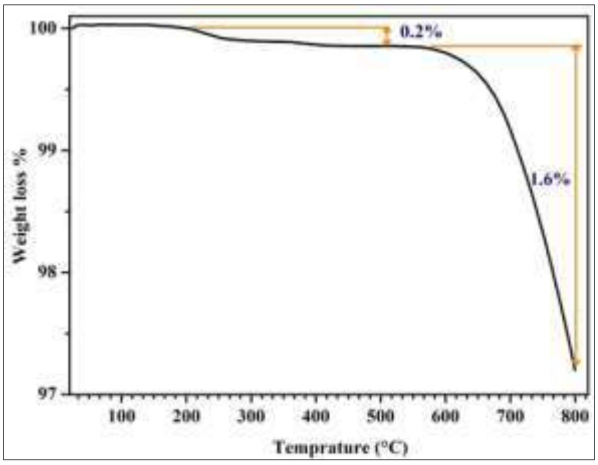


Fig 5: TG curve of L-alanine potassium nitrate

Vicker's microhardness measurement is one of the suitable methods for the analysis of mechanical property for crystal. The hardness of the solid crystal depends on the structure, number of bonds per unit volume, interatomic spacing, lattice energy and heat formation and the composition of crystalline solids [10, 11]. Calculation of microhardness on various loads gives more information about the mechanical properties of the solid such as resistance, yield strength and stiffness constant. Vickers hardness tester fitted with pyramidal diamond indenter at the room temperature. In the present study applied load P was varied in the range of 25-100 g with depression time of 10 s for each depression. The average two diagonal lengths (d) of depression mark were measured through the microscope attached to it. The Vickers microhardness value (Hv) (Table 3) was calculated using the relation [2],

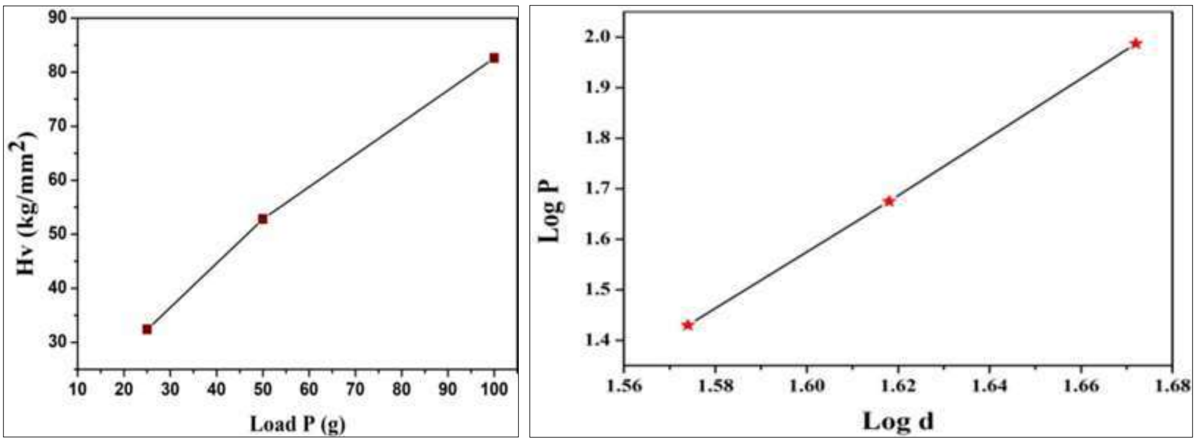
$$Hv = 1.8544 \frac{P}{d^2} \text{ (Kg/mm}^2\text{)} \quad (2)$$

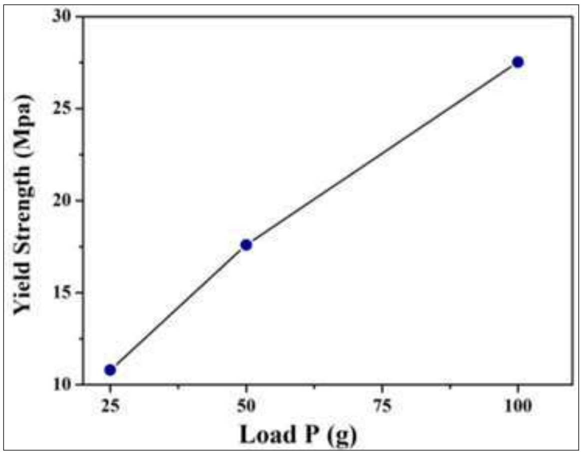
where 1.8544 is a constant called geometrical factor for pyramidal indenter, d is the diagonal length of depression and P is the applied load. The graph (Fig 6a) is a plot against the hardness value with varying load. It is clearly shown that the grown crystal LAPN undergoes a reverse indentation size effect (RISE) which means that Hv increase with the increase of applied load (P). The increase in hardness value is due to the work hardening of surface layers, and the RISE may be subjected to the generation of cracks around the indentation [12]. The work hardening coefficient (Meyer's index number) is 5.7 calibrated by the least square fitting (Fig 6b). Thus, the calibrated value suggests that this grown crystal belongs to soft material category [13]. Using Hv and Mayer's index value (n), the yield strength (Fig 6c) of the grown crystal was measured by following relation [3],

$$\sigma_y = \frac{H_v}{3} \quad (3)$$

The elastic stiffness constant (Fig. 9d) gives an idea about the nature of bonding between neighbouring atoms. It can be measured by the Wooster's empirical formula [14],

$$C_{11} = H_v^{(7/4)} \quad (4)$$





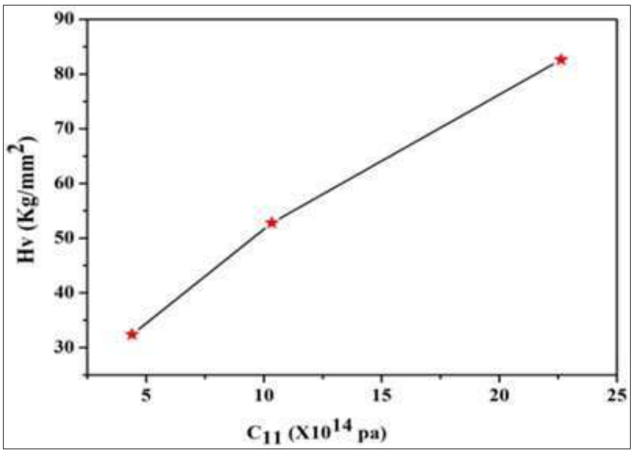


Fig 6: (a) Hardness value (b) Mayer's plot, (c) Yield strength, (d) Stiffness constant

Table 3: H_v, Elastic stiffness constant, yield strength and H_k values of LAPN crystal

Load p (g)	H_v (kg/mm^2)	C_{11} x10^{14}(Pa)	Yield strength (MPa)
25	32.4	4.40	10.8
50	52.8	10.34	17.6
100	82.6	22.63	27.53

Conclusion

High quality optically transparent single crystals of L-Alanine potassium nitrate (LAPN) were grown by slow evaporation technique. The grown LAPN crystal possessed an orthorhombic structure and the crystalline quality was assessed from the sharp peaks in the XRD patterns. Various functional groups presented in the grown crystal were identified using the FTIR spectrum. The crystal exhibited about 98% of transparency in the visible region and had a UV cut-off wavelength of LASS at 301 nm recommends that material is a potential candidate for NLO applications. The TGA studies ascertain the thermal stability of the sample of LAPN up to 211 °C. Microhardness measurements on the grown crystals revealed the increase of Vicker's hardness for various applied load signified the presence of rising effect and the high stiffness constant revealed the better hardness property of the grown LAPN crystal. The mechanical study shows that the title crystal belongs to soft material category (n = 5.7). The Vicker's hardness (Hv) value increases with increasing load and crack develop above 100 g. From Vicker's hardness measurement yield strength and elastic stiffness constant was calculated for the device fabrication.

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