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GROWTH AND CHARACTERIZATION OF GLYCINIUM MALEATE ORGANIC CRYSTAL

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ABSTRACT

Single crystals of organic glycinium maleate were grown from the aqueous solution of glycine and maleic acid in an equimolar ratio by the slow solvent evaporation technique at ambient temperature. Optically good and colorless prismatic single crystals were harvested with the dimension of 40 × 16 × 10 mm^3 in a fortnight. The grown crystals were subjected to single crystal X-ray diffraction and the resultant cell parameter values were compared with the reported values to confirm the coordination formed. In order to identify the functional groups present in the grown crystals, FTIR studies were carried out from 4000 to 450 cm^{-1}. They were further characterized by UV-Vis-NIR transmission and Laser damage threshold studies to determine its optical properties. Powder X-ray diffraction of the grown crystal was recorded and indexed on the corresponding major peaks. Thermal studies such as thermogravimetric (TGA) and differential thermal analysis (DTA) were carried out to find the thermal stability of the grown crystal. Dielectric properties such as dielectric constant and dielectric loss were studied at different frequencies with the function of temperature. To reveal the surface hardness, Vicker's microhardness testing was made on the as-grown crystal, from which yield strength was calculated.

KEYWORDS: Crystal Growth, Crystal Structure, X-ray Diffraction, Nonlinear Optical Crystals, Organic Compounds, Deformation, Harmonic Generation & Dielectric Properties

INTRODUCTION

Crystals grown from organic compounds are usually assembled from discrete units of organic molecules. They have attracted great attention due to their ability to combine with other compounds at low cost and ease of processing in the assembly of optical devices. Maleic acid combined with some amino acid such as l-alanine, l-arginine and l-phenylalanine to form crystalline compound [1-3], which exhibit noncentro symmetric structure and hence they behave as a nonlinear organic optical crystals. Since the amino acid glycine as an amphoteric can assume cationic and anionic forms, the molecule can combine with anionic, cationic and overall neutral chemical constituents, and thus a large number of possible glycine compounds exist [4]. Moreover organic materials have been known for their applications in semiconductors [5] and superconductors [6]. In the course of investigation of noncentro symmetric crystal for nonlinear optical devices, many attempts of growth and various characterizations is being made on glycine based organic compounds, since it has a chemical nature to produce many compounds. Efficient second harmonic generation is possible in organic media like polar crystals and poled polymers. In such systems, the more or less parallel alignment of molecules with a high hyperpolarize ability result in large values of the second order nonlinear susceptibility [7]. In this paper, we are presenting the report for the growth and characterization of glycinium maleate, a Centro symmetric crystal.

MATERIALS AND METHODS

Glycinium Maleate single crystals were grown from a supersaturated aqueous solution containing glycine (Merck) and Maleic acid (Lobo) in a stoichiometric ratio. After preparing the supersaturated solution, it was allowed to evaporate slowly at ambient temperature. The pH value of the solution was tested as 2. Colorless and elongated prismatic single crystals of Glycinium Maleate of size 40 × 16 × 10 mm^3 were harvested in a fortnight. But the crystals harvested were cloudy in nature due to the rapid growth process taking place. So they were subjected to recrystallization to get the quality crystal. The photograph of the as grown, and cut and polished single crystals of Glycinium Maleate is shown in Figure 1. The cut and polished crystals are optically good and transparent in nature. In the Glycinium Maleate compound $C_2H_6NO_2^+C_4H_3O_4^-$, the glycine molecule exists in the cationic form (Figure 2) with a positively charged amino group and an uncharged carboxylic acid group. The maleic acid molecule exists in a mono-ionized state [8].

EXPERIMENTAL DETAILS

In order to confirm the grown crystalline material as glycinium maleate, it was subjected to single crystal X-ray diffraction, which was carried out using a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite monochromated Mo (Kα) (λ= 0.7107Å) radiation. The goniometer equipped with the diffractometer is four-circle goniometer with φ, χ, ω and 2θ axes by which the crystal is rotated. The crystals of sized 0.30 x 0.20 x 0.20 mm^3 were cut and mounted on a glass fiber using cyanoacrylate. The unit cell parameters were determined by collecting the diffracted intensities from 36 frames measured in three different crystallographic zones and using the method of difference vectors followed by data collection using ω-φ scan modes. Data collection and data reduction were done using APEX2, SAINT/XPREP (Bruker, 2004) software. The structure was solved by direct methods using SHELXS97 (Sheldrick, 2008) and refined using SHELXL97 (Sheldrick, 2008) by the methods of full-matrix least squares refinement. The powder X-ray diffraction pattern of the grown glycinium maleate single crystal was recorded using Seifert dyz 2002 model powder X-ray diffractometer with CuKα (λ = 1.540598 A^0) radiation for showing crystallinity of the sample. The grown glycinium maleate single crystal was crushed into fine powder and it was scanned over the range of 10-70° at a scanning rate of 1°/minute. The intensity of the diffracted beam was recorded as a function of 2θ and the peaks were indexed. In order to identify functional groups present in the glycinium maleate compound, Fourier Transform Infrared analysis of glycinium maleate single crystal was carried out between 4000 and 450 cm^{-1} using Perkin Elmer spectrum one FT-IR spectrometer. Optical transmittance is a prominent one for any kind of optical devices. To determine the transmittance in the ultraviolet and visible region, the UV-Vis-NIR transmission spectrum of glycinium maleate crystal was recorded in the range of 200 to 1100 nm using Perkin Elmer Lambda 35 UV/VIS spectrometer. A polished crystal of thickness 2mm was used to find the transmittance.

Laser threshold studies were made in the as grown crystal of 1mm thickness using Nd:YAG laser of wavelength 532 nm and spot size about 70.849 μm in multiple shots mode. A lens of focal length 8 cm was used to focus the light spot on the crystal. The pulse rate and frequency of the laser were adjusted to 7 ns and 10 pulse/sec respective. In order to find the decomposition of the grown crystal, thermal analysis, such as thermogravimetric and differential thermal analysis were carried out between 30 ^{0}C and 1100 ^{0}C in a nitrogen atmosphere at a heating rate of 10 ^{0}C/min using NETZSCH STA 409 C/CD TG/DTA instrument. Dielectric properties such as dielectric constant and dielectric loss of glycinium maleate single crystal were studied, which were carried out using Precision LCR meter AGILENT 4284A model at various frequencies and temperatures. The required sample was prepared from the transparent part of the crystal about 2mm thickness and was

made equivalent to the size of the electrode. In order to make a contact with the electrodes, both the sides of the crystal were coated with graphite paste. Then it was placed between the two electrodes and heated from 40 ^{0}C to 100 ^{0}C using the thermostat. Capacitance and dielectric loss factors were measured at the frequency range of 100 Hz to 1 MHz and hence dielectric constant was calculated using the formula $\varepsilon_r = C_{crystal} / C_{air}$. The dielectric constant determines the property of the grown crystal. In order to reveal the mechanical behavior of the grown crystal, Vicker's microhardness studies were carried out using a HMV2T Microhardness tester. The hardness values were calculated from the formula $H_v = 1.8544\ P/d^2$ kg/mm^2, where P is the applied load and d is the mean diagonal length of the indentation.

RESULTS AND DISCUSSIONS

The unit cell parameters of the grown glycinium maleate single crystal are a=18.10Å, b=5.76Å, c=17.64Å, α=90.00(0)°, β=112.73° γ=90.00(0)° and volume=1696Å^3. It exhibits monoclinic crystal system with the centrosymmetric space group of C2/c. When they are compared, the result is in good agreement with the reported values [8]. The indexed XRD pattern of the grown crystal is shown in Figure 3. The peak obtained corresponding to the intensity shows the crystalline nature of the compound. Figure 4. shown the resulting spectrum of Fourier transforms infrared analysis, in which the functional groups present in the molecules, can be identified by stretching vibration. In this spectrum, the broadband obtaining between 2647 and 3208 cm^{-1} is due to the NH_3^+ stretching vibration [9]. A weak asymmetrical NH_3^+ bending band occurs at 1616 cm^{-1} and a strong symmetrical bending occurs at 1523 cm^{-1}. The more weakly absorption of carboxylate ion group COO^- is obtained at 1395 cm^{-1} which results from symmetrical $C(=O)_2$ stretching. The absorption peaks characterizing different functional groups are shown in Table 1. The corresponding UV-Vis-NIR transmittance spectrum is shown in the Figure 5, in which the lower cutoff region is obtained at 338 nm. Further, it is found that the glycinium maleate single crystal has almost steady transmittance from the visible region to nearinfrared region (400 to 1100 nm). The maximum transmittance in the a visible region is found to be 40%. In the laser damage threshold studies, when the laser beam of energies 10 mj and 20 mj were made to be incident on the glycinium maleate single crystal for 30 seconds respectively, there were no remarkable changes. But, when the beam energy was adjusted to 30 mj for 30 seconds, the crystal got damaged. Thus, from these observations, the energy density was calculated from the relation D = E/A GW/cm^2, where E is the input energy in milli jouls and A is the area of the circular spot size. For the title compound glycinium maleate, laser damage threshold was found to be 27 GW/cm^2.

The resulting traces of thermo gravimetric and differential thermal analysis for the glycinium maleate crystal are shown in Figure 6, which shows that there is no weight loss up to 155 ^{0}C. Hence the crystal is devoid of any physically adsorbed water on it and also it is observed that there is a continuous weight loss occurring from the temperature 155 ^{0}C. The DTA response curve too shows a sharp endothermic peak at the same temperature. Thus, from the thermal analysis, it is observed that glycinium maleate decomposes without melting and is stable up to approximately 155 ^{0}C. This was also confirmed by Monatch Melting Point apparatus. A small quantity of the crystalline substance in the form of powder was taken in a microcapillary tube and was heated up using the melting point apparatus. During decomposition at 155 ^{0}C, the glycinium maleate substance was found to be moving upward in the capillary tube by the initial force acting on the substance due to evaporation. Hence the grown glycinium maleate crystal can be designed for device application up to 155 ^{0}C. The Figure 7 and Figure 8 represent the dielectric constant and dielectric loss respectively. It is observed that dielectric constant is maximum at 100 Hz since all types of polarization such as electronic, ionic, orientation and space charge polarizations occur at a lower frequency. Also, it is found that the dielectric constant is maximum at the temperature 90 ^{0}C

and decreases gradually. Above this temperature, the randomizing action of thermal energy decreases the tendency of the permanent dipoles to align themselves with the applied field. This results in a decrease in the dielectric constant with increasing temperature. Moreover, due to the inertia of the molecules and ions at high frequencies, the orientation and ionic contribution of polarization are small [11]. So, the magnitude of polarization increases with the decrease of frequencies. Dielectric loss of the grown crystal is corresponding to the dielectric constant at all the frequencies. The graph for the Vicker's microhardness of the grown glycinium maleate single crystal is shown in Figure 9, from which it is observed that the hardness increases with the increase of load up to 100 gm and crack developed at the higher load. The strengthening of the crystal by plastic deformation is measured by a work hardening coefficient (n). Another graph (Figure10) was drawn between log P and log d to find work hardening coefficient (n) of the grown crystal. From the Meyer's law $P = ad^n$ connecting the applied load and diagonal length of the indentation, work hardening coefficient or Meyer index was calculated. Here, 'a' is the constant for the given material. The work hardening coefficient was calculated as 2.3 from the Figure. 10. According to Onitsch [12] n lies between 1 and 1.6 for hard material and it is more than 1.6 for soft materials [13, 14]. Since the 'n' value obtained is more than 1.6, the grown crystal comes under the category of soft materials. The yield strength of the grown glycinium maleate single crystalline material was also calculated using the formula [15] $\sigma_y = (H_v/3)(0.1)^{n-2}$, where σ_y is the yield strength, H_v is the Vicker's hardness and 'n' is the logarithmic exponent. It was found to be 8.77 MPa from the relation and hence the grown glycinium maleate single crystal has relatively low mechanical strength.

CONCLUSIONS

The Glycinium maleate single crystal was grown by slow solvent evaporation technique from a supersaturated aqueous solution of glycine and maleic acid at room temperature. The grown crystal was confirmed by X-ray diffraction analysis, and FTIR studies confirm the presence of functional groups in the crystal. From the optical transmittance analysis, the steady transmittance is found in the visible region and the maximum transmittance is obtained as 40%. Thermal analysis shows that the crystal has thermal stability up to 155 ^oC. The dielectric constant is maximum 4.7 at 90 ^oC temperature at 100 Hz frequency. The grown glycinium maleate crystal is a relatively soft material and having low yield strength from the investigations of microhardness testing.

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REFERENCES

1. S. Natarajan, S. A. Martin Britto, E. Ramachandran, Cryst. Growth Desi. 6 (2006) 137-140.
2. Zhi-Hua Sun, Wen-Tao Yu, Jian-Dong Fan, Dong Xu, Xin-Qiang Wang, Acta E 63 (2007) o2805-o2807.
3. M. Alagar, R. V. Krishnakumar, S, Natarajan, Acta E 57 (2001) o968-o970.
4. Michel Fleck, Ladislav Bohaty, Acta C 60 (2004) 291.
5. J. P. Farges, Organic Conductors, Marcel Dekker, New York, 1994.

6. T. Ishiguro, K. Yamaji, Organic Superconductors, Springer, Berlin, 1990.
7. E. W. Meijer, E. E. Havinga, G. L. J. Rikken, Phys. Rev. 65 (1990) 1.
8. K. Rajagopal, R. V. Krishnakumar, A. Mostad, S. Natarajan, Acta E 57 (2001) o751- o753.
9. M. Robert Silverstein, X. Francis Webstar, Spectrometric Identification of Organic
10. Compounds, john Willey & Sons, Inc, New York, 1998.
11. Y. R. Sharma, Elementary Organic Spectroscopy, S. Chand & Company Ltd, New Delhi, 2007.
12. Charles Kittel, Introduction to Solid State Physics, Wiley Eastern Limited, New Delhi, 1993.
13. E. M. Onitsch, Microscope 12 (1950) 95.
14. M. Esthaku Peter, P. Ramasamy, Mater. Chem. Phys. 137 (2012) 258-263.
15. N. P. Rajesh, V. Kannan, M. Ashok, K. Sivaji, P. Santhana Raghavan, P. Ramasamy, J. cryst. Growth 262 (2004) 561-566.
16. M. Esthaku Peter, P. Ramasamy, Adv. Mater. Lett, 7 (2016) 83-88.

APPENDICES

Figure Captions

Figure 1: Photograph of (a) as grown and (b) cut and polished Glycinium maleate crystals.

Figure 2: Structure of Glycinium Maleate crystal.

Figure 3: Powder XRD pattern of glycinium maleate crystal.

Figure 4: FTIR spectrum of Glycinium Maleate crystal.

Figure 5: UV-Vis-NIR spectrum of Glycinium Maleate crystal.

Figure 6: TG/DTA curves of Glycinium Maleate crystal.

Figure 7: Dielectric constant of Glycinium Maleate crystal.

Figure 8: Dielectric loss of Glycinium Maleate crystal.

Figure 9: Hardness V_s load graph of Glycinium Maleate crystal.

Figure 10: Plot of log P and log d of Glycinium Maleate crystal.

Table Caption

Table 1: Frequencies of the Fundamental Vibrations of Glycinium Maleate Crystal

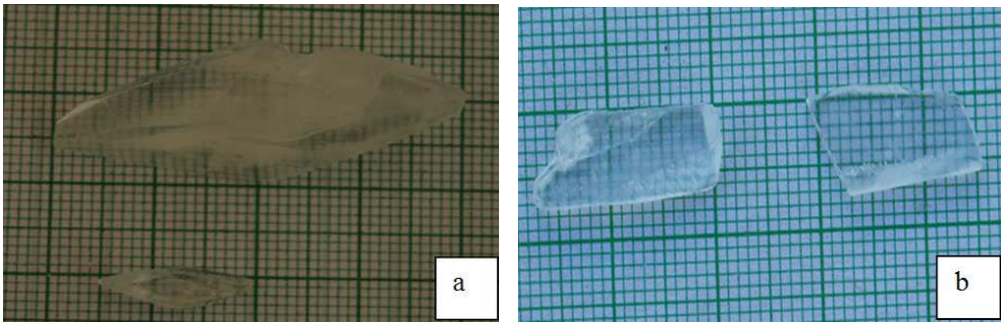

Figure 1: Photograph of (a) as Grown (b) Cut and Polished Glycinium Maleate Crystals

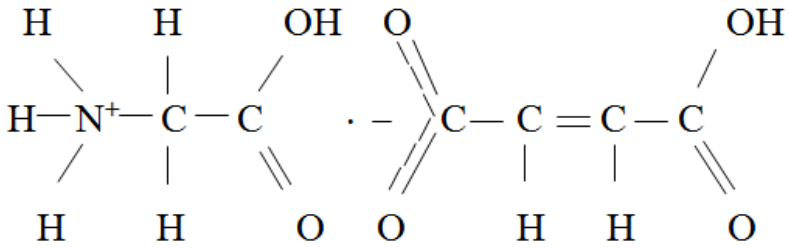

Figure 2: Structure of Glycinium Maleate Crystal

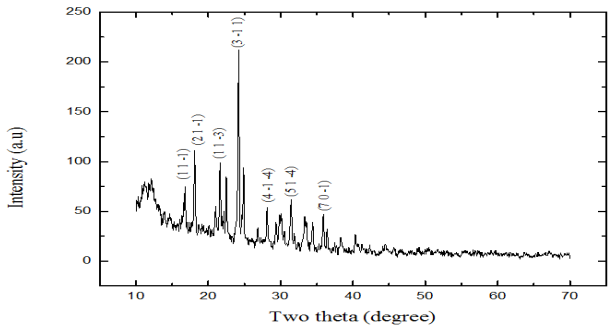

Figure 3: Powder XRD Pattern of Glycinium Maleate Crystal

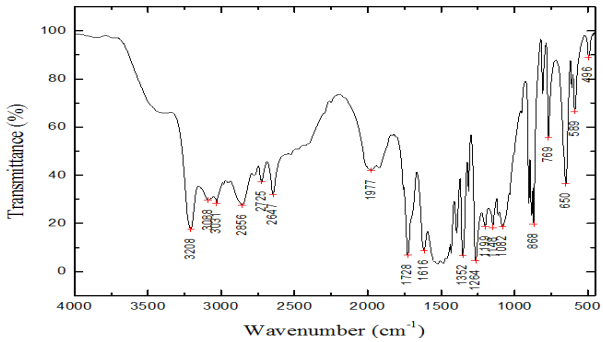

Figure 4: FTIR Spectrum of Glycinium Maleate Crystal

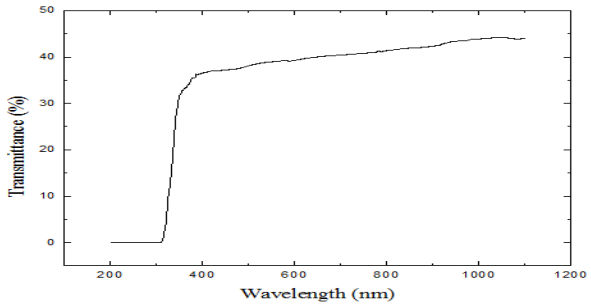

Figure 5: UV-Vis-NIR Spectrum of Glycinium Maleate Crystal

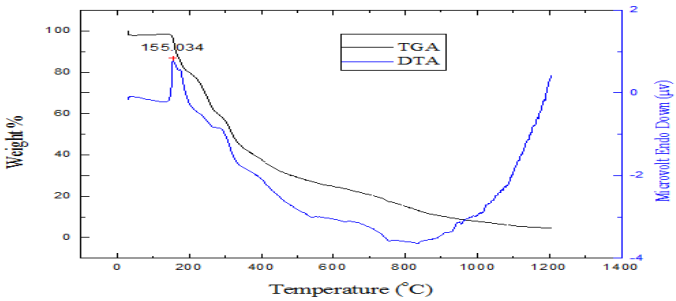

Figure 6: TG/DTA Curves of Glycinium Maleate Crystal

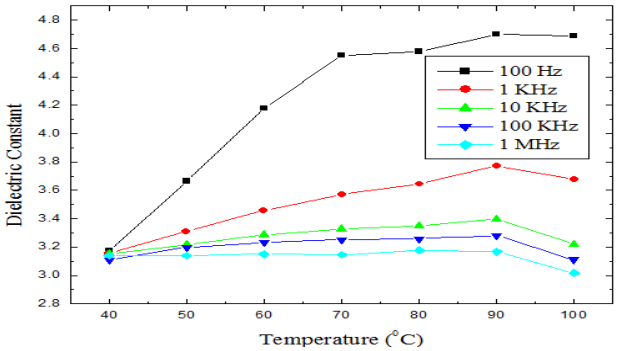

Figure 7: Dielectric Constant of Glycinium Maleate Crystal

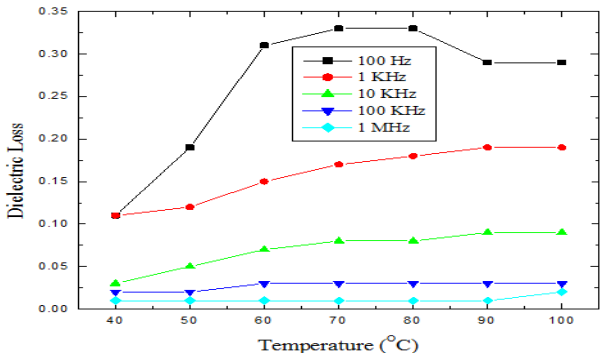

Figure 8: Dielectric Loss of Glycinium Maleate Crystal

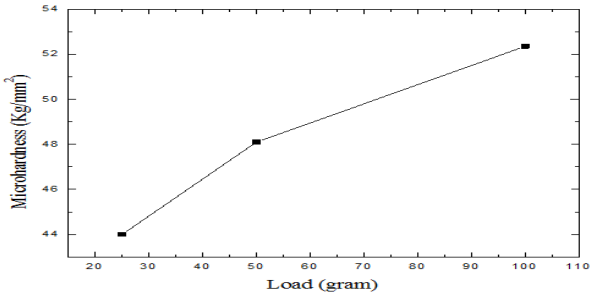

Figure 9: Hardness V_s Load Graph of Glycinium Maleate Crystal

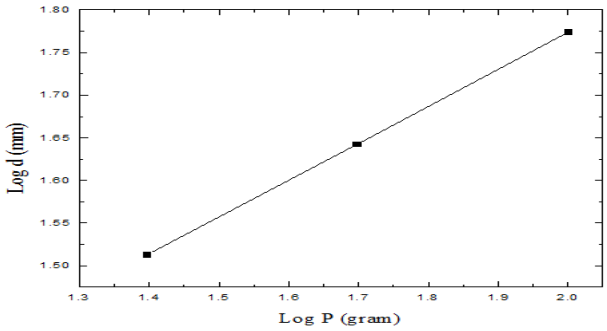

Figure 10: Plot of Log P and Log d of Glycinium Maleate Crystal

Table 1: Frequencies of the Fundamental Vibrations of Glycinium Maleate Crystal

Frequency in Wave Number (cm^{-1})	Assignment of Vibrations Ref.[9, 10]
3088, 3031	N-H stretching
2647, 3208	NH_3^+ Stretching
1728	Asymmetric C=O stretching
1616	Weak asymmetrical NH_3^+ stretching
1523	Strong symmetrical NH_3^+ stretching
1395	Symmetrical CO_2 stretching
1082	CN stretching
650	–COO- bending vibration
589	$-COO^-$wag
496	$-COO^-$rock