

## Synthesis and characterization of a new nonlinear optical single crystal: L-Lysinium trifluoroacetate

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Single crystals of a new L-Lysine salt: L-Lysinium trifluoroacetate {abbreviated as LLyTFA;  $[(\text{NH}_2)-(\text{CH}_2)_4-\text{CH}-(\text{NH}_3)-(\text{COOH})]^+ \text{CF}_3\text{COO}^-$ } were grown by slow evaporation of an aqueous solution at room temperature. The grown crystals were subjected to single crystal X-ray diffraction, FTIR and UV-Vis-NIR spectrum analyses. The UV-Vis-NIR spectrum shows that the absorption is very less in the whole of the region from ultraviolet to near IR. The Kurtz-Perry powder SHG measurement using a Nd:YAG laser of wavelength 1064nm confirms the frequency doubling of the crystal and its powder SHG efficiency was measured as  $d_{\text{eff}} = 0.96 d_{\text{eff}}(\text{KDP})$ .

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### 1 Introduction

A major effort was developed to use the nonlinear optical effect in materials to generate frequencies that are not available and also to develop the capability of generating tunable coherent beams [1]. Much of this research has been directed towards materials that produce second-harmonic generation (SHG), the frequency doubling of laser light. As a result, a variety of both organic and inorganic materials have been developed [2-4]. In recent years, organic crystals are rated high as compared to inorganics in view of their large electro-optic coefficients with low frequency dispersion, low cost, fast and large nonlinear response over a broad frequency range, inherent synthetic flexibility and intrinsic tailorability [5,6].

Many new organic crystals have been found based on the predictive molecular engineering approach and have been shown to have potential applications in nonlinear optics. Moreover, crystals capable of generating second harmonics must have a unit cell with no centre of inversion and this requirement is always met by the crystals of pure amino acids because these molecules themselves are dissymmetric [8,9]. The key factor of material selection depend not only on laser conditions but also on the physical properties of the crystal, such as transparency, damage threshold, conversion efficiency, phase matching and temperature stability. Among the organic crystals for NLO applications, amino acids display special features of interest [10], such as

- Molecular chirality which secures acentric crystallographic structure
- Wide transparency in the visible and UV range
- Zwitter-ionic nature of the molecule which favours the hardness of the crystal

In the present work a new nonlinear optical material L-Lysinium trifluoroacetate (LLyTFA) was synthesized and its spectral and thermal properties were investigated in detail for the first time.

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## 2 Experimental procedure

**Crystal growth** L-Lysinium trifluoroacetate (LLyTFA) solution was prepared by dissolving equimolar quantities of L-Lysine (Lancaster 98 % purity) and trifluoroacetic acid (Lancaster 99 % purity) in deionised water. The reaction undergoes as follows:



The molecular structure of the LLyTFA crystal is shown in figure 1. Purity of the solution was improved by successive recrystallization process. The solution was stirred for 24 hours continuously and the homogeneous solution was allowed to stand for several days. Good quality seed crystals of L-Lysinium trifluoroacetate were grown by slow evaporation from an aqueous solution.

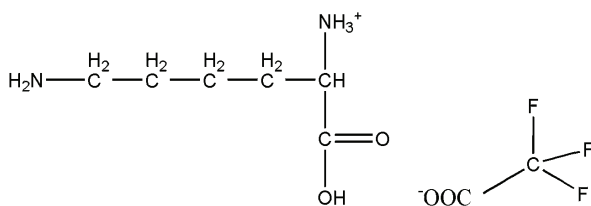


Fig. 1 Molecular Structure LLyTFA single crystals.

**Single crystal X-ray diffraction studies** The single crystal diffraction analysis of L-Lysinium trifluoroacetate was carried out using Bruker apex2 Single crystal X-ray diffractometer equipped with MoK $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The cell parameters were obtained from least square refinement of the setting angles of 50 reflections. The compound crystallizes in monoclinic form with a space group P2<sub>1</sub>. The crystallographic parameters are listed in table 1.

Table 1 Crystal data for L-Lysinium trifluoroacetate (LLyTFA).

Identification code	LLyTFA
Empirical formula	C <sub>8</sub> H <sub>15</sub> F <sub>3</sub> N <sub>2</sub> O <sub>4</sub>
Formula weight	260.22
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, Space group	Monoclinic, P2 <sub>1</sub>
Unit cell dimensions	a = 5.6904(4) Å, b = 23.497(2) Å, c = 8.4859(8) Å and $\beta = 91.385(5)^\circ$
Cell Volume	1134.32(16) Å <sup>3</sup>

## 3 Results and discussion

Fourier transform Infrared (FTIR) spectra of LLyTFA was recorded using a Bruker IFS66 FTIR spectrophotometer at room temperature in the range 400 – 4000 cm<sup>-1</sup> by KBr pellet method is shown in figure 2. The absorption spectrum of the crystal was recorded using a Varian Cary 5E UV-Vis-NIR spectrophotometer in the wavelength range of 200 – 1000 nm is shown in figure 3. The second harmonic generation (SHG) measurement of LLyTFA was also performed using the Kurtz-Perry powder SHG technique [11].

The existence of COO<sup>-</sup> or COOH groups in the studied crystals was deduced on the basis of vibrational spectra. It is clearly seen that the existence of COOH is illustrated by the very strong infrared band located at 1710 cm<sup>-1</sup>. The fact that some of the COOH groups are ionized implicates an appearance of the NH<sub>3</sub><sup>+</sup> group in lysine molecules. The coexistence of both forms of carboxylic groups (ionized and protonated) resulting the annihilation of centrosymmetry appears to be a fruitful idea underlined by Guru Row [12]. Such mutual orientation of one protonated and the second ionized carboxylic groups allows asymmetric chain formation. Accordingly LLyTFA crystallizes in non-centrosymmetry space group P2<sub>1</sub> of monoclinic system.

The strong shoulder at 3421 cm<sup>-1</sup> and very strong band at 3075 cm<sup>-1</sup> in the infrared spectrum are attributed to stretching vibrations of O-H and NH<sub>3</sub><sup>+</sup> groups. Bands corresponding to symmetry type of stretching vibrations for NH<sub>2</sub> group is observed at 2364 cm<sup>-1</sup>. A peak at 1678 cm<sup>-1</sup> has been assigned to COO<sup>-</sup> asymmetric

stretching vibration. Bending vibration of  $\text{NH}_3^+$  is observed in the IR spectrum at  $1600\text{ cm}^{-1}$ . Asymmetric stretching vibration of  $\text{COO}^-$  is observed at  $1580\text{ cm}^{-1}$ . The bands at  $1441$ ,  $1350$  and  $1037\text{ cm}^{-1}$  corresponds to scissoring, twisting and wagging vibrations of  $\text{CH}_2$  group. Out-plane bending vibration of OH group is assigned at  $920\text{ cm}^{-1}$ . The stretching type of vibrations of C-F bonds gives rise to several bands in the region of  $1128$ - $1350\text{ cm}^{-1}$ . The wagging of  $\text{CO}_2^-$  vibration is assigned at  $545\text{ cm}^{-1}$ . The wavenumbers and their corresponding assignments are listed in table 2.

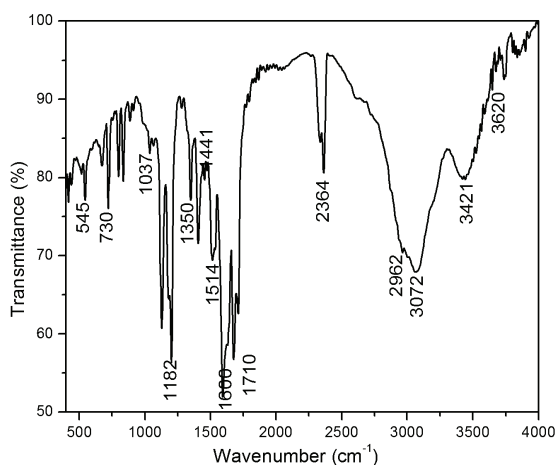


Fig. 2 FTIR spectrum of LLYTFA single crystals.

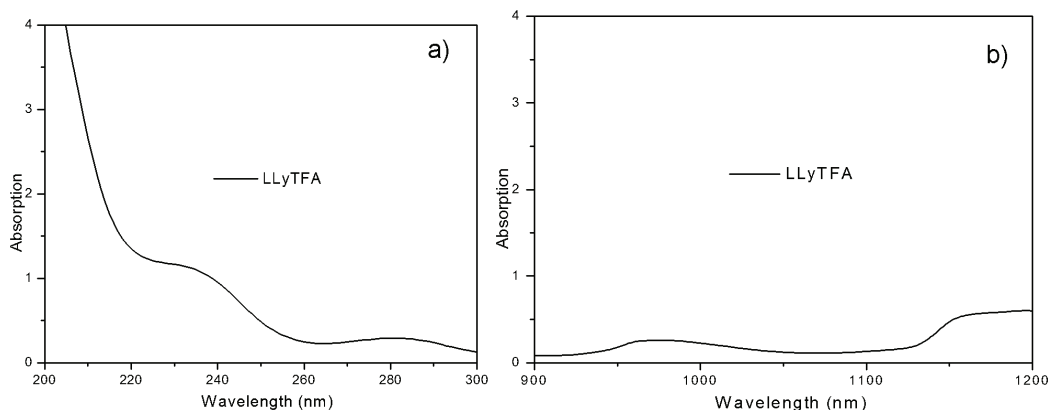


Fig. 3 UV-Vis-NIR spectra of LLYTFA single crystals.

Table 2 Bands assignments of FTIR spectrum of LLYTFA [13].

Wavenumber ( $\text{cm}^{-1}$ )	Assignments
3620, 3421	O-H stretching vibrations
2962	C-H asymmetric stretching
2337, 2364	$\text{NH}_2$ symmetric stretching
1710	C=O stretching of COOH
1678	$\text{COO}^-$ asymmetric stretching
1600	$\text{NH}_3^+$ asymmetric bending
1580	$\text{COO}^-$ asymmetric stretching
1514	$\text{NH}_3^+$ symmetric deformation
1450, 1440	$\text{CH}_2$ - scissoring
1310	$\text{CH}_2$ twisting
1128, 1182, and 1350	C-F stretching vibrations
1037	$\text{CH}_2$ -wagging
920	O-H out of plane bending
784	$\text{CH}_2$ -rocking
723	$\text{COO}^-$ scissoring
545	$\text{COO}^-$ wagging

The optical absorption spectra of LLyTFA crystals show that there is very less absorption in the whole of visible spectrum. Also the transparency window (~90%) lies in the range 270-940 nm and the lower UV cutoff of LLyTFA occurs at 240 nm.

Differential Scanning Calorimetric measurement has been carried out for LLyTFA using Netzsch DSC 200 in the temperature range 30-400°C in nitrogen atmosphere at a heating rate of 5 K/min is shown in figure 4. The onset of endothermic peak starts at 210°C and it attains a maximum at 224°C, which represents the partial decomposition of the compound and a large endothermic peak between 200 - 224°C indicates the complete decomposition of LLyTFA crystals. The study reveals that the crystal is chemically stable up to 210°C, which is comparable to the reported values of 210°C and 215°C respectively for L-histidinium trifluoroacetate and L-arginine trifluoroacetate single crystals [14, 15].

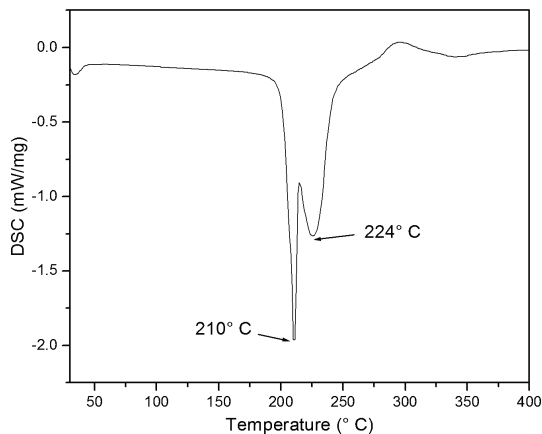


Fig. 4 Thermal analysis of LLyTFA crystals.

The Kurtz-Perry powder second harmonic generation (SHG) measurements was carried out using a Spectra-Physics Quanta-ray ProLab 170 Nd:YAG laser with the first harmonics output at 1064 nm and a pulse width of 10 ns at a repetition rate of 10 Hz. The second harmonic signal generated by the LLyTFA compound was confirmed by the emission of green radiation and the powder SHG efficiency of LLyTFA was found to be comparable to that of potassium dihydrogen phosphate (KDP).

I. V. Kityk et al. [16] reported that SHG efficiency of guest-host systems enhances considerably due to the delocalisation of pi electrons. They have also correlated the SHG susceptibilities with the dipole moments of different chromophores and revealed the substantial contribution of guest molecule in tuning the second order SHG co-efficients. Following this, we assign that the complexation of organic and inorganic molecules, highly polarizable cation (L-Lysine) has been linked to the highly polarizable anion (trifluoroacetate) through H-bonded networks. The bonding energy present in the H-bonds linking the organic and inorganic groups counteracts the tendencies of the organic dipoles to form parallel pairs and drive the formation of new crystals with high SHG susceptibilities. Hence the SHG efficiency of L-lysine trifluoroacetate has shown an appreciable increase when compared to pure L-lysine molecules (0.1 times that of KDP). The results agreed well with the earlier reports on L-histidine derivatives [14,17].

#### 4 Summary and conclusions

L-lysine trifluoroacetate, single crystals have been grown from aqueous solution by slow evaporation method. The presence of various functional groups in the crystal has been confirmed through FTIR analysis. The UV-Vis-NIR spectrum of the crystal shows minimum absorption in the range 270 nm – 940 nm. LLyTFA is thermally stable up to 210°C. The NLO property of the grown crystal was confirmed by Kurtz SHG test. Its SHG efficiency was found to be 0.96 times that of KDP. Owing to its good transparency, high thermal strength and good SHG efficiency, LLyTFA can act as a good optical second harmonic generator.

**Supplementary material** Full crystallographic data (cif file) relating to the crystal structure have been deposited with the Cambridge Crystallographic Data Centre as CCDC 627397. Copies of this information can

be obtained free of charge from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk; www: <http://www.ccdc.cam.ac.uk>).

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