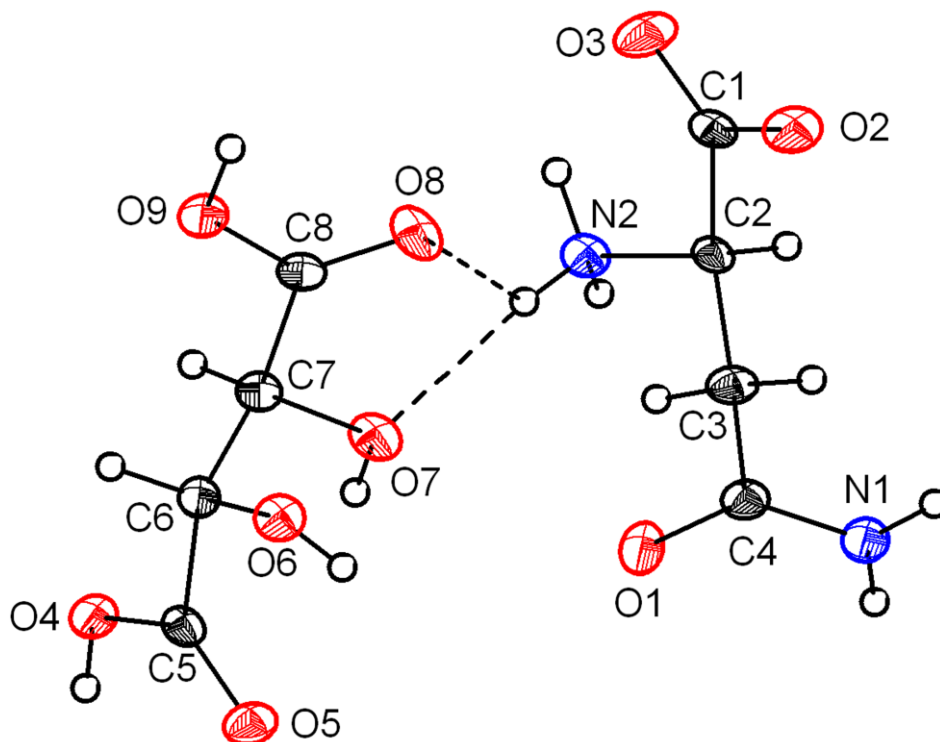


Graphical abstract

The material reported, viz., L-asparagine-L-tartaric acid (LALT) is a new nonlinear optical (NLO) material. Second harmonic generation (SHG) conversion efficiency is about 31% of that of the standard KDP crystals. The compound is stable upto 195 °C and transparent for the fundamental and second harmonic of Nd: YAG ($\lambda = 1064$ nm) laser. The compound may have possible applications in non-linear optics. Thermal ellipsoids plot of the compound are drawn at the 50% probability level excepting for H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown by broken lines.



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Highlights

- The material reported, viz., L-asparagine-L-tartaric acid (LALT) is a new nonlinear optical (NLO) material
- This is a new amino acid compound reported for the first time and its structure is elucidated
- Second harmonic generation (SHG) conversion efficiency is about 31% of that of the standard KDP crystals
- The compound is stable upto 195 °C and transparent for the fundamental and second harmonic of Nd: YAG ($\lambda = 1064$ nm) laser
- The compound may have possible applications in non-linear optics.

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Structural, vibrational and thermal studies of a new nonlinear optical material: L-Asparagine-L-Tartaric acid

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Abstract

Crystals of a new nonlinear optical (NLO) material, viz., L-asparagine-L-tartaric acid (LALT) (**1**) were grown by slow evaporation of an aqueous solution containing equimolar concentrations of L-asparagine and L-tartaric acid. The structure of the title compound which crystallizes in the non-centrosymmetric monoclinic space group $P2_1$ consists of a molecule of L-asparagine and a molecule of free L-tartaric acid both of which are interlinked by three varieties of H-bonding interactions namely O-H \cdots O, N-H \cdots O and C-H \cdots O. The UV-Vis-NIR spectrum of **1** reveals its transparent nature while the vibrational spectra confirm the presence of the functional groups in **1**. The thermal stability and second harmonic generation (SHG) conversion efficiency of **1** were investigated.

Keywords: Crystal growth, L-Asparagine L-Tartaric acid, Crystal structure, Non-linear optical material, Single crystal

1. Introduction

In recent years, there is a growing need for nonlinear optical (NLO) materials in view of their applications in opto-electronic and photonic devices [1]. In terms of nonlinear optical properties, organic compounds possess more advantages as compared to their inorganic counterparts [2-3]. Organic NLO crystals have attracted much attention because of their low cost and flexibility of molecular design. The naturally occurring α -amino acids are ideal precursors for the synthesis of new materials for NLO applications in view of their chiral nature (excepting glycine) and ready availability. Although the simplest α -amino acid glycine is achiral, it is known to form several solids which crystallize in non-centrosymmetric space groups. Based on a study of about thirty five crystal structures containing glycine, metal cations and halogenide ions, Fleck [4] has recently reported that the percentage (28%) of non-centrosymmetric structures in this class of compounds is high and much more than the usual 15%. In a more recent study, we have observed a similar feature in a smaller subset of glycine compounds containing calcium [5]. In the group of calcium halide-glycine compounds, four out of ten compounds (40%) crystallize in non-centrosymmetric space groups. In the case of the other α -amino acids which are used to build the protein skeleton, non-centrosymmetric compounds are expected in view of the chiral nature of the α -carbon. In the solid state, amino acids exhibit a zwitterionic behaviour in that they contain a protonated amino group (NH_3^+) and deprotonated carboxylic acid group (COO^-). This dipolar nature leads to some interesting physical and chemical properties in amino acids making them suitable candidates for NLO applications [6]. The naturally occurring amino acid L-asparagine plays a role in the metabolic control of some cell functions in nerve and brain tissues and is also used by many plants as a nitrogen reserve source [7]. Recently, the growth and characterization of the single crystals of the NLO materials, viz., L-asparaginium picrate [8] and L-asparagine

monohydrate [9] have been reported. A brief report of the crystal structure of L-asparagine-L-tartaric acid (LALT) **1** was published by our group [10]. In this paper, the full details of crystal growth, spectral and structural characterization, thermal studies and SHG efficiency of **1** are reported.

2. Crystal growth of LALT (1)

L-Asparagine (99.7% purity) and L-tartaric acid (99% purity) purchased from M/s. Loba Chemie Pvt. Ltd., were taken in 1:1 mole ratio and dissolved completely in double-distilled water, to obtain a supersaturated solution, which was kept in an undisturbed environment for slow evaporation solution growth. After about three weeks, transparent single crystals of good quality (approximate size: $4 \times 2 \times 2 \text{ mm}^3$, Fig.1) were obtained. The density of the crystal was determined as $1.63(3) \text{ g/cm}^3$ using the floatation method and the melting point was measured as $195(2) \text{ }^\circ\text{C}$. The morphology of the LALT crystal is shown in Fig. 2 and is rhombic with eighteen developed faces. Of these, the largest faces are (001), (00-1), (0-11) and (011) and the smallest faces are (1-1-1), (11-1), (-111) and (-1-11). The figure showing the morphology of the crystal was drawn using the single crystal data making use of the program MERCURY [11].

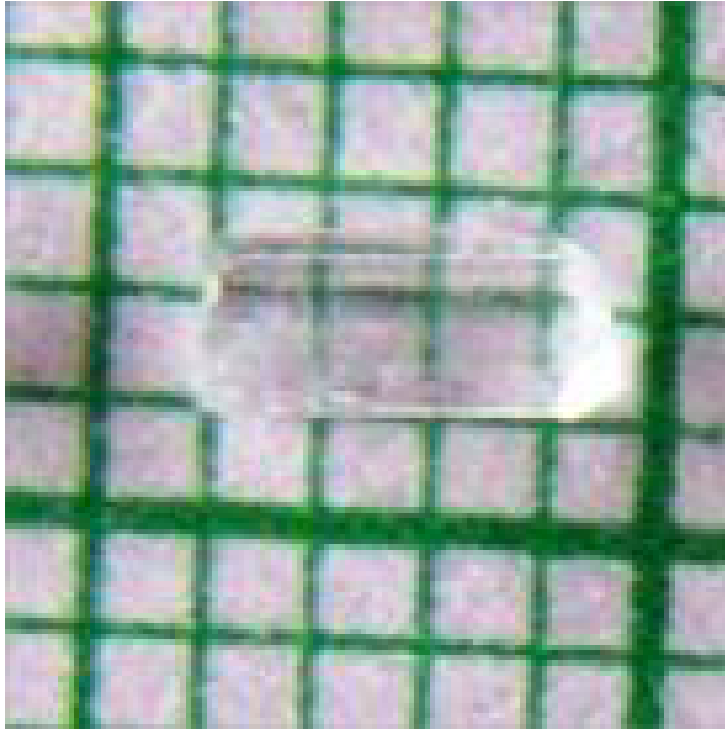


Fig.1. Photograph of grown LALT crystal

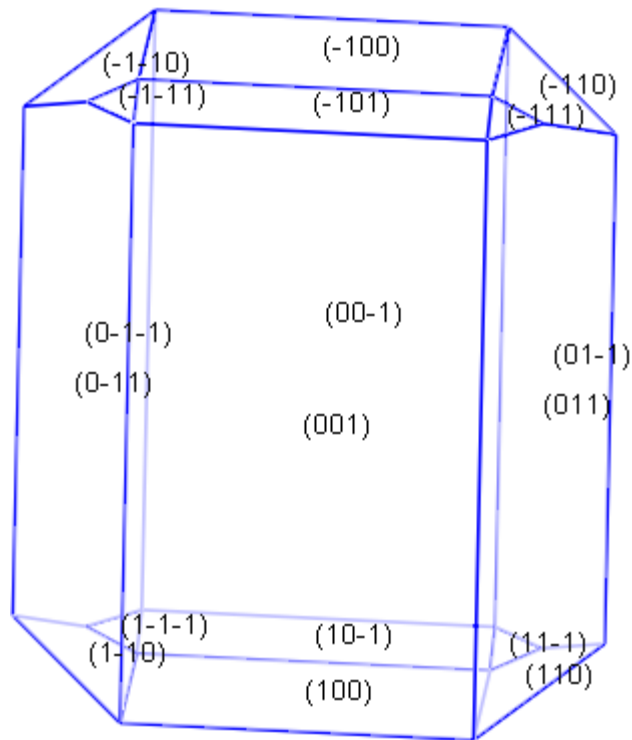


Fig.2. Morphology of LALT crystal

2.1 Characterization

Nonius CAD-4/MACH3 diffractometer with MoK α (0.71073 Å) radiation was used to obtain the accurate unit cell parameters. The crystal structure was determined from single crystal X-ray intensity data, collected at room temperature (293 K). The program XCAD4 [12] was used for the data reduction, while absorption correction was applied using the method of ψ -scan [13]. The structure solution and refinement were performed using the program SHELX97 [14]. The structure was solved by direct methods using all the unique reflections. The crystal data, experimental conditions and structure refinement parameters are presented in Table 1. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The H atoms were placed at calculated positions [O-H = 0.82 Å, N-H = 0.86 or 0.89 Å and C-H = 0.98 Å] and were allowed to ride on their respective parent atoms with $U_{\text{iso}}(\text{H})=1.2U_{\text{eq}}(\text{C,N})$ and $1.5U_{\text{eq}}(\text{O})$. In the absence of significant anomalous scattering effects, Friedel pairs were averaged. The absolute configuration was assigned based on the known configuration of L-asparagine and L-tartaric acid. Infrared spectra of the samples were recorded in the KBr phase in the frequency region of 4000 – 400 cm $^{-1}$ using a Shimadzu Spectrometer (FTIR, model 8400s), at a resolution of 4 cm $^{-1}$. Raman spectral measurements were made with a model RFS 100/S Bruker instrument with a Nd:YAG laser operated at 1064 nm with a power output of 200 mW. The spectrum was recorded over the range 4000–500 cm $^{-1}$. The sample was finely powdered and pressed into a small depression on a metal disc and mounted on the sample compartment. This instrument has a resolution of 4 cm $^{-1}$. The transmission spectra were recorded using Perkin Elmer Lambda 750 UV–Vis–NIR spectrophotometer in the range of 200–1100 nm. Simultaneous thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out for the crystals, using a SDT Q600 V8.3 build 101 thermal analyzer. A powder sample was used for the analysis in the temperature range of 25°C to 900°C with a

heating rate of 20°C/min. The crucible used was of alumina (Al₂O₃), which also served as a reference for the sample. The second harmonic generation (SHG) conversion efficiency was tested using a modified setup of Kurtz and Perry. The fundamental beam of wavelength 1064 nm from a Q switched Nd:YAG laser was used to test the SHG efficiency of LALT crystals. The laser beam used had an energy of 3.9 mJ/pulse and pulse width of 8 ns, the repetition rate being 10 Hz.

Table 1 The crystal data, experimental conditions and structure refinement parameters

Empirical formula	C ₈ H ₁₄ N ₂ O ₉
Formula weight	282.21
Temperature	293 K
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P2 ₁
Unit cell dimensions	$a = 5.0860(4)$ Å $b = 9.6720(6)$ Å $c = 11.8340(8)$ Å $\beta = 95.311(8)^\circ$
Volume	579.64(7) Å ³
Z, Calculated density	2, 1.617 mg/m ³
Absorption coefficient	0.15 mm ⁻¹
F(000)	296
Crystal size	0.28 x 0.23 x 0.21 mm ³
Theta range for data collection	2.7° to 25.0°
Limiting indices	0 ≤ h ≤ 6, -1 ≤ k ≤ 11, -14 ≤ l ≤ 13
Reflections collected / unique	1339 / 1015 [R(int) = 0.095]
Max. and min. transmission	0.969 and 0.959
Data / restraints / parameters	1073 / 1 / 172
Goodness-of-fit on F ²	1.38
Final R indices [I > 2σ(I)]	R1 = 0.053, wR2 = 0.226
Largest diff. peak and hole	0.34 and -0.40 e.Å ⁻³

3. Results and discussion

3.1. Synthetic aspects

The reaction of L-asparagine or DL-asparagine with inorganic acids like nitric acid or perchloric acid has been shown to result in proton transfer to the amino group of amino acid, resulting in the formation of asparaginium compounds like L-asparaginium nitrate [15], DL-asparaginium nitrate [16] and DL-asparaginium perchlorate [17]. A similar proton transfer has been observed from the more acidic phenolic proton of picric acid to the amino group in L-asparaginium picrate [18]. However no proton transfer was observed, during the synthesis of compounds like L-phenylalanine fumaric acid [19] and L-phenylalanine benzoic acid [20], in our earlier studies of amino acid (L-phenylalanine) with organic acids. In view of our interest on the hybrid compounds of amino acids with organic acids [19, 20], the reaction of L-asparagine was investigated with L-tartaric acid in this study. As in L-phenylalanine, no proton transfer took place and the observed product (**1**) was a simple 1:1 adduct containing both the starting materials. The formation of a new compound could be evidenced by its characteristic thermal behavior and infrared spectrum which are different from that of the starting materials. The presence of the free L-tartaric acid in (**1**) could be inferred from the characteristic O-H stretching vibration (*vide infra*) and unambiguously confirmed by X-ray crystallography as shown below.

3.2. Structural features

The title compound **1** crystallizes in the non-centrosymmetric monoclinic space group $P2_1$ and its structure consists of a unique L-asparagine molecule and an independent free L-tartaric acid molecule (Fig. 3) with all atoms located in general positions. The L-asparagine molecule exists as a zwitterion and is interlinked to the organic acid with the aid of several H-bonding interactions. Of these, the two intramolecular N-H \cdots O bonds

(Table 2) involving the hydrogen atom (H2C) attached to nitrogen (N2) of the zwitterionic amino acid appear to be important for the formation of the 1:1 crystalline adduct.

Table 2 Hydrogen bond geometry [\AA , $^\circ$]

D-H\cdotsA	d(D-H)	d(H\cdotsA)	d(D\cdotsA)	\angleD-H\cdotsA
N1-H1A \cdots O5 ^d	0.86	2.23	3.053(8)	160
N1-H1B \cdots O3 ⁱⁱ	0.86	2.04	2.856(9)	159
N2-H2A \cdots O8 ⁱⁱⁱ	0.89	2.19	2.895(8)	136
N2-H2B \cdots O2 ^v	0.89	2.28	2.921(9)	129
N2-H2C \cdots O7	0.89	2.06	2.912(8)	160
N2-H2C \cdots O8	0.89	2.30	2.916(8)	126
O4-H4 \cdots O1 ^v	0.82	1.69	2.500(6)	168
O6-H6 \cdots O4 ⁱ	0.82	2.19	2.959(8)	156
O7-H7 \cdots O6 ⁱⁱⁱ	0.82	2.05	2.850(7)	166
O9-H9 \cdots O2 ⁱⁱ	0.82	2.12	2.860(7)	180
O9-H9 \cdots O3 ⁱⁱ	0.82	2.69	3.226(13)	125
C2-H2 \cdots O2 ⁱⁱ	0.98	2.56	3.426(9)	147
C3-H3A \cdots O3 ⁱ	0.97	2.40	3.158(10)	134

Symmetry codes: i) $-x, y+1/2, z$; ii) $-x+1, y+1/2, -z+1$; iii) $x-1, y, z$; iv) $-x+1, y-1/2, -z+1$; v) $-x, y-1/2, -z$; vi) $-x+1, y+1/2, -z$; vii) $-x+2, y-1/2, -z+1$.

The asparagine carboxylate skeleton, which includes O2, O3, C1 and C2 is nearly planar.

The deviation of the amine N atom from the plane of the carboxylate group is 0.516 (2) \AA .

The twist of the carboxylate group of the asparagine molecule is described by $\psi^1 =$

160.4(6) $^\circ$ and $\psi^2 = -24.9(9)^\circ$, corresponding to *trans* and *cis* arrangements. The side-

chain conformations are observed as $\chi^1 = 63.9(8)^\circ$, $\chi^{21} = -80.7(9)^\circ$ and $\chi^{22} = 95.9(8)^\circ$ for

the asparagine molecule. The tartaric acid molecule is in the unionized state. The angle

between the planes of the half molecules, O9/O8/C8/C7/O7 and O4/O5/C5/C6/O6 is

57.6(3)°, which is closer to the value of 54.6° found in the structure of tartaric acid. The carbon skeleton of tartaric acid molecule is non-planar, with a C5—C6—C7—C8 torsion angle of -168.5(6)°.

An analysis of the structure reveals several H-bonding interactions with all the oxygen atoms excepting O9 functioning as H-acceptors. All H-atoms attached to the nitrogen atoms N1 and N2 and the oxygen atoms O4, O6, O7 and O9 function as H-donors (Table 2). The H atoms attached to the C atoms in L-tartaric acid are not involved in C-H···O bonds although two of the H atoms namely H2 and H3A in L-asparagine are H-bonded in an intermolecular fashion to the oxygen atoms O2 and O3 respectively, in neighbouring symmetry related L-asparagine molecules. Each independent L-asparagine is H-bonded to four symmetry related L-tartaric acid and four unique L-asparagine molecules with the aid of three varieties of H-bonding interactions (Fig 4). Each unique L-tartaric acid is linked by H-bonding to four symmetry related L-asparagine molecules and four neighboring L-tartaric acid with the aid of seven O-H···O and three N-H···O interactions (Fig 4). As a result of H-bonding, the tartaric acid and amino acid molecules are organized into alternating layers which are linked into an intricate H-bonded network.

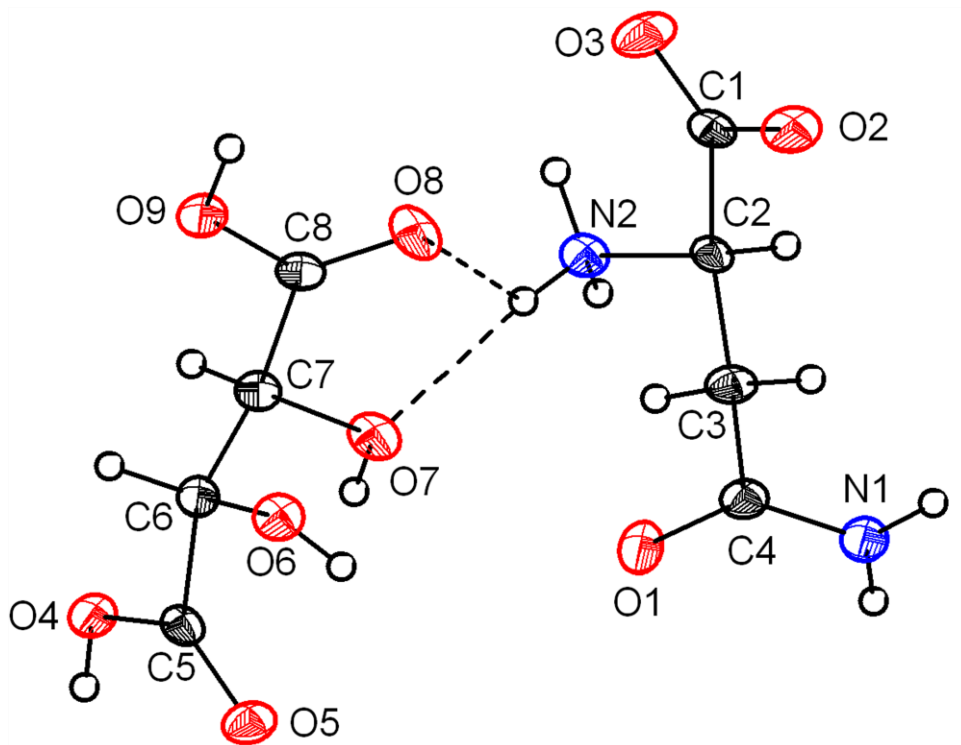
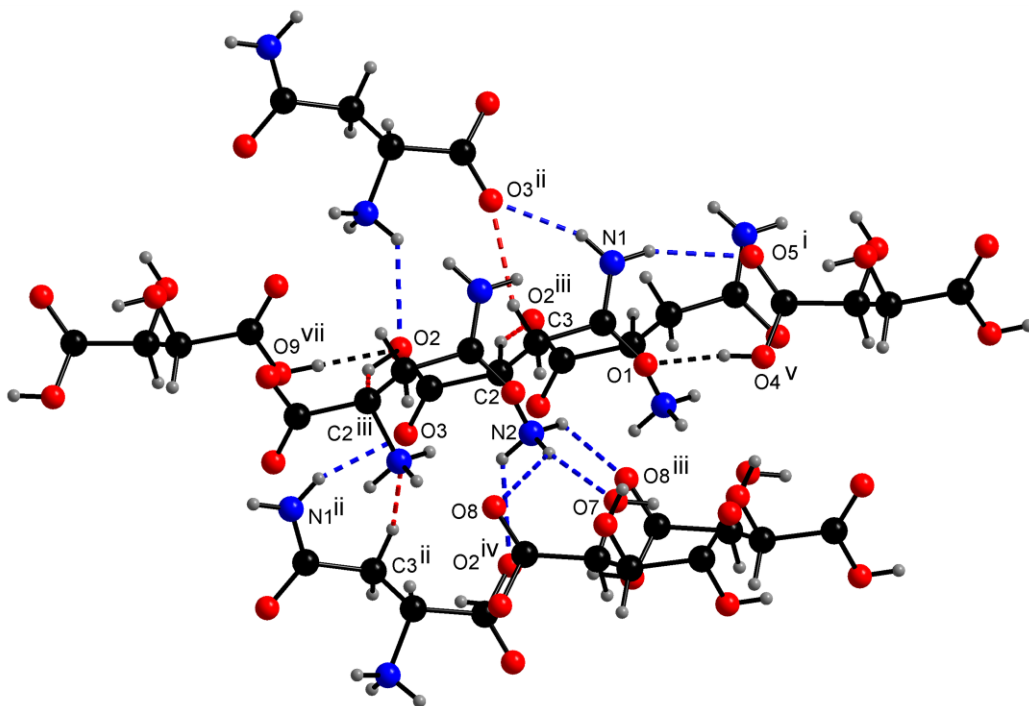


Fig. 3. Molecular structure of LALT (**1**), showing the atom labeling scheme. Thermal ellipsoids are drawn at the 50% probability level excepting for H atoms, which are shown as circles of arbitrary radius. Intramolecular H-bonding is shown by broken lines.



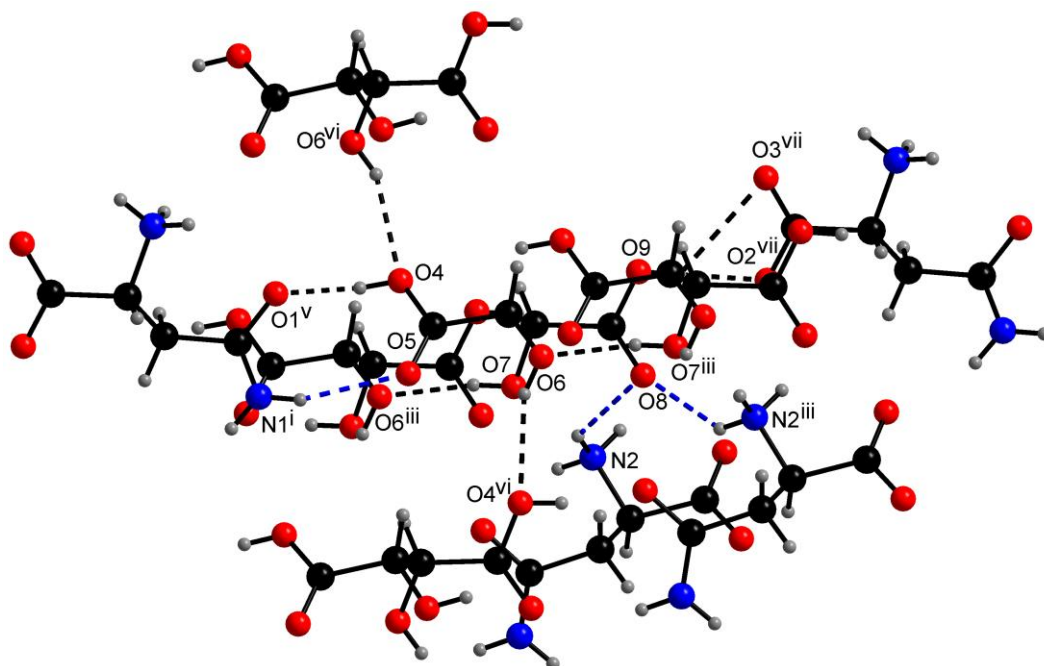


Fig.4. H-bonding situation around L-asparagine (top) showing the three varieties of H-bonds (broken lines) namely O-H \cdots O, N-H \cdots O (blue) and C-H \cdots O (red). The H-bonding surroundings of L-tartaric acid (bottom). For explanation of symmetry code see Table 2.

3.3 Infrared and Raman Spectra

A combination of infrared and Raman spectra was used to characterize the functional groups in **1**. Based on a comparison of the reported data for functional groups [21-22] and amino acid compounds [23-26] with those of the experimentally observed spectra (Fig 5 & 6) assignments have been made for the functional groups in the title compound (Table 3).

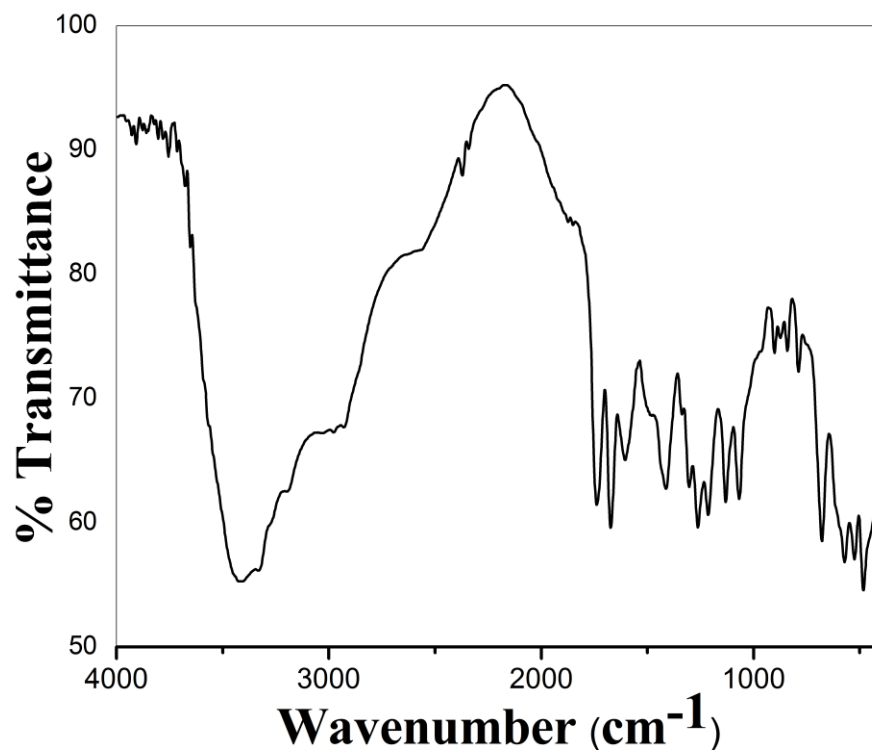


Fig. 5. Infrared spectrum of LALT

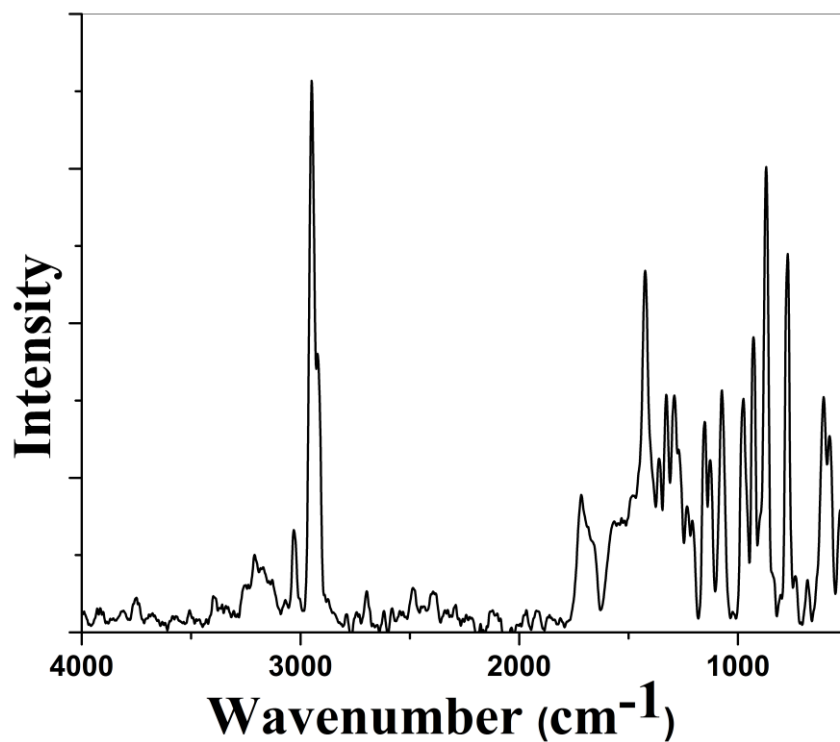


Fig.6. Raman spectrum of LALT

Table 3 Assignments of infrared and Raman bands for functional groups

Infrared (in cm^{-1})	Raman (in cm^{-1})	Tentative Assignments
3404 b,s		O-H str
3331 sh		NH ₂ asym. str
3276 vw	3217 w	NH ₃ ⁺ asym. str
3199 vw		NH ₂ sym. str
	3033 w	NH ₃ ⁺ sym. str
2970 vw	2952 vs	CH ₂ sym. str
2926 vw		CH ₂ str
	2915 sh	CH ₂ asym. str
1736 s	1723 s	C=O str
1672 s		NH ₃ ⁺ asym.def
1601 s	1568 vw	NH ₃ ⁺ sym.def
	1430 s	CH ₂ def
1416 s		COO ⁻ sym. str
	1364 w	C-N str
1338w,	1329 m	CH ₂ wag
1304 w		
1261 m	1293 m	C-C str
	1264 sh	CH ₂ twist
	1237 w	C-OH i.p.def
1213 w	1208 w	CH ₂ twist
1130 m	1153 m	NH ₃ ⁺ rock
	1127 m	O-H str
1069 m	1070 m	C-C str
954 m	981 m	NH ₃ ⁺ rock
901 w	934 s	C-C str
874 vw	870 vs	C-C-N sym. str
841 w		C-C str
787 m		C-C str
742 vw	768 w,	CH ₂ rock
	743 vw	

679 s	688 w	COO ⁻ sci
617 vw	614 m	COO ⁻ wag
	589 m	C-C=O i.p. def
571 m		COO ⁻ wag
525 m	539 m	O-H str
484 s	471 m	NH ₃ ⁺ tor

s:strong, vs:very strong, sh: shoulder, b:broad, m:medium, w:weak, vw: very weak, sym:symmetric, asym:asymmetric, str:stretch, wag:wagging, def:deformation, sci:scissoring, i.p:in-plane, tor:torsion

The strong and broad signal at 3404 cm⁻¹ in the IR spectrum can be attributed to the O–H stretching vibration of the carboxylic acid group of the free L-tartaric acid. The peaks at 3217 cm⁻¹ in Raman and 3276 cm⁻¹ in IR are assigned to the asymmetric stretching vibration of NH₃⁺ group while the band at 3033 cm⁻¹ in Raman is assigned to the symmetric stretching vibration of the NH₃⁺ group. The carbonyl C=O stretching vibration occurs as a strong signal in the region 1800–1740 cm⁻¹. The strong bands at 1736 cm⁻¹ in IR and at 1723 cm⁻¹ in Raman can be attributed to the carbonyl vibration of the amide functionality of L-asparagine. The deprotonated carboxylic group (COO⁻) has characteristic absorption band around 1416 cm⁻¹ in the IR spectrum, which is the symmetric stretching mode. The strong IR band at 679 cm⁻¹ and the weak band at 688 cm⁻¹ in the Raman spectrum are assigned to the scissoring of the COO⁻ group.

3.4 UV-Vis-NIR spectrum

The UV-Vis-NIR spectrum of 1 (Fig 7) reveals that the UV transparency cutoff occurs around 200 nm and there is no remarkable absorption in the entire region of the spectrum. Such a transparent behavior is a favorable characteristic of NLO materials for possible applications [27].

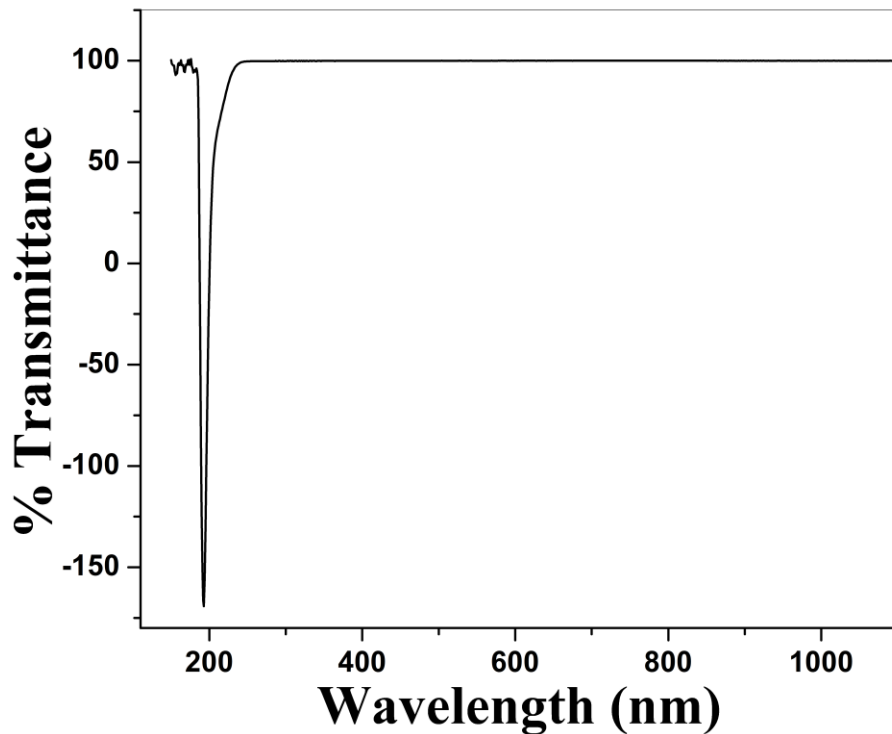


Fig. 7. Transmission spectrum of LALT

3.5 Thermal studies

The TG-DTA thermogram of **1** (Fig.8) exhibits no thermal events till 195 °C and its thermal behaviour is different from that of L-asparagine which melts at 234-235 °C and L-tartaric acid (m.p. 168-170 °C) indicating that compound **1** is thermally more stable as compared to that of free L-tartaric acid. The endothermic peak around 195 °C in the DTA curve accompanied by a rapid drop in mass can be attributed to the simultaneous occurrence of melting and decomposition of **1**.

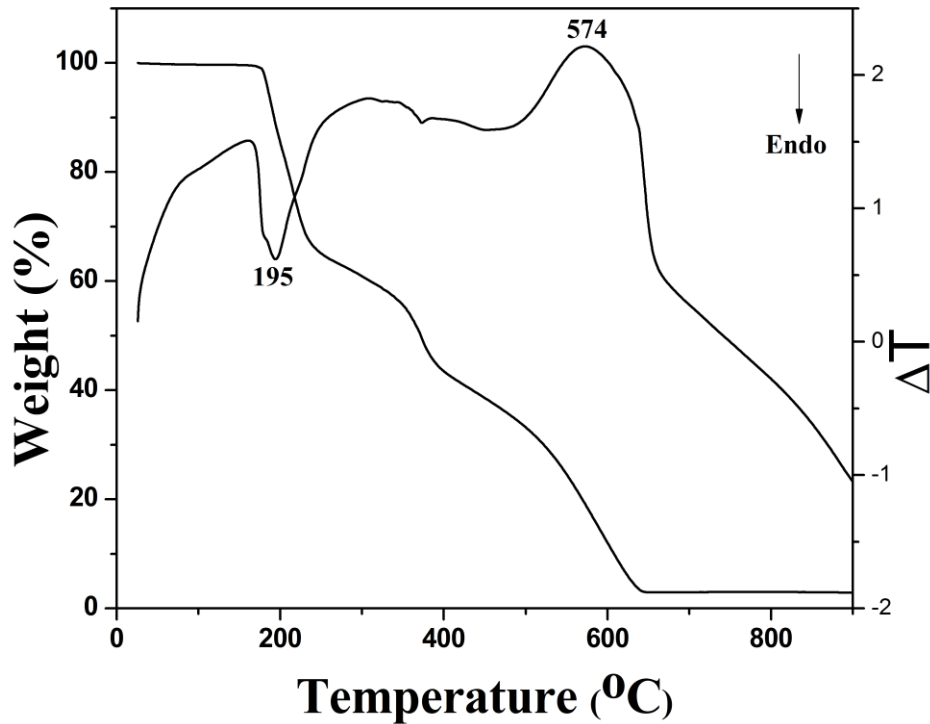


Fig.8. TG-DTA thermogram of LALT

3.6 Second harmonic generation

Since the specimen has crystallized in a non-centrosymmetric space group, a preliminary study of the powder SHG was made using a laser beam of wavelength 1064 nm, using Kurtz and Perry technique [28]. The crystals were ground to a uniform particle size of about 125–150 μm and then packed in capillaries of uniform bore and exposed to the laser radiation. A powder of KDP, with the same particle size was used as a reference. The output from the sample was monochromated to collect only the second harmonic ($\lambda= 532$ nm), eliminating the fundamental and the intensity was measured using a photomultiplier tube. It was found that the SHG conversion efficiency is about 31% of that of the standard KDP crystals.

Conclusions

Transparent optical quality crystals of LALT were grown from aqueous solution by the slow evaporation method. The crystal structure was elucidated using standard crystallographic procedures. Infrared and Raman spectra revealed the presence of the various functional groups. UV-Vis-NIR study shows that the crystal is transparent for the fundamental and second harmonic of Nd: YAG ($\lambda = 1064$ nm) laser. Thermal analyses showed the good thermal stability of the material revealing its suitability for NLO applications.

Acknowledgments

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