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Growth, structural and opto-electrical studies of glycine doped malic acid crystal for nonlinear applications

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Abstract

The present communication reports impact on structural, optical and dielectric properties of optically active glycine doped malic acid crystal. The grown crystal was subjected to powder XRD, UV-Vis studies, FT-IR analysis and SEM characterizations. The structure and surface morphology has been examined by powder XRD and SEM analysis. The UV-Vis studies revealed high transparency and cut off was found to be 361 nm imperative to evaluate the electronic band structure and optical properties. The grown crystal inherits wide band gap, low susceptibility and high optical conductivity eminent for optical device fabrication. The lower dielectric characteristics were ascertained from dielectric studies. The imprints of glycine were evaluated by FTIR analysis.

Keywords: XRD, UV-vis studies, delectric studies, SEM analysis, FTIR analysis.

Introduction

In past decade more attention had been drawn by the organic NLO materials due to their vital physico-chemical properties essential for electro-optic modulation, laser applications, optical switching and data storage, phase matching and NLO applications. Organic materials posses high chirality, exceptionally wide bandwidth potential, excellent nonlinear activity than inorganic materials[1-3]. Many researchers had attributed studies on improved structural, thermal, optical and electrical properties due to mixing equimolar ratios of L-alanine, L-arginine with malic acid, oxalic acid, nitric acid acetic acid cited in literature[2-6]. Amino acids posses proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH_2) group. The amino acids glycine, arginine, l-alanine and lysine are evidently showing NLO activity due to donor-acceptor groups and also intermediate charge transfer was possible. Glycine ($C_2H_5NO_2$) is the simplest of all amino acid, has three polymeric crystalline forms: α, β and γ. The α and β forms crystallize in centrosymmetric while γ-glycine crystallizes in non-centrosymmetric space group[7]. As per the literature survey glycine had been doped in host materials KDP and thiourea complexes by hussaini et.al[8-9]. In present investigation crystal of glycine doped malic acid crystal has been synthesized and characterized by powder XRD, UV-Vis and dielectric studies, FT-IR analysis and SEM analysis.

Methodology

The supersaturation of host material malic acid was attained in deionized water at room temperature. 1 mole% of optically active glycine had been mixed and was stirred well for six hours at a constant speed to achieve the homogeneity throughout the volume. The solution is then filtered and kept for evaporation at room temperature. The purity was achieved by successive recrystallisation. The photograph shows good quality transparent crystals of glycine doped malic acid cited in figure 1.

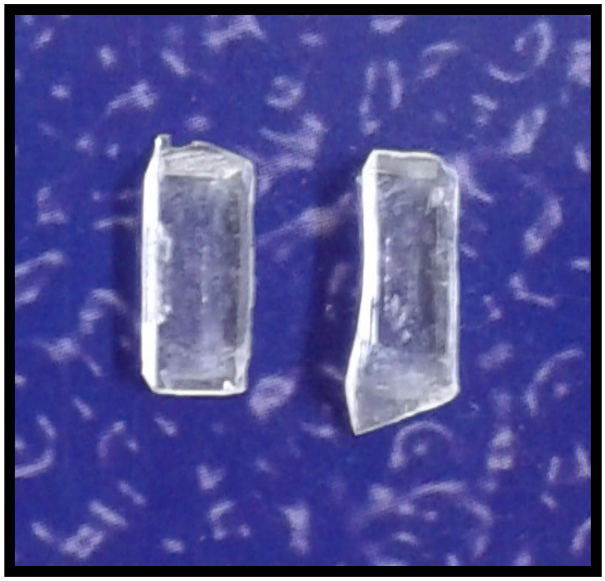

Figure-1
Photograph of glycine doped malic acid

Results and Discussion

X-Ray Diffraction Analysis: The sample of the grown crystal was subjected to powder X-ray diffraction analysis using Panalytical, XPert PRO powder X-ray diffractrometer employing CuKα radiation (λ = 1.5418 Å). The XRD pattern of glycine doped malic acid crystal, seen in figure 2. The observed peaks in the spectrum indicates the resemblance of grown

crystal to orthorhombic structure. The evaluated cell parameters are a=7.255A^0, b= 10.7A^0, c= 8.746A^0.

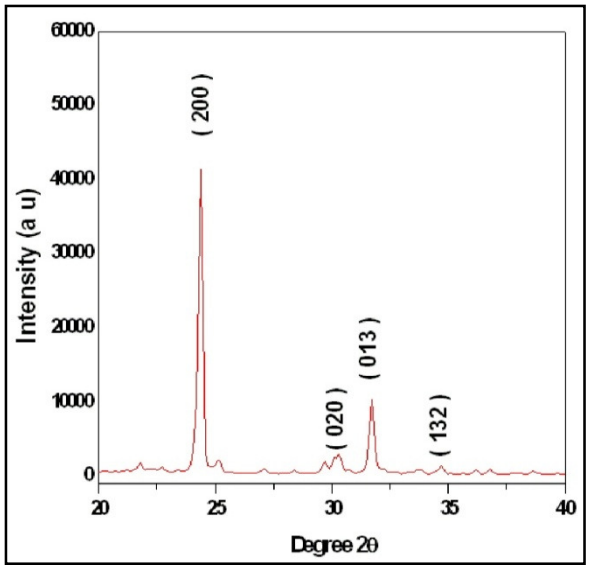

Figure-2
XRD pattern of Glycine doped Malic Acid

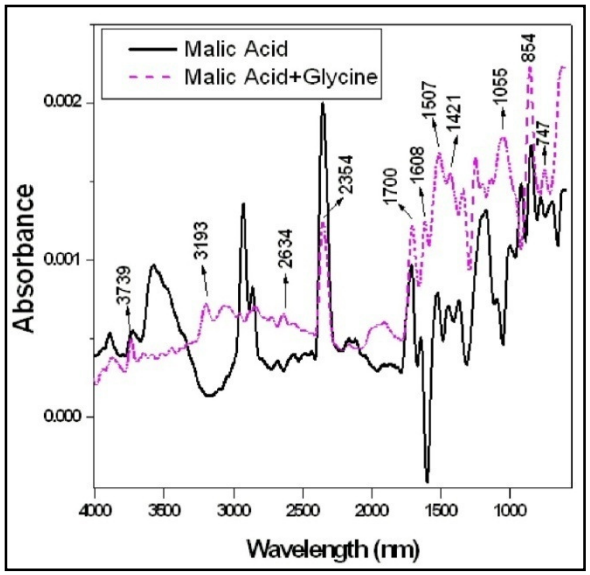

Figure-3
FT-IR Spectrum

FTIR Analysis: The incorporation of glycine in malic acid was evaluated by FTIR analysis. The absorption spectrum was recorded within the range of 600 to 4000 cm^{-1} by Bruker α-ATR visualized in figure 3. Glycine shows characteristic functional groups at 504, 658, 858, 1410, 1501, 1613, cm^{-1} [10]. The absorption peaks at 639 and 747 cm^{-1} contributes to the -COO$^-$ plane deformation. The C-C stretching is observed at 854 cm^{-1}. The absorption peak at 1055 cm^{-1} is evident of C-C-N bond stretching. The NH_3^+ asymmetric stretching is observed at 1507, 1608, 1700 cm^{-1} which appears to be in good agreement with the characteristic wavelengths of glycine. The absorption peaks within the range of 2000 to 3750 cm^{-1} contributes to the N-H and C-H stretching vibrations.

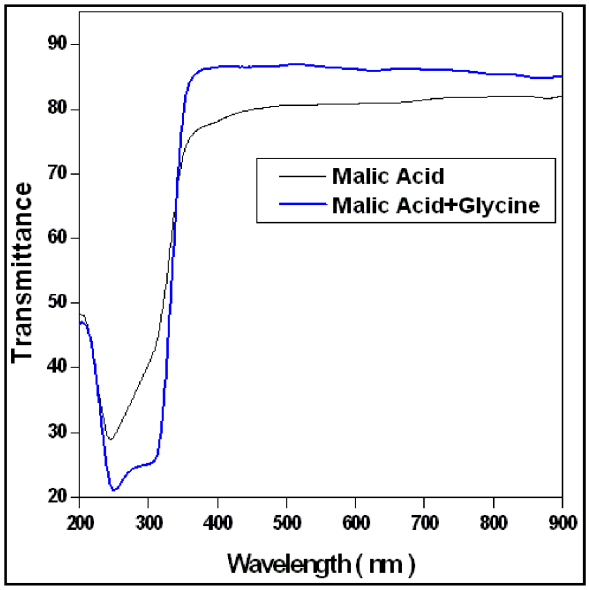

Figure-4
UV Transmittance Spectrum

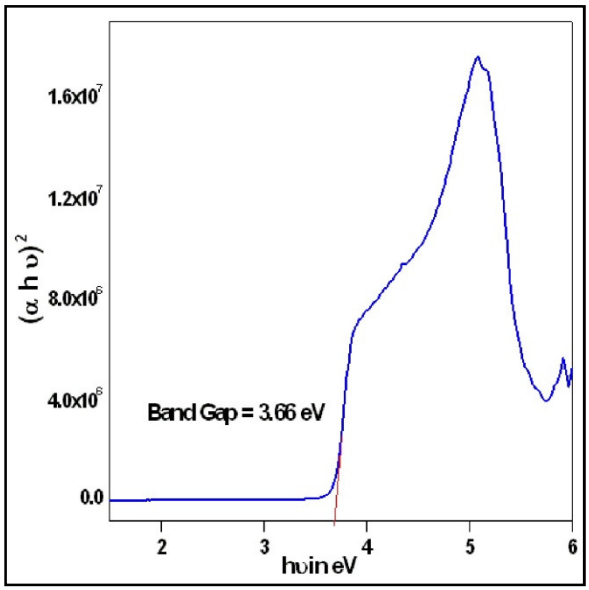

Figure-5
$(\alpha h\nu)^2$ vs. hν in eV

UV-Vis Studies: The transmittance spectrum shown in figure 4 was recorded using Shimadzu UV-2450 spectrophotometer within the range of 200-900 nm. The lower cutoff wavelength of 361 nm and high transmittance above 85% led least absorption in entire visible region affirms high optical transparency and wide transmittance range of the grown crystal imperative for NLO applications. The absorption coefficient is evaluated using the transmittance spectrum as

$$\alpha = \frac{2.303 \log\left[\frac{1}{T}\right]}{d} \quad (1)$$

Where T is the transmittance, α is the absorption coefficient, d is the thickness of the crystal Optical band gap (Eg) depicted in figure 3 was calculated by

$$\alpha = A(h\nu - E_g)^{\frac{1}{2}} \quad (2)$$

Extinction coefficient can be obtained by the following relation,

$$k = \frac{\propto \lambda}{4\pi} \quad (3)$$

Reflectance in terms of refractive index (n) is given by relations respectively,

$$R = \frac{(n-1)^2}{(n+1)^2} \quad (4)$$

The variation of $(\alpha h\upsilon)^2$ versus hυ in the fundamental absorption region is plotted in figure 5 and E_g is evaluated by extrapolation of the linear part. The remarkably wide optical band gap of 3.66 eV highly imperative for optical device fabrication. The figure 6 & 8 display decrementing values of refractive index, extinction coefficient, reflectance with increasing wavelength essential optical parameters for antireflection coating in solar thermal devices and high optical conductivity (10^{10} s^{-1}) response depicted in figure-9 is requisite for device applications in information processing and computing[11]. The ac susceptibility observed from figure-10 found to be greater than 1 which indicates material is more prone to polarize in intense light [12].The electrical susceptibility was calculated using the relation,

$$\chi_c = n^2 - 1 \quad (5)$$

The relation between band gap and refractive index is given as

$$E_g\ e^n = 18.12 \quad (6)$$

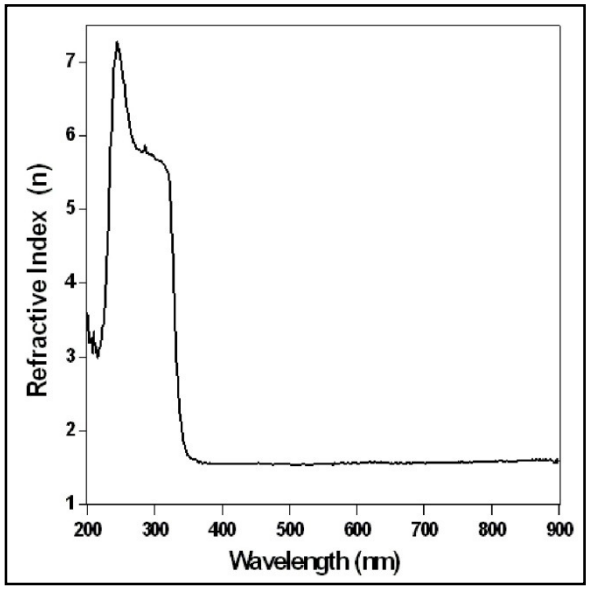

Figure-6
Refractive Index vs. Wavelength

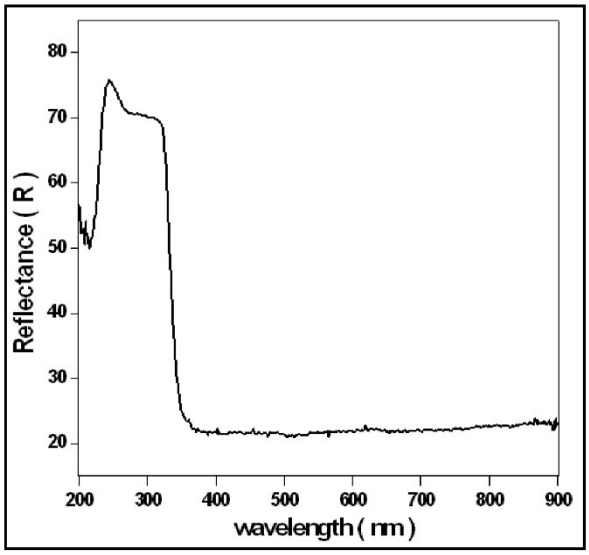

Figure-7
Reflectance vs. Wavelength

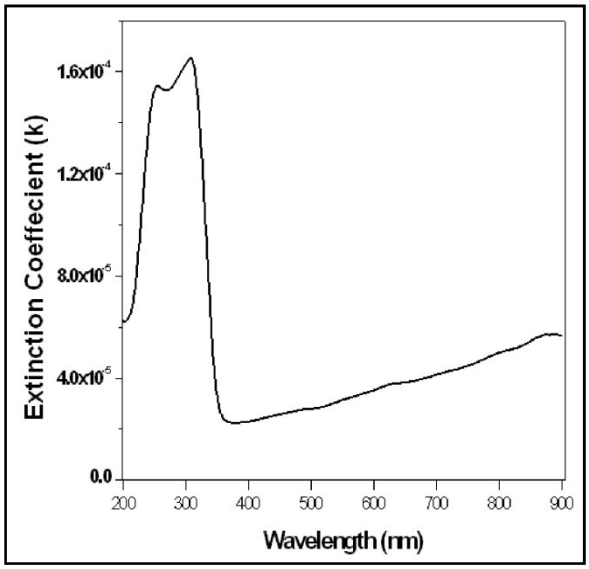

Figure-8
Extinction Coefficient vs. Wavelength

Dielectric Studies: The dielectric studies were carried at room temperature using Gwinstek LCR-819 meter within the range 10 Hz to 100 KHz. The variation of dielectric constant and dielectric loss are represented in figure-11 and 12 respectively. The higher values of dielectric constant at lower frequency are attributed due to four polarization mechanism. The lower values of dielectric constant at higher frequencies are due to low contribution of polarization mechanism. However grown crystal exhibited lower dielectric constant over entire frequency which is eminently needed for enhancement of SHG coefficient and optical quality of grown crystal[12]. The lower dielectric loss at higher frequency confirmed the lower defects concentration and the low energy dissipation[12]. The lower dielectric constant and

dielectric loss indicated the grown crystal is potential candidate for NLO applications[12].

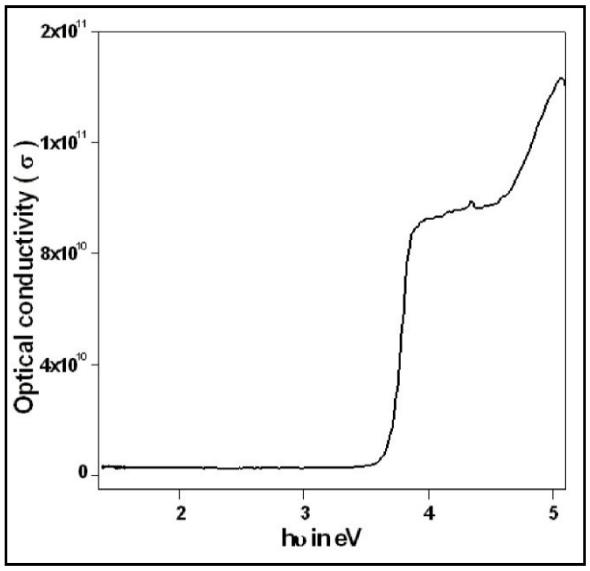

Figure-9
Optical Conductivity vs. hν in eV

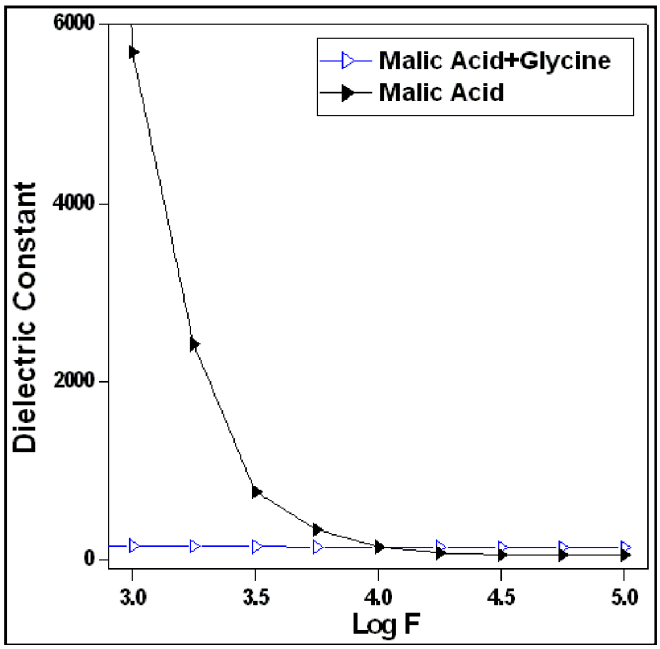

Figure-11
Dielectric Constant vs. Log F

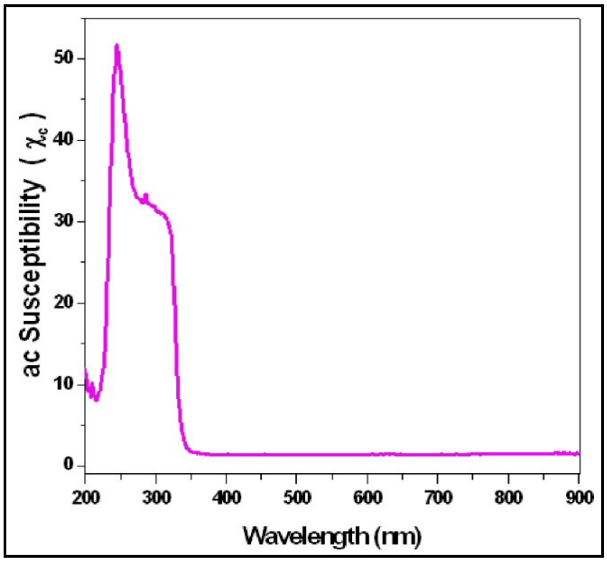

Figure-10
ac susceptibility vs. Wavelength

Table-1
Optical constants

Parameters	Malic Acid + Glycine 1Mole	Potassium Dihydrogen Phosphate [KDP]
Refractive Index	1.61	2.04
Reflectance	23	34.09
Extinction coefficient	2.41×10^{-5}	9.6×10^{-5}
ac susceptibility	1.59	3.16
E_g e^n	18.12	36.14

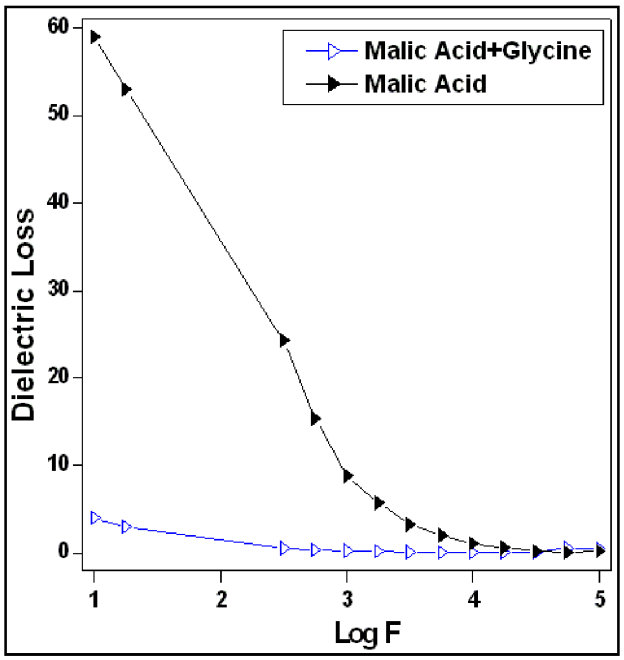

Figure-12
Dielectric Loss vs. Log F

Scan Electron Microscopy Analysis: The Scanning electron microscopy (SEM) image of the grown crystal was recorded using HITACHI S4800 to study the surface morphology of glycine doped malic acid crystal. The figure 13 depicts the layer formations on the surface of the grown crystal at a 100µm scale. It is evident that the grown crystal shows stepped growth which may be the consequence of constant rate of evaporation of solvent at room temperature.

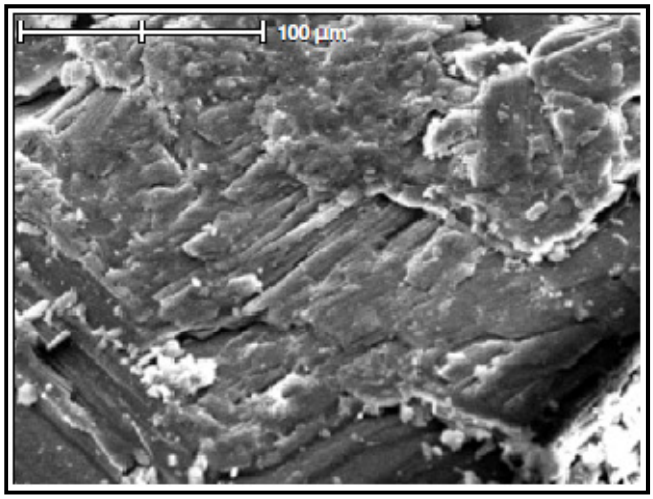

Figure-13
SEM Photograph

Conclusion

The good quality transparent glycine doped malic acid crystal has been grown and structural and optical studies were performed. The employed powder XRD verified the orthorhombic structure of the grown crystal. FT-IR analysis confirmed the incorporation of different functional groups of glycine. The cut off wavelength was ascertained to be 361nm from UV spectrum. The attribution of glycine had employed to enhance optical parameters eminently better than KDP substantive for NLO applications. The band gap of grown crystal was found to be 3.66 eV highly demanded for optoelectronic device fabrications. The dielectric studies confirmed high optical quality and lower defects concentration in grown crystal. The SEM study revealed the stepped growth of the grown crystal.

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