Synthesis, Growth, Spectroscopic, Optical and Thermal studies of Glycinium Maleate single crystals

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ABSTRACT

Organic single crystal of glycinium maleate (GM) of size 14x7x8 mm³ was grown by the solvent evaporation technique at room temperature. The solubility of GM material was studied. Unit cell parameters of the grown GM crystal were determined by single crystal X- ray studies. Powder X- ray diffraction spectrum confirms the crystalline nature. Functional groups of the crystallized molecules were confirmed by FT-IR analysis. Transmission range of the grown crystal was determined by UV-vis-NIR spectrum. The thermal characteristics of GM were analyzed by thermo gravimetric and differential thermal analysis and differential scanning calorimetry. Vickers microhardness test was performed on the prominent plane (001) of the grown crystal.

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INTRODUCTION

Nonlinear optical materials have attracted researchers because of their excellent applications in emerging optoelectronic technologies [1]. Among NLO materials, organic NLO materials are generally preferred to be more efficient than their inorganic counterparts due to their favorable nonlinear response. Organic NLO materials are widely used in second harmonic generation (SHG), frequency mixing, electro- optic modulation, optical parametric oscillation, optical bi- stability, optical image procession, color displays, under water communications and medical diagnostics, etc., [2,3]. These applications are in turn based on various properties of materials such as transparency, dielectric constant, refractive index and mechanical capability, and their thermal, photochemical and chemical stabilities [4]. In the recent past, considerable efforts have been made to combine amino acid with interesting organic and inorganic matrices to produce outstanding NLO materials to challenge the established inorganic materials like KDP, the borates and niobates. In solid-state, many amino acids contain a deprotonated carboxylic acid group (COO^-) and protonated amino group (NH_3^+). This dipolar nature gives some special features [5] such as molecular chirality, the absence of strong conjugated bonds, wide transparency ranges in the visible and UV spectral regions and zwitterionic nature of the molecule which favors crystal hardness [6].

Glycine is the simplest amino acid found in the protein of all living organisms. Structurally glycine has no asymmetric carbon atom and is optically inactive. Glycine crystallizes in three different forms namely α, β and γ [7]. Since the glycine molecule can exist in zwitterionic form, it is quite capable to coordinate with anionic, cationic and neutral chemical compounds. Some organic compounds of glycine like benzoyal glycine [8], glycine picrate [9] and glycinium oxalate [10] are reported to have good NLO efficiency comparable to KDP with better transparency window. Many of the dicarboxylic salts are reported to b e active in second harmonic generation (SHG) and it may be useful to study complexes with carboxylic acid and their properties. Maleic acid with relatively large π-conjugation has attracted our attention. The intramolecular hydrogen bond in maleic acid is very strong. Maleic acid

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forms crystalline maleate of various organic molecules through hydrogen bonding and π- π interactions [11]. It is known that maleic acid acts not only as an acceptor to form various π stacking complexes with other aromatic molecules but also as an acidic ligand to form salts through specific electrostatic or hydrogen bond interactions. Some of the organic compounds of maleate like L-arginine maleate dehydrate [12], L- Phenylalaninium maleate [13], L- alaninium maleate [14], L- arginine formomaleate [15] and a 2 aminopyridinium maleate [16] ate reported to have better NLO efficiency than KDP. The crystal structure of glycinium maleate was reported by K. Rajagopal et al. [17]. γ- glycine structure of bisglycine maleate was reported by D. Balasubramanian et al [18]. However, to the best of our knowledge, no thorough report is available on solubility and growth of GM. Hence in this work, the growth, structural, optical, thermal and mechanical properties of GM crystals are reported.

MATERIALS AND METHODS

2.1 Synthesis and solubility
Glycinium maleate (GM) was synthesized by dissolving the analytical grade glycine and maleic acid in a stoichiometric ratio of 1:1 in an aqueous medium. The solution was prepared with continuous stirring at a temperature slightly more than the room temperature. The prepared solution was left to dry and the GM salt was obtained. The purity of the synthesized salt was improved by successive recrystallization process and filtration. The reaction mechanism of the GM salt is as follows.

$$C_2H_5NO_2 \ + \ C_4H_4O_4 \ \rightarrow \ C_2H_6NO_2^+. \ C_4H_3O_4^-$$
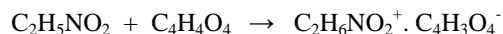
The solubility of material in a solvent plays an important role in growing large size single crystal. The synthesized salt of GM was dissolved in double distilled water and it was kept in a constant temperature bath at 30°C. After attaining supersaturation, the equilibrium concentration of the solute was analyzed gravimetrically [19]. The same process was repeated for various temperatures 35- 45°C in 5°C intervals. The solubility curve (Fig. 1) shows that the solubility increases linearly with temperature, exhibiting a high solubililty gradient, which reveals the fact that slow evaporation technique is appropriate to grow bulk single crystal.

2.2 Crystal growth
Bulk single crystals of the GM were grown by slow evaporation technique in an aqueous solution. The calculated amount of recrystallized salt of GM was dissolved in distilled water using magnetic stirrer and the solution was saturated at 35°C. The pH value of the solution was 5.2. Then the solution was kept in a constant temperature bath controlled to an accuracy of ±0.01°C. After that optical quality seed crystal obtained by slow evaporation method was suspended in the growth solution. The bath temperature was maintained at 35°C. Optically good single crystal (Fig. 2) of dimension 14x7x8 mm^3 was obtained within a period of 20 days.

RESULTS AND DISCUSSION

3.1 Single crystal X- ray diffraction analysis
Crystal structure of the grown crystal of GM was confirmed by single crystal X- ray diffraction analysis. A transparent single crystal of GM was selected for single crystal X- ray diffraction study. X- ray diffraction data were collected using an ENRAF NONNIUS- CAD 4 single crystal X- ray diffractometer with MoKα (λ= 0.71073 Å) radiation at room temperature. The unit cell parameters obtained are compared with the reported values in Table 1. In glycinium maleate, the glycine molecule exists in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The maleic acid molecule exists in a mono- ionized state. In the semi maleate ion, an intramolecular OH…O hydrogen bond is found to be asymmetric [17]. A C-H…O hydrogen bond is also observed. The glycinium and semi maleate ions aggregate into alternate columns extending along the c- axis.

3.2 Powder X- ray diffraction analysis
The grown crystal of GM was subjected to powder X-ray diffraction. Powder form of GM crystal was taken for the analysis using a Rich Seifert diffractometer with Cu Kα (λ= 1.54059Å) radiation. The indexed powder X- ray diffraction pattern of the GM crystal is given in Fig. 3. The obtained 2θ values are used for indexing using Check cell software package. The well defined and sharp peaks imply the good crystalline nature of the compound.

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3.3 FT-IR spectral analysis
Fourier transform infrared (FT-IR) spectrum was recorded using KBr pellet technique with a Perkin- Elemer RXI spectrometer. Fig. 4 shows the recorded FT-IR spectrum of GM crystal in the range 400- 4000 cm^{-1} to identify the functional groups present in the grown crystal. The FT- IR spectrum shows a very broad intense band observed at 3213 cm^{-1} corresponding to NH_3^+ asymmetric stretching mode. The position and broadness of this band clearly indicates the presence of NH_3^+ group in the crystal [20]. Thus, the protonation of the amino group can be inferred from the vibrational spectrum. The NH_3^+ symmetric stretching frequencies are overlapping with vibrations of CH_2 group. The observed NH_3^+ asymmetric stretching frequencies are lowered due to the intermolecular N-H…O hydrogen bond interactions.

The NH_3^+ asymmetric deformation mode appears at 1532 cm^{-1} [21]. The NH_3^+ rocking modes occur at frequencies around 1100 cm^{-1} for glycine and its derivatives and exact band position depends, on the position and strength of the hydrogen bond [22]. The IR band at around 1071 cm^{-1} is assigned to NH_3^+ rocking mode. The medium intense band at 449 cm^{-1} is assigned to the NH_3^+ torsion mode. The CH symmetric stretching vibrations are observed at 2863 cm^{-1}. The combination and overtone vibrations overlap in the range 2646- 1990 cm^{-1}. The frequency at 1347 cm^{-1} corresponds to CH_2 wagging vibrations. The carbonyl stretching vibrations are found in the region 1780-1700 cm^{-1} [23]. The sharp intense band in IR spectrum at 1721 cm^{-1} can be assigned to C=O stretching vibration. The symmetric C-O stretching frequency is observed at 1255 cm^{-1} in the spectrum. The COO^- bending, wagging and rocking vibrations are observed at 755, 591 and 496 cm^{-1} respectively [24]. The absorption bands arising due to C-C stretching vibrations are usually observed in the region 1150- 850 cm^{-1} [21]. The C-C stretching is observed at 870 cm^{-1}. The vibrational study confirms the existence of NH_3^+ group in glycinium maleate. The IR band positions and their assignments are given in Table 2.

3.4 UV- vis- NIR spectral analysis
Single crystals are used in optical applications. Due to this, optical transparency and UV- cut off are important. UV- vis transmittance spectrum of GM crystal of thickenss 2mm was recorded using Perkin Elmer- Lambda 35 UV-vis spectrophotometer in the range of 190- 1100 nm. The recorded spectrum is shown in Fig. 5. The crystal has sufficient transmission in the entire visible and IR region. The absence of absorption of light in the visible region is an intrinsic property of all amino acids. The lower UV- cut off wavelength is around 310 nm.

3.5 Thermal analysis
The thermo gravimetric analysis (TGA) and the differential thermal analysis (DTA) are very important to find the thermal stability of the substance. Thermal analysis was carried out using SDT Q600V 8.3 build 101 simultaneous DTA/TGA analyzer in the nitrogen atmosphere at a heating rate of 20°C/min in the temperature range 20-1200°C. A small piece of crystal weighing 2.0280 mg was used for this investigation. From Fig. 6, it is evident that the compound GM has good thermal stability up to 153.47°C as there is no major weight loss below that temperature. The TGA curve also shows that there was a weight loss of about 59% in the temperature range 153-520°C due to the liberation of volatile substance in the compound. The DTA curve shows the initial exothermic peak at 144.85°C, the melting point of the substance. Then it undergoes an irreversible endothermic at 167.66°C which shows that the decomposition of the material. The second endothermic peak at 308.68°C may be due to the liberation of glycine in GM, as glycine is known to decompose at 233°C [25]. Major decomposition of the compound is indicated by endothermic peak at 521.78°C. The heat capacity at constant pressure C_p, of GM crystal was measured by differential scanning calorimetric (DSC) analysis in the temperature range 20- 1200°C at the heating rate for the system calibration. Crystal weighing about 2.0280 mg was placed in a sealed alumina DSC pan. The DSC curve of GM is shown in Fig. 7. The specific heat of GM crystal at 167.53°C was found to be 543.3 J/g/°C. This endothermic peak temperature is well agreed with DTA curve.

3.6 Microhardness studies
Microhardness measurement is a general microprobe technique for assessing the bond strength, apart being a measure of bulk strength. The hardness of a crystal is an important solid state phenomenon. The hardness of a material is influenced by various parameters such as Debye temperature, the lattice energy, heat of formation and interatomic spacing [26]. The crystal slices are well polished with a thickness of 10µm to avoid the surface defects which influence the hardness value strongly. Microhardness studies were carried out along the growth plane (001) at room temperature using a Shimadzu HMV-2000 fitted with a Vickers pyramidal indentor. The indentations were made on the flat surface with the load ranging from 25 to 100 g and the time of indentation was kept constant at 5s for all the trials. The GM crystal can withstand a maximum load of 100 g, after which cracks developed around the

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indentation mark. The diagonal lengths of the indentation were measured. The hardness of the material (H_v) was calculated by the relation [27],

$H_v = 1.8544P/d^2$ (kg/mm^2)

Where P is the applied load (kg) and d is the diagonal length of the indentation impression (mm). The variation of H_v, with the applied load P is shown in Fig. 8. The plot between log P and log d was a straight line graph and its slope gave the work hardening index n, which was found to be 2.2. According to the Onistch concept, if n < 2, H_v decreases with increasing load, whereas for n >2, H_v increases with increasing load. In the present study of GM n>2, the material belongs to the soft materials category.

Fig. 1: Solubility curve of GM

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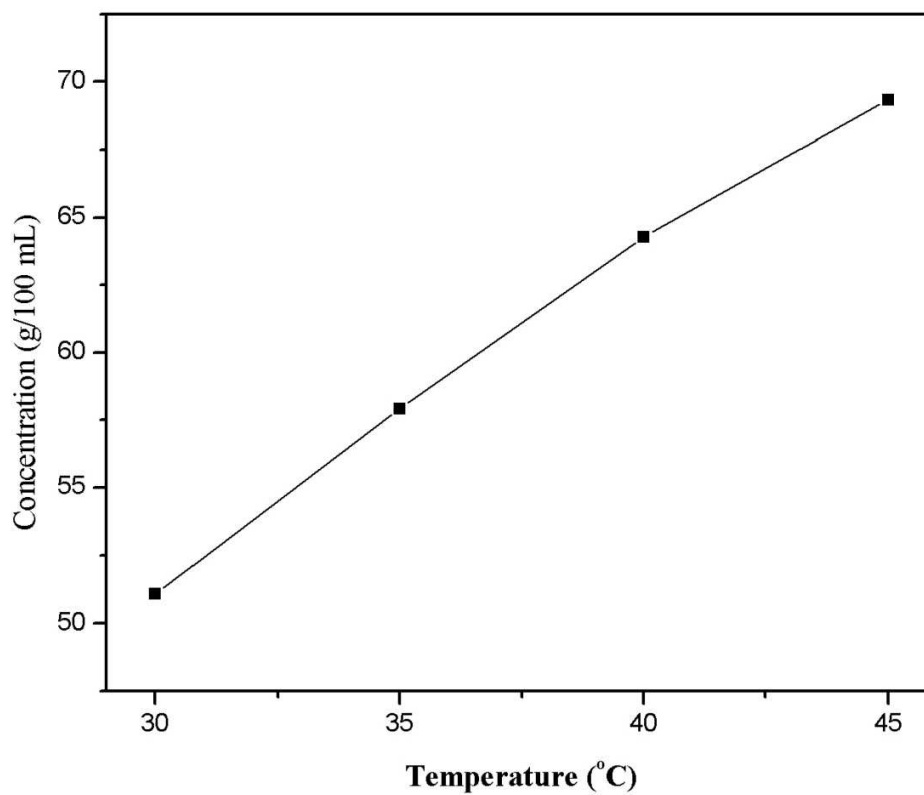
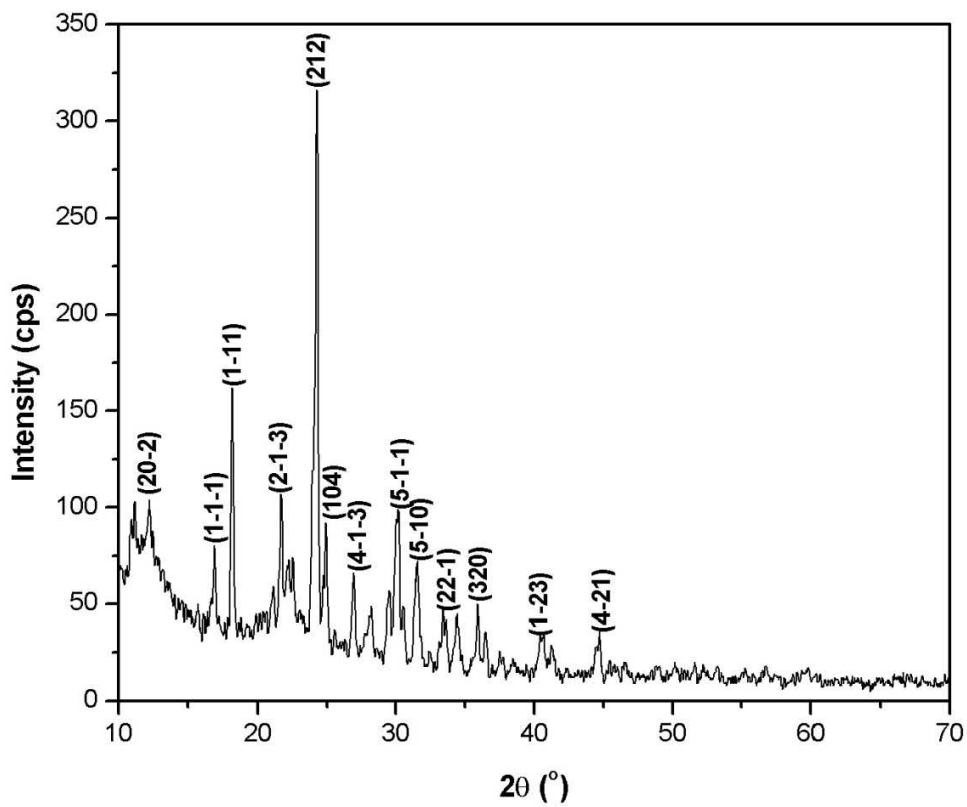**Fig. 2: Photograph of as- grown crystal of GM**
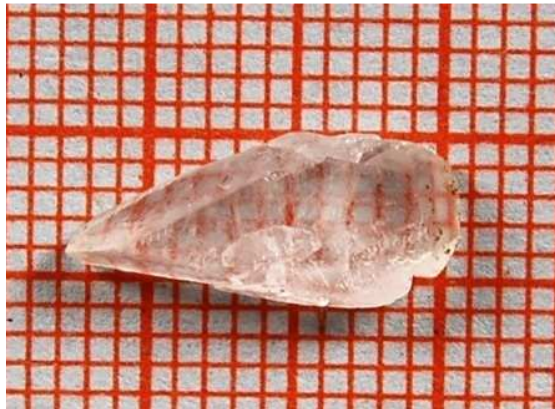
Fig. 3: Powder XRD spectrum of GM

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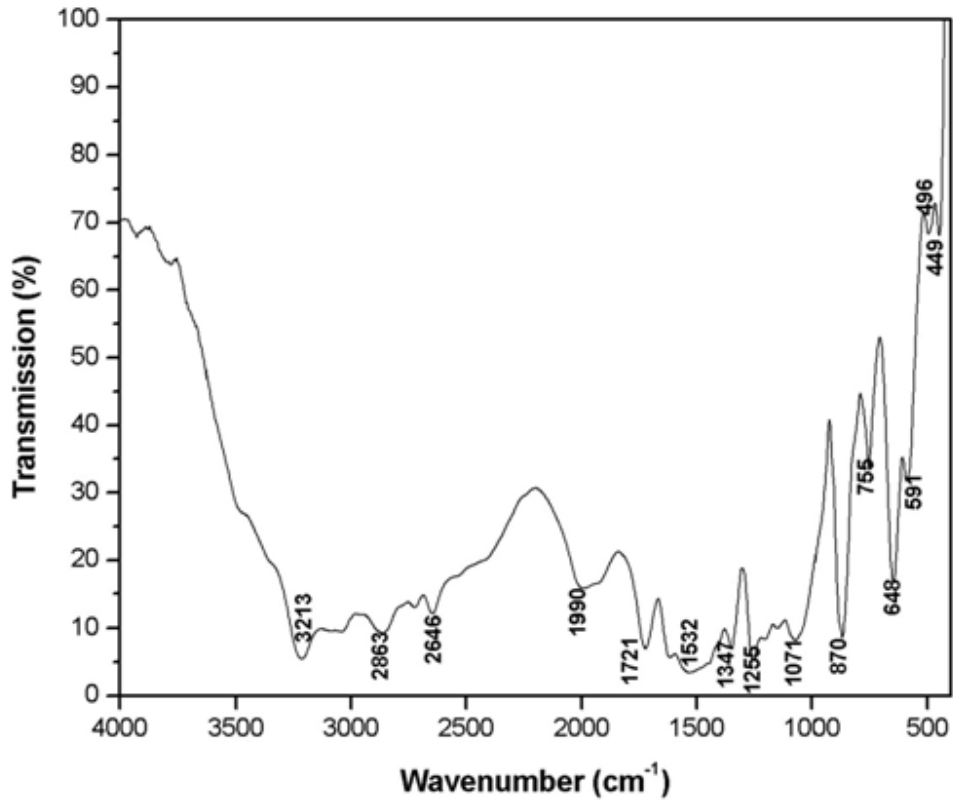**Fig. 4: FT-IR spectrum of GM**

Fig. 5: Transmission spectrum of GM crystal

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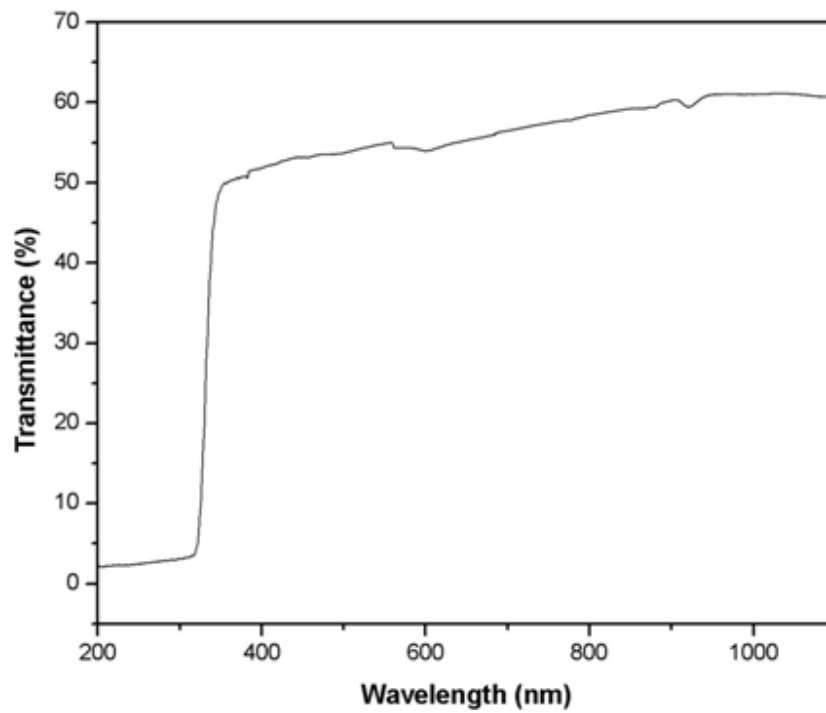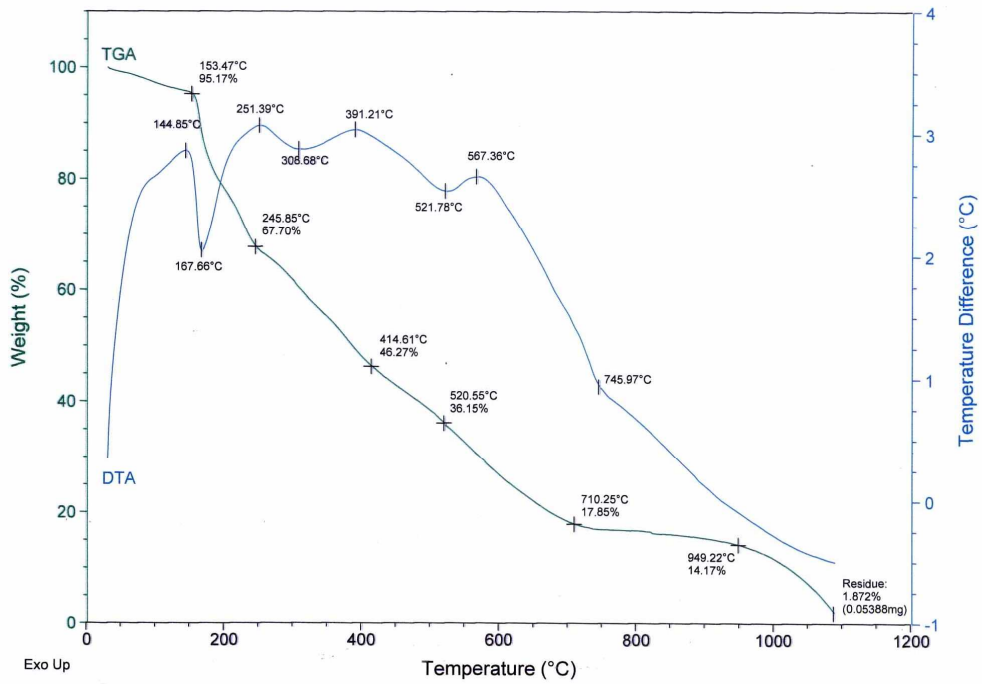**Fig. 6: TGA/DTA curve of GM**

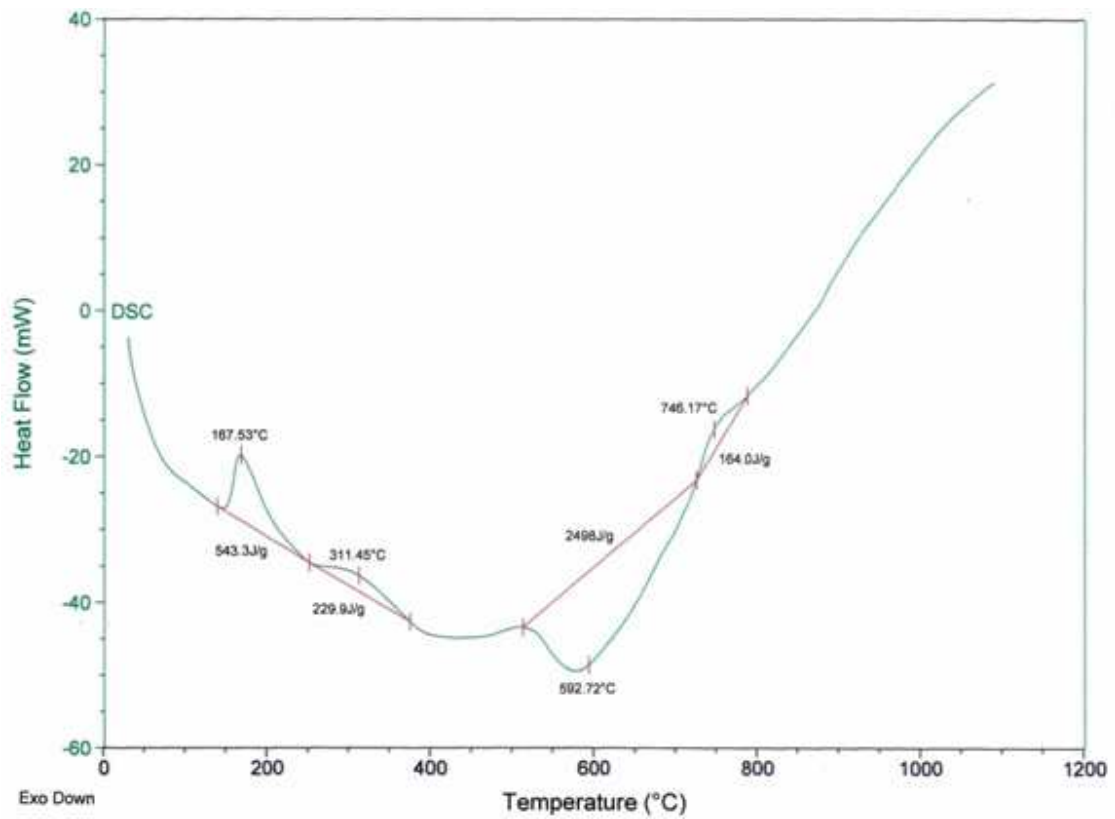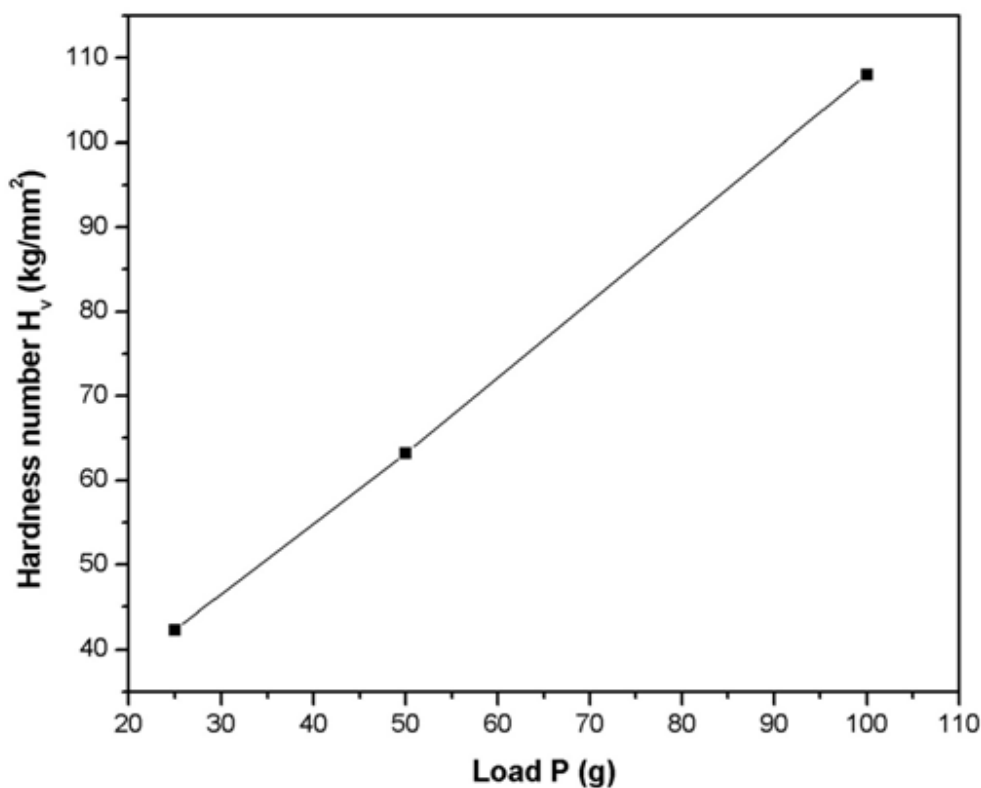**Fig. 7: DSC curve of GM**

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Fig. 8: Variation of hardness H_v versus Load P of GM

Table 1 Unit cell parameters of GM

Parameters	Present work	Rajagopal et al [17]
a (Å)	17.77	17.689
b (Å)	5.62	5.610
c (Å)	17.24	17.328
V (Å^3)	1588	1605.4
B	112.70°	112.30°
System	Monoclinic	Monoclinic
Space group	C2/c	C2/c

Table 2 FTIR band positions and assignments for glycinium maleate

Wavenumber (cm^{-1})	assignment
3213	asymmetric stretching of (NH_3^+)
2863	symmetric stretching of (CH)
2646	Combination band
1990	overtone
1727	stretching of (C=O)
1532	asymmetric deformation of (NH_3^+)
1347	wagging of (CH_2)
1255	symmetric stretching of (C-O)
1071	rocking of (NH_3^+)
870	Stretching of (C-C)
755	bending of (COO^-)
648	Bending of (COO^-)
591	wagging of (COO^-)
496	rocking of (COO^-)
449	torsion of (NH_3^+)

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CONCLUSION

An organic material glycinium maleate (GM) was synthesized and its solubility was studied. The solubility curve indicates moderate solubility of GM in water with positive solubility temperature gradient. Good optical quality single crystals of GM were grown by slow solvent evaporation technique at room temperature. From the single crystal X-ray analysis, lattice parameters were estimated and obtained values agree well with the reported values. Sharp peaks of powder XRD of the crystal show good crystalline nature of the compound. Vibrational frequencies of various functional groups present in the grown crystal were confirmed by FT-IR spectral analysis. UV-visible spectrum showed that the crystal has a wide transmission range with a lower UV-cut off wavelength 310 nm. Vickers hardness values measured on (001) plane reveals its mechanical strength as soft.

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