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CONTENTS

Structural, Dielectric and Spectroscopic Analysis of L-Glycinium Oxalate Single Crystal for Optoelectronic Applications

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ABSTRACT

L-Glycinium Oxalate single crystals were grown from aqueous solution by adopting slow evaporation solution growth technique. Single crystal X-ray diffraction studies confirms Monoclinic crystal system with lattice parameters a = 10.57 Å, b = 5.67 Å, c = 12.07 Å, crystallographic axis α = 90°, β = 113.71°, γ = 90°. FTIR spectroscopic analyses of the grown crystals were recorded in the wave number range 400-4000cm^{-1}. The functional groups associated with the L-Glycinium Oxalate crystals were identified and their respective peaks were assigned. The Fluorescence spectrum gives information about excitation of molecule brought by absorption of photon. The emission spectrum of the crystals was recorded in the range of 250-900 nm using Perkin Elmer fluorescence spectrometer. UV spectroscopy is one of the important characterization techniques to study the optical properties of the crystal. UV analysis was also carried out to determine the transmittance spectra and the optical energy gap of the grown crystal. Dielectric Measurements were carried out using the LCR meter the capacitance and dielectric loss (tan δ) of the samples prepared from these crystals were measured at the different frequency of 100 Hz, 1 KHz, 10 KHz, 100KHz, 1MHz and 5MHz at various temperatures.

Keywords: *Spectroscopic techniques; XRD; FTIR; Dielectric studies; Band gap.*

1. Introduction

In recent years, one has witnessed increasing interest in the study of amino acids base organic and their derivative crystals. This interest has been stimulated by the standpoint of understanding a system where the hydrogen bonding plays a fundamental role. In order to fabricate some biological importance crystals a better knowledge and the mechanism of hydrogen bonding can be known. Organic crystals mainly amino acid with delocalized π electrons usually displays larger nonlinear optical response and these crystals are potential candidates for applications in the emerging areas of photonics [1]. L-Glycine is a simplest stable amino acid with single hydrogen atom as its side chain [2]. L- Glycine has no centre of chirality and the crystals have been subjected to extensive research by several researchers for their efficient optical properties [3]. Oxalic acid is also an organic compound considered as a simplest dicarboxylic acid [4]. Due to its charge transfer complex of glycine and oxalic acid-glycinium oxalate, both the compounds are readily soluble in water therefore double distilled water can be used as a solvent during the synthesis process. When the amino acid L-glycine combines with the oxalic acid it offers new applications in the field of materials science [5]. Most of such crystals are composed of dipolar aromatic molecules, which exhibit intra molecular charge transfer that shows asymmetric polarization induced by electron donor and acceptor groups in π electron conjugated molecules are responsible for electro optic and NLO properties [6]. In this paper we report the growth of L-Glycinium Oxalate crystal. The grown crystals were subjected to characterization methods such as Single Crystal XRD, FTIR, Fluorescence spectrum, UV analysis and Dielectric Measurement.

2. Experimental Methods

L-Glycinium Oxalate single crystal was grown by slow evaporation solution growth method. The homogeneous solution was prepared by dissolving 1:1 molar ratio of organic solutes L-Glycine and Oxalic acid. The calculated amount of L-Glycine solute is dissolving in deionised water and stirrer well using magnetic stirrer. After dissolving, calculated amount of Oxalic acid is added to the above solution and heated at 40°C with continuous stirrering for 4 hours. Then the solution is filter using the whatmann filter paper and transferred to beaker with porously sealed and kept for nucleation. Nucleation occurs after 9 days and good quality crystals are harvested after 30 days shown in Fig.1.

Fig. 1. L-Glycinium Oxalate crystal

3. Result and Discussion

Single crystal XRD studies were carried out to determine the crystal structure. The miller indices (h k l) values are generated using the INDEX software package. Fourier transform infrared spectroscopy is effectively used to identify the functional groups present in the crystal. The Fluorescence spectrum gives information about excitation of molecule brought by absorption of photon. UV spectroscopy is one of the important characterization techniques to study the optical properties of the crystal. Using the LCR meter, the capacitance and dielectric loss (tan δ) of the samples prepared from these crystals were measured at the frequency of 100 Hz, 1 KHz, 10 KHz, 100 KHz, 1 MHz and 5 MHz at various temperatures.

3.1 Single crystal XRD

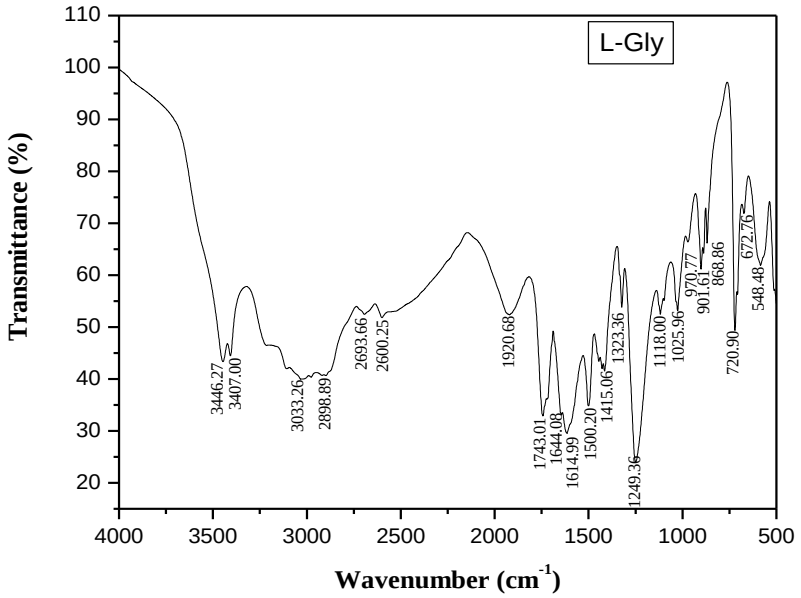
The single crystal X-ray diffraction studies of L-Glycinium Oxalate was carried out using Single Crystal X-ray Diffractometer Model Enraf Nonius CAD-4 with MoKα radiation of wavelength λ = 0.71073 Å. The X-ray diffraction analysis it was conforms the crystalline nature of the grown crystal. From the result, it was found that the crystals belong to Monoclinic system with a = 10.57 Å, b = 5.67 Å, c = 12.07 Å, α = 90°, β = 113.71°, γ = 90° and volume 660Å^3. The crystal system corelated with the reported literature [7]. Using the unit cell parameters obtained from the single crystal XRD, the Miller Indices values are generated using INDEX software package. The generated miller indexes are tabulated in table 1.

Table. 1. Miler Indices of L-Glycinium Oxalate

h	K	l	Theta
-1	2	4	20.182
-3	2	3	21.144
-1	1	6	21.920
1	3	0	22.054
0	3	1	21.974
1	3	0	22.054
-5	1	3	23.031
4	2	3	23.521
0	3	3	24.001
-3	1	6	24.537
-5	2	2	25.138
-3	3	2	25.590
-2	1	7	26.038
3	0	7	26.475
7	0	0	27.168
6	2	1	27.663
-7	0	2	28.022
-7	0	3	29.057
-5	3	2	30.016

3.2 FTIR Analysis

FTIR spectra of the grown crystals were recorded using perkin Elmer FTIR spectrometer in the wave number range 400-4000cm^{-1}. The functional groups associated with the crystals were identified and their respective peaks were assigned. The FTIR spectra of L-Glycinium Oxalate crystal was shown in fig 2 and the spectral assignments are tabulated in Table.2.



Fig; 2 FTIR Spectrum of L-Glycinium Oxalate Crystal

The spectrum of L-Glycinium Oxalate shows the broad absorptions band near 3446.27 cm^{-1} are assigned to O-H stretching. The medium intensity broad band near the wave number 2898.89 cm^{-1} is due to N-H stretching present in the amino acid molecules. Sharp peak around 2693.66 and 1920.68 cm^{-1} are assigned to the C-H stretching and N-H deformation respectively. The absorption peaks at 1614.99 cm^{-1} arises due to the presence of NH_2deformation. The absorption peaks at 1415.06, 1323.36 and 1249.36 cm^{-1} are assigned to the, C-N stretching, C-C-N asymmetric stretching and asymmetric $–CH_3$ deformation respectively. The peak at 901.61 cm^{-1} is attributed to NO_3 asymmetric stretching and the peak 868.86 cm^{-1} is due to C-C stretching [8].

Table: 2 The Frequency spectral Assignment for L-Glycinium Oxalate

Wavenumbers (cm^{-1})	**Assigned Wavenumbers (cm^{-1})**	**Assignment**
3446.27, 3407, 3033.26	3350 – 3000	O-H Stretching
2898.89	2800 – 3000	N-H Stretching
2693.66	2830 – 2695	C-H Stretching
2600.25	2600 – 2550	C-H Stretching
1920.68	2000 – 1650	N-H deformation
1743.01	2000 – 1650	N-H deformation
1614.99	1621	NH_2 deformation
1415.06	1410	C-N Stretching
1323.36	1400 – 1000	C-C-N Asymmetric Stretching
1249.36	1234	Asymmetric $–CH_3$ Deformation
1118.00	1115 – 1119	-C-H Wagging
970.77	994 – 951	CH_2 Rocking
901.61	1000 – 640	NO_3 Asymmetric Stretching
868.86	852	C-C Stretching
672.76	705 – 671	COO in plane deformation
548.48	531 – 538	COO^- Wagging

3.3 Fluorescence Analysis

The Fluorescence spectrum of the L-Glycinium Oxalate crystal was recorded using Perkin Elmer Fluorescence spectrophotometer LS45 model. The spectrum was recorded in the range between 200nm to 900nm. The Fluorescence spectra of the grown crystals are shown in fig 3. The Fluorescence gives information about excitation of molecule brought by absorption of photon.

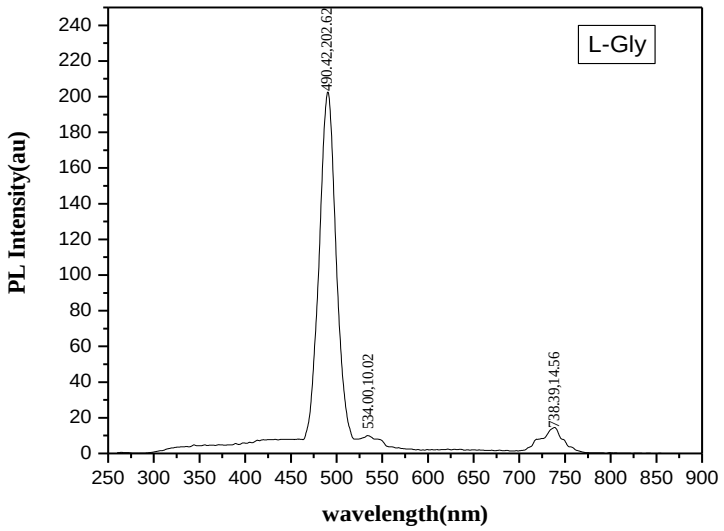


Fig: 3 Fluorescence Spectrum of L-Glycinium Oxalate

To investigate the optical phenomena like recombination of electron transitions, Fluorescence Spectroscopy analysis was carried out in the wavelength range between 250 to 900 nm. The Fluorescence excitation wavelength is 240 nm and emission wavelength is around 490. L-Glycinium Oxalate emission spectrum exhibits three peaks at different wavelengths 490.42, 534 and 738.39 nm. But variation in the intensity arises in which L-Glycinium Oxalate exhibits maximum value around 202.6 nm. The higher value is mainly due to the organic nature of the crystal. L-Glycinium Oxalate crystal was low electrical conductivity. The emission wavelength around 490nm can act as a better candidate for optoelectronic device fabrications.

3.4 UV Analysis

UV-Vis spectroscopy is one of the most important analytical and characterization techniques which are useful in characterizing absorption, transmission and reflectivity of a variety of technologically important materials. The UV-Vis spectrum was recorded for Glycinium Oxalate crystal using a U-2900 spectrophotometer in the range 200-1100 nm. The recorded UV-Vis transmittance spectra for L-Glycinium Oxalate crystal was shown in fig 4.

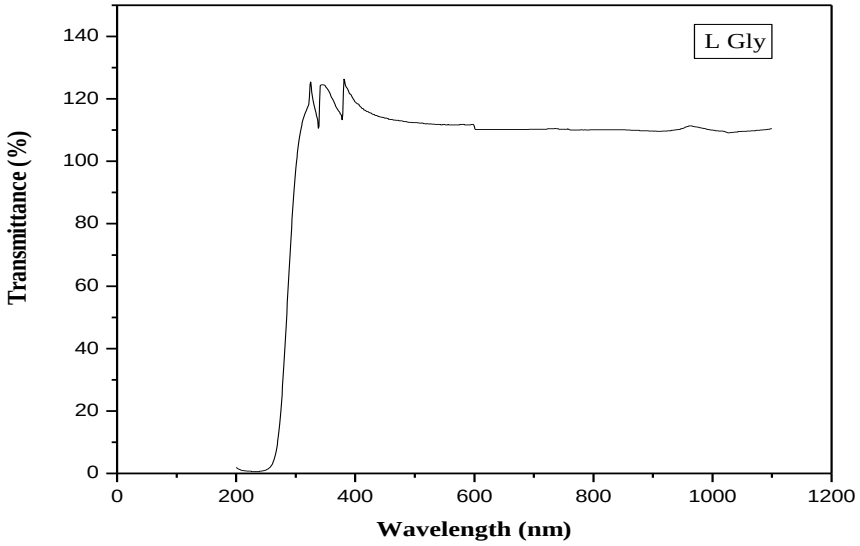


Fig: 4 UV Spectrum of L-Glcinium Oxalate

From the UV spectrum of L-Glycinium Oxalate it was confirmed that the grown crystal shows high transparent in nature. High transparency and lower cut off wavelength shows that the grown crystals are due to the organic nature which is suitable for non linear optical response and opto electronic applications. The optical band gap is the threshold for photon to be absorbed, while the transport gap is the threshold for creating an electron-hole pair that is not bound together. The optical band gap (E_g) (λ) for the crystal is evaluated using the relation,

$$E_g = \frac{hc}{\lambda}$$

L-Glycinium Oxalate shows lower cut off wavelength around 310 nm and optical band gap 6.41 eV. Furthermore it was confirmed that the crystal have lower cut off wavelengths of 240-400 nm near the UV region and exhibits absorption in the range of the blue light. These properties arise due to the combination of $\pi \rightarrow \pi^*$ transitions and change between organic-organic ligands. The lower cut off wavelength in the order of 200-400 nm is the necessary requirement of the crystal capable for blue light by second harmonic generation from diode laser. Hence the grown crystal was considered as a better candidate for NLO application. From the band gap calculation it was confirmed that L-Glycinium Oxalate act as a better insulator.

3.5 Dielectric Measurement

Using the LCR meter, the capacitance and dielectric loss (tan δ) of the samples prepared from these crystals were measured at the frequency of 100 Hz, 1 KHz, 10 KHz, 100 KHz, 1 MHz and 5 MHz at various temperatures. The dielectric permittivity of the crystals was calculated using the relation,

$$\varepsilon_r = C_{crys} / C_{air}$$

Where C_{crys} is the capacitance of the crystal and C_{air} is the capacitance of the same dimension of air. Dielectric properties are correlated with the electro-optic property of the crystals. The magnitude of

dielectric permittivity depends on the degree of polarization depends on the degree of polarization charge displacement present in the crystals.

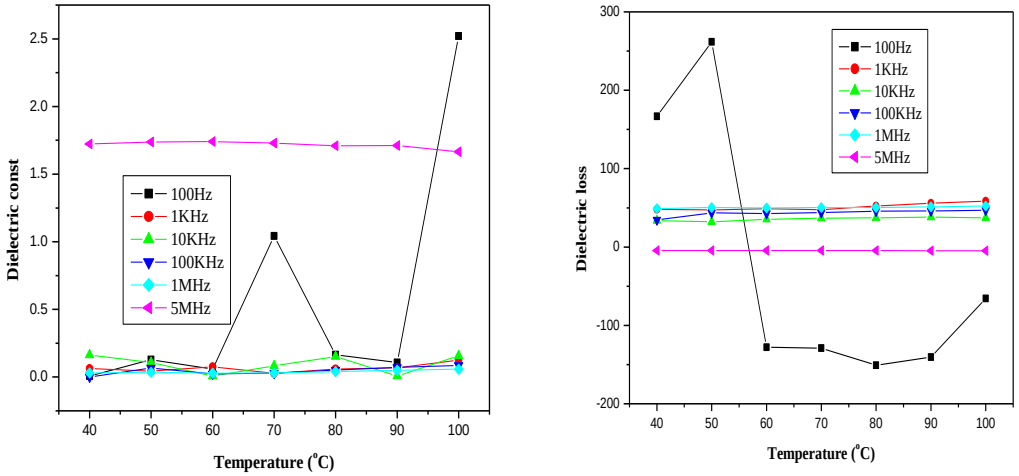


Fig: 5 Dielectric constant and Dielectric loss of L-Glycinium Oxalate

In the case of L-Glycinium Oxalate crystal, as the temperature increases dielectric constant decreases and exhibits maximum value of dielectric constant at high temperature. For 1KHz, 10KHz, 100KHz, 1MHz and 5MHz the dielectric constant remain same values with different temperature. The polarization of the crystal arises due to electronic, ionic and dipole polarization. Ionic polarization arises due to the relative displacement of potassium metal ions and amino acid ions which results lattice vibration of the crystal. Dipole polarisation requires greater time compared to other polarisations, therefore the static permittivity drops at certain temperature. The dipoles cannot orient at lower temperature, as temperature increases dielectric constant increases [9,10].

4. Conclusion

A single crystal L-Glycinium Oxalate has been crystallized successfully by slow evaporation solution growth method. Single crystal X-Ray diffraction studies were carried out and confirms that L-Glycinium Oxalate belongs to Monoclinic crystal system. FTIR studies revealed the presence of various functional groups in the crystal. Using the fluorescence spectroscopy the emission spectrum was recorded, which confirms that the material is suitable for NLO response and optical device fabrications. From UV analysis, the crystal shows high transmittance percentage and the calculated optical energy gap of the grown crystals confirms insulators. Dielectric Measurements were carried out using the LCR meter, the capacitance and dielectric loss (tan δ) of the samples prepared from these crystals were measured at various temperatures. Dielectric studies further confirms L-Glycinium Oxalate crystal is a better dielectric materials suitable for optoelectronic device fabrications.

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