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Growth and characterization of Glycine Magnesium Chloride single crystals for NLO applications

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ABSTRACT

A new semi-organic nonlinear optical crystal of Glycine Magnesium Chloride (GMC) has been grown by slow evaporation solution growth technique. The crystal system and lattice parameters were determined from the single crystal X-ray diffraction analysis. Fourier transform infrared (FTIR) studies confirm the various functional groups present in the grown crystal. The transmittance and absorbance of electromagnetic radiation is studied through UV-Visible spectrum. The mechanical property of grown crystals has been analyzed by Vicker's microhardness method. The thermal behavior of the grown crystals has been investigated by DTA and TGA analysis. The second harmonic generation test has been confirmed by the Kurtz powder test.

Key words: Crystal growth, nonlinear optical materials, solution growth, X-ray diffraction.

INTRODUCTION

Non-linear optical materials (NLO) exhibiting second harmonic generation have been in great demand over the last few decades due to technological importance in the fields of optical communication, signal processing and instrumentation [1-3]. Most of the organic NLO crystals usually have poor mechanical and thermal properties and are susceptible for damage during processing even though they have large NLO efficiency. Also it is difficult to grow larger size optical-quality crystals of these materials for device applications. Purely inorganic NLO materials have excellent mechanical and thermal properties but possess relatively modest optical nonlinearity because of the lack of extended π-electron delocalization [4,5]. Hence it may be useful to prepare semi-organic crystals which combine the positive aspects of organic and inorganic materials resulting in useful NLO properties. In semi-organic materials, the organic ligand is ionically bonded with inorganics. These crystals have higher mechanical strength, chemical stability, large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness [6, 7].

Amino acids are interesting materials, as they contain a proton donor carboxyl acid (-COOH) group and proton acceptor amino (-NH_2) group which provide the ground state charge asymmetry of the molecule required for second order nonlinearity [8, 9]. Literature reveals that amino acid impurities have improved the material properties [10]. Glycine is the simplest amino acid. It is reported that glycine addition has enhanced the nonlinear optical property of Zinc-Tris-thiourea sulphate [11]. Glycine hydrofluoride [12], Glycine barium dichloride [13], Glycine thiourea [14], and Glycine sodium chloride [15] are some of the examples which proved their applications in the field of Nonlinear optics.

In this paper, we report the growth of glycine magnesium chloride (GMC) single crystals by slow evaporation solution growth technique and to study its characterization.

MATERIALS AND METHODS

Synthesis

The starting material was synthesized by taking glycine and magnesium chloride in a 3:1 ratio. The required amount of starting materials fir the synthesis of glycine magnesium chloride (GMC) salt was calculated according to the relation

$$3\ C_2H_5NO_2 + MgCl_2 \rightarrow \{C_2H_5NO_2\}_3.\ MgCl_2$$

The calculated amount of glycine was first dissolved in deionized water. Magnesium chloride was then added to the solution slowly by stirring. The prepared solution was allowed to dry at room temperature and the salts were obtained by slow evaporation technique. The purity of the synthesized salt was further improved by successive recrytallization process.

2.1. Crystal growth

The saturated solution of GMC was prepared at room temperature from the recrystallized salt. The solution was then filtered twice to remove the suspended impurities and allowed to crystalline by slow evaporation technique at room temperature. A good optical transparent crystal harvested in a growth period of four weeks is shown in Fig.1.

Characterization

The grown crystals of GMC were confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. The functional groups were identified by Fourier transform infrared studies using Perkin Elmer spectrum RXI FTIR spectrometer in the range of 400-4000 cm^{-1}. The optical properties of the crystals were examined by using Lambda 35 UV-Vis spectrometer. The thermal behavior of the grown crystal was tested by SDT Q600 V8.3 thermal analyzer. The microhardness measurements of GMC crystal were carried out using a Leitz Weitzler Vicker's microhardness tester. To confirm the nonlinear property, Kurtz powder SHG test was performed in the GMC crystals.

3.1. Single crystal X-ray diffraction analysis

The grown crystals were subjected to single crystal X-ray diffraction analysis to confirm the crystallinity and also to estimate the lattice parameters by employing Enraf Nonis CAD4 diffractometer. From the single crystal X-ray diffraction data, it is observed that the GMC crystal is hexagonal in structure. The lattice parameters were observed to be a = 7.024 Å, b = 7.013 Å, c = 5.479 Å, $\alpha = \beta = 90^o$, $\gamma = 120^o$ and V = 233.5 $Å^3$.

3.2. Fourier transform infrared analysis

The FTIR spectrum of GMC revealed at room temperature in the range of 400-4000 cm^{-1} is shown in Fig.2 and all the functional group assignments are summarized in Table. 1. The absorption due to carboxylate group of free glycine is observed at 504.2, 892.8 and 1614 cm^{-1} respectively. In GMC, these peaks are shifted to 511.8, 883.2 and 1636.8 cm^{-1} respectively. Similarly, the absorption peaks due to NH_2^+ group of free glycine are observed at 1131 and 1505 cm^{-1} respectively. In GMC, these peaks are shifted to 1116.6 and 1401.8 cm^{-1} respectively. In the same manner, the other peaks at 1384 and 2837 cm^{-1} are attributed to COO group and CH_2 group respectively from a comparison of the spectra with that of glycine [16].

3.3. Optical studies

The UV-Vis spectrum gives limited information about the structure if the materials because of the absorption of UV and visible light involve promotion of the electron in σ and π orbital from the ground state to higher energy states. Transmission spectra are very important for any NLO material because a NLO material can be practical use only it has wide transparency window. To find the transmission range of GMC, the optical transmission spectrum of the

GMC for the wavelength between 190 and 1100 nm was recorded. The recorded transmission and absorption spectra are shown in Fig.3. From the spectrum, it is evident that the GMC crystal has a very low cut off wavelength 230 nm along with a large transmission window in the entire visible region. Hence, it can be utilized for SHG from a laser operating at 1064 nm or other optical application in the blue region.

3.4. Thermal studies

The thermogravimetric analysis (TGA) and the differential thermal analysis (DTA) give information regarding phase transition and different stages of decomposition of the crystal system [17]. The TG/DTA curves for GMC were recorded for the range of temperature from 25 to 700^o C with a simultaneous thermal analyzer SDT Q600 V8.3. A powdered sample weighing 2.822 mg was used for the analyses. The analyses were carried out simultaneously in air at a heating rate of 20^o C min^{-1} and it is represented in Fig.4.

From the TGA curve, it is observed that there is a single stage of weight loss starting at 222^o C but the range between 25 and 200^o C no loss in weight is recorded. This illustrates the absence of physically absorbed or lattice water in the crystal. Hence the compound is stable up to 223^o C. between 223 and 271^o C, there is a conspicuous loss in weight. From DTA curve, the sharp endothermic peak observed at 270^o C corresponds to the decomposition of the material. The peak of the endothermic represents the temperature at which the melting terminates which corresponds to its melting point.

3.5. Microhardness studies

Microhardness measurements were carried out using Leitz Weitzler hardness tester fitted with a diamond indentor. The mechanical behavior of the GMC crystals was analyzed using Vicker's microhardness test at room temperature. The selected surface of the grown crystals were lapped, polished, washed and dried. Hardness measurements were taken for applied load s varying from 25 to 100 gm keeping the indentation constant at 10 sec. for all cases. The Vocker's hardness number (VHN) of grown crystals were calculated using the relation $Hv=1.8544\ P/d^2$ kg.mm^{-2}, where Hv is VHN, P-is the applied load in kg, d-is the average diagonal length in mm of the indentation mark. A graph was plotted between hardness number (Hv) and applied load P as shown in Fig.5. From the graph, it is found that the hardness value increases with the increase of load. This might be due to the release of internal stress generated locally by indentation.

3.6. Second Harmonic Generation Test

The second harmonic generation (SHG) test on the GMC crystal was performed by Kurtz powder SHG method [18]. The powdered sample of crystal was illuminated using the fundamental beam of 1064 nm from Q-switched Nd:YAG laser. Pulse energy 4ml/pulse and pulse width of 8 ns and repetition rate of 10Hz were used. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation of wavelength 532 nm collected a monochromator after separating the 1064 nm pump beam with an IR-blocking filter. A photomultiplier tube is used as a detector. It is observed that the measured SHG efficiency of GMC crystal was 0.5 times that of potassium dihydrogen phosphate (KDP).

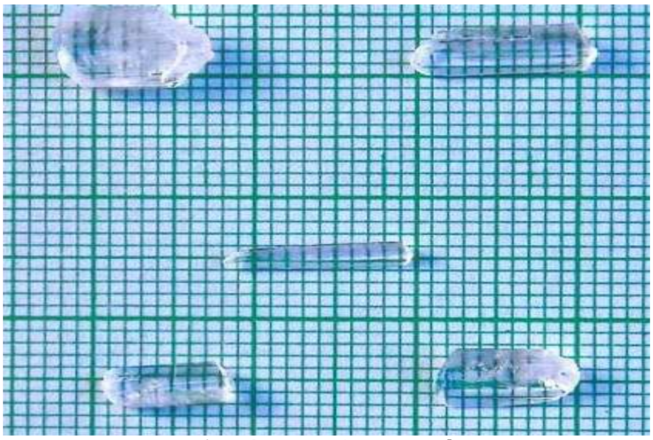

Fig.1. As grown GMC crystals

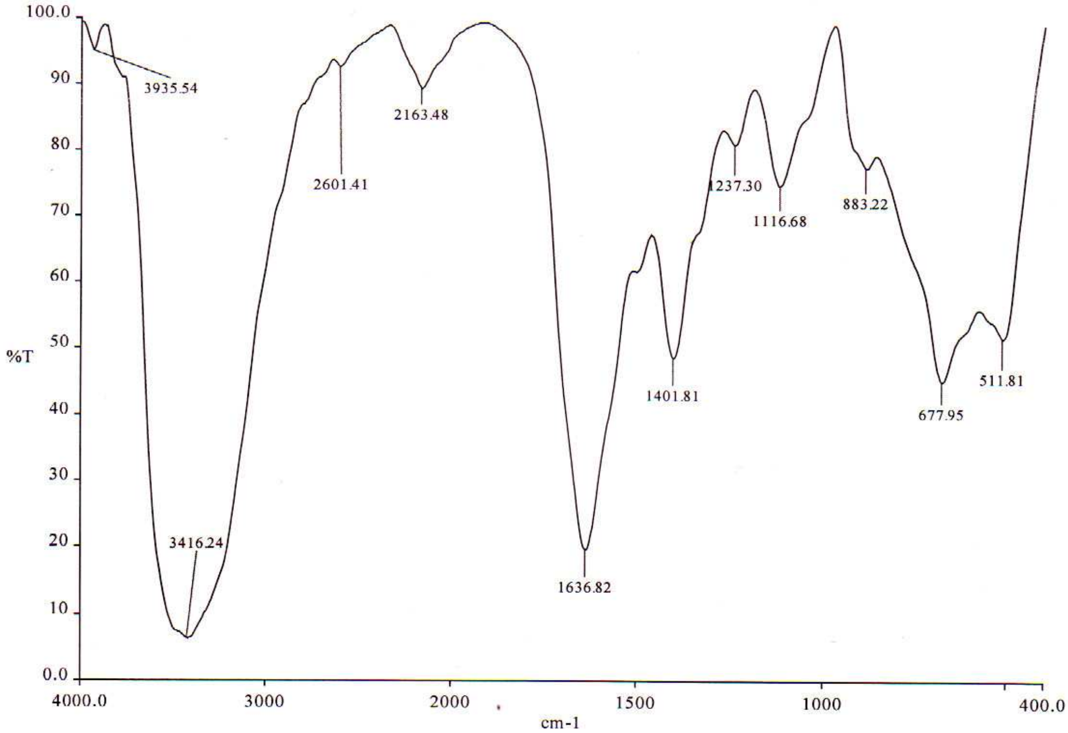

Fig.2. FTIR spectrum of GMC crystals

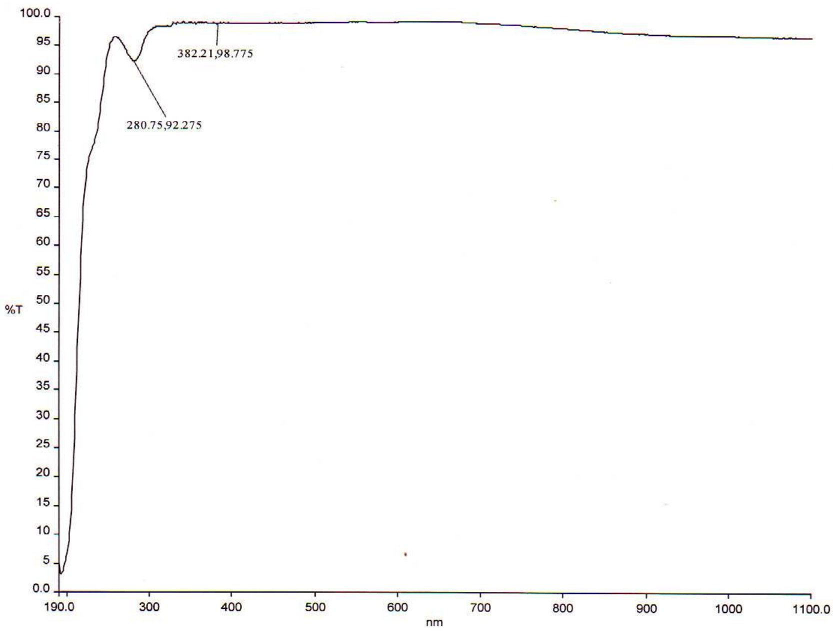

Fig.3(a). UV-Vis-NIR spectrum of GMC crystals

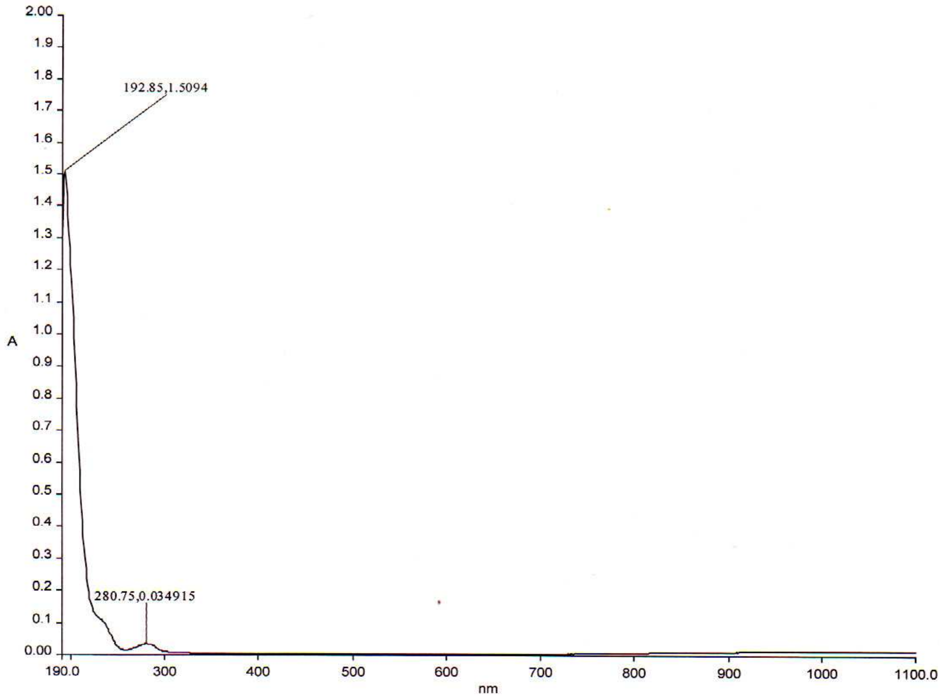

Fig.3(b). UV-Vis-NIR spectrum of GMC crystals

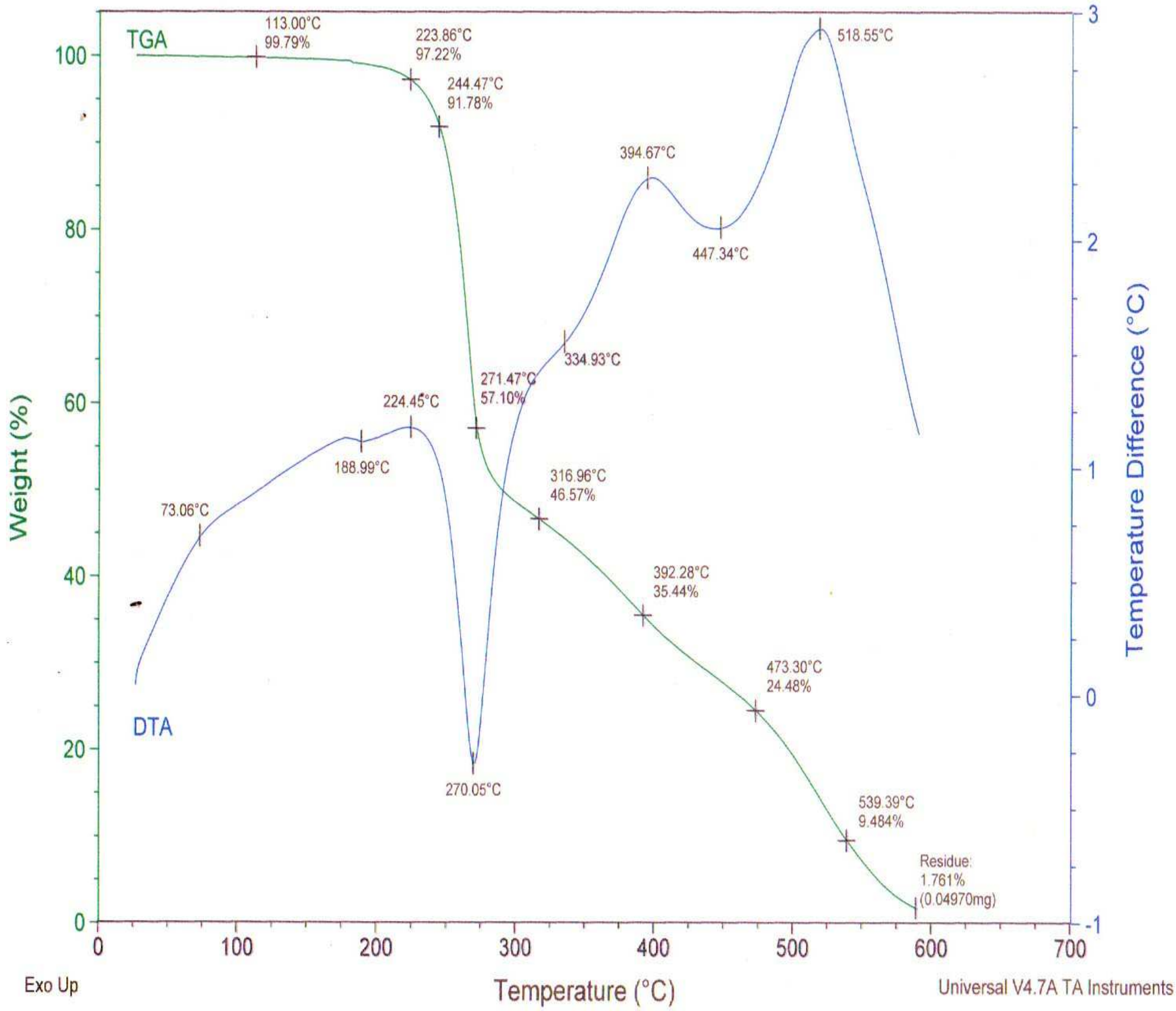

Fig.4. TG/DTA curves of GMC crystals

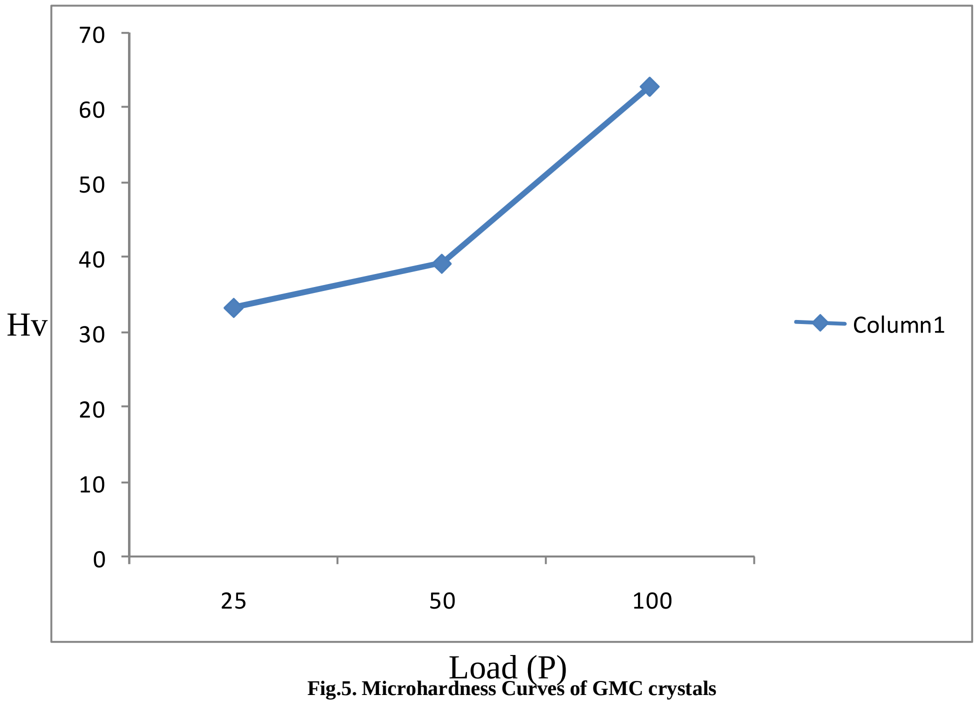

Fig.5. Microhardness Curves of GMC crystals

Table. 1. FT–IR assignments for GMC crystals

Wavelength cm^{-1}		Assignments
Glycine [16]	GMC	
504.2	511.81	Corboxylate group
892.8	883.22	Corboxylate group
1131	1116.68	Absorption due to NH_2^+
1384	1237.30	COO group
1505	1401.81	Absorption due to NH_2^+
1614	1636.82	Corboxylate group
2837	2601.41	CH_2 group

CONCLUSION

Single crystals of GMC, a new semi organic non linear optical material has been grown in solution growth technique. The lattice parameters were found by single crystal X-ray diffraction technique. The FTIR spectrum reveals that the functional groups of the grown crystal. From the UV-visible spectrum it has a good optical transmittance in the visible IR region. Mechanical property of the grown crystal has been studied by microhardness test and noticed that there is an increase of microhardness number. The thermal behavior of the crystals has been investigated by DTA and TGA analysis. The powder second harmonic generation efficiency measurement shows the grown GMC crystal having 0.5 times higher nonlinear optical efficiency than potassium dihydrogen phosphate (KDP).

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