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Study on Growth, Optical and Dielectric Properties of Zinc Doped Glycinium Maleate Single Crystal

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Abstract: An organic compound of glycinium maleate (GM) single crystal was grown by constant temperature solution growth method. New doping method was attempted to dope the zinc metal with GM single crystal. Few peak intensities of the GM crystal were suppressed after doping zinc metal, it was observed from the FT-IR spectrum. Increase in some of the Raman peak intensities shows the presence of zinc metal present in the doped GM crystal. Dielectric constant and dielectric loss measurements were observed for the Zn doped GM crystal (Zn-GM). High value of dielectric loss at lower frequency region indicates the purity of the crystal. The percentage of the metal present in the grown crystal was found using Atomic Absorption Spectroscopy.
Keywords: Growth, Optical and Dielectric Properties,Zinc Doped Glycinium Maleate Single Crystal.

Introduction:

Amino acids and their complexes plays a vital role during these past decades, due to their role in electro optical switching, second harmonic generation efficiency, frequency conversion, optical memory storage and signal processing[1]. These organic crystals are capable of giving raise to dielectric, ferroelectric and piezoelectric materials which have many industrial applications. Presence of piezoelectric resonance peaks at lower frequency region were observed for the 2,6-diaminopyridinium -4-nitrophenolate-4-nitrophenol co-crystals during the dielectric measurements. These piezoelectric resonance peaks are capable of increasing the electro-optic coefficient of the material hence, can be used as electro-optic modulators[2].

Dielectric behavior of a new organic compound bis-glycine maleate single crystal and the existence of glycine in zwitter ionic form were discussed in detail by [3]. Glycine is the simplest amino acid which mostly reacts in zwitterionic form due to their dipole nature. Likewise glycine successfully reacts as zwitter ion with D-tartaric acid and forms a new complex compound of glycine-D-tartaric acid[4]. Optical and dielectric property of L-alanine formate proves it as a potential material for the optoelectronic devices[5].

This article explains about a doping method which was successfully attempted to dope Zn metal with glycinium maleate (GM) single crystal. Zinc doped glycinium maleate (Zn-GM) single crystal was grown and it's spectral, optical, dielectric and thermal property were reported.

Experimental Methods:

Commercially available analytical grade glycine and maleic acid were taken in equal weight ratio and dissolved in double distilled water at room temperature. The prepared solution was stirred well and sonicated for about 10 minutes in ultrasonic cleaner to make it as a homogeneous solution, similarly another solution was prepared and kept for doping. In a separate beaker 5 g of Zn metal was dissolved in 40 ml of aqua regia solution.

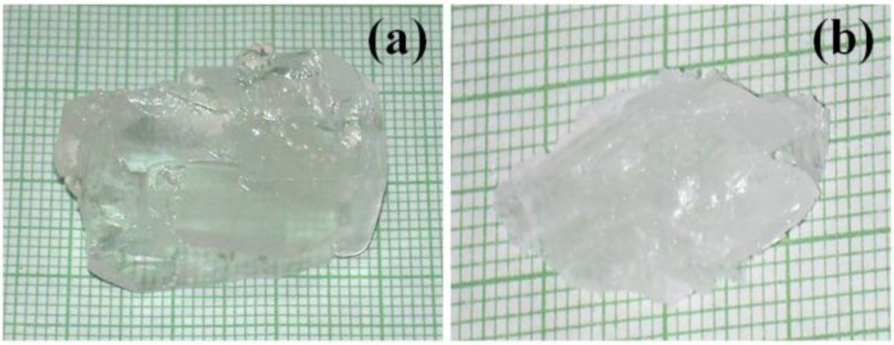

Figure 1: (a) Photograph of the GM and (b) Zn-GM single crystals.

From this aqua regia, 0.1 ml was added to one of the glycine and maleic acid prepared solution mixture. Both the solutions were separately filtered using watman fiter paper and closed with aluminium foil with few holes in order to restrict fast evaporation of the solvent.

The prepared solutions were kept in constant temperature bath of accuracy ±0.05 ^{o}C. After 3 days, nucleation was observed, after full growth period was over GM and Zn-GM crystals with dimension of 38 X 25 X 18 mm^3 and 28 X 13 X 9 mm^3 were harvested respectively. Fig.1 (a) and (b) shows the digital photograph of GM and Zn-GM crystals.

Result and Discussion:

The FTIR spectrum of the GM and Zn-GM crystals were recorded using Perkin Elmer spectrophotometer by KBr pellet method, in the region 4000-400 cm^{-1}. FT-IR plot of the GM and Zn-GM crystal were shown in Fig.2. From the spectrum the functional groups of the parent compounds present in the grown crystal were confirmed, and the frequency assignments explains the nature of the bonding between them. The small peaks at 497 and 583 cm^{-1} belongs to the COO^- rocking and COO^- wagging respectively, similarly the peak at 761 cm^{-1} denotes CH_2 rocking absorption [6]. The absorption peak at 867 cm^{-1} corresponds to the C-C stretching vibration. The symmetric and asymmetric deformation mode of COO^- belongs to the peaks 1393 and 1622 cm^{-1} [7] respectively. The intense sharp peak in the band at 3217 cm^{-1} may be assigned to N-H stretching vibrations of the amino group.

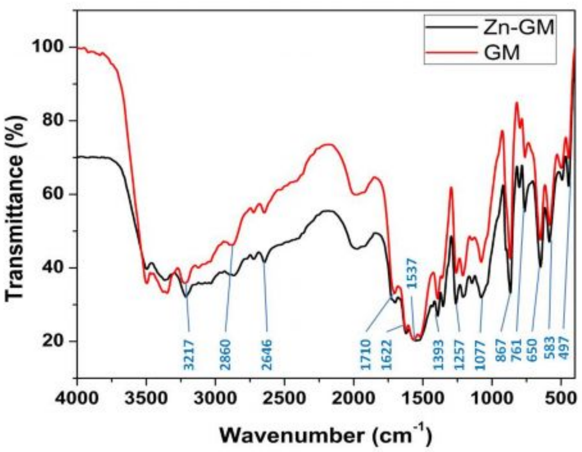

Figure 2: **FT-IR spectrum for GM and Zn-GM single crystal.**

The absorption band at 1537 cm^{-1} belongs to NH_3+ symmetric stretching. The C=O stretching band of carboxilic group seems to have peak at 1710 cm^{-1}. The peaks at 2860 and 2646 cm^{-1} are attributed to the C-H stretching mode vibrations. The vibration of C-N group appears at 1257 cm^{-1}. Here the variations of high and low intensity peaks are clearly visible between the GM and Zn-GM spectrum. The zinc metal doped with the GM crystal suppresses the peak intensity of the pure GM crystal respectively.

The Raman spectra are measured using Shimadzu UV-2600 with Ar^+ laser line λ = 513.4 nm as the excitation source with 1 nm resolution. The spectrum was recorded for both GM and Zn-GM crystals as shown in the Fig. 3. The increased intensity peaks at 3035 cm^{-1} corresponds to the N-H stretching vibration. Similarly the peaks at 2981, 877 and 497 cm^{-1} belongs to the C-H stretching, C-C stretching and COO^- rocking respectively. The intensity of Zn-GM peaks observed at 3035, 2981, 877 and 497 cm^{-1} increases significantly when compared with the undoped GM sample. Also, the higher frequency phonon mode at 1684 cm^{-1} is attributed to C=O stretching vibration and the peaks intensity have rapidly reduces due to the incorporation of Zn metal ions.

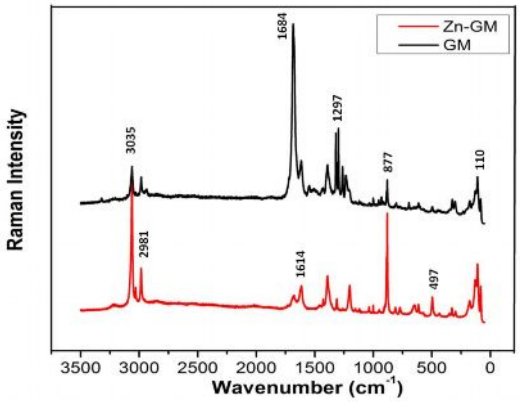

Figure 3: Raman spectrum for Zn-GM and GM single crystal.

The remaining peaks located at 1614 and 110 cm^{-1} has the similar trends when compared to doped and undoped samples. The asymmetric deformation mode of COO^- corresponds to the 1614 cm^{-1} respectively.

The transmittance spectrum of the Zn-GM was recorded using Perkin Elmer Lambda 35 spectrum in the range of 200 to 1100 nm. The transmittance and optical cut-off are necessary parameters for a material to undergo any device applications.

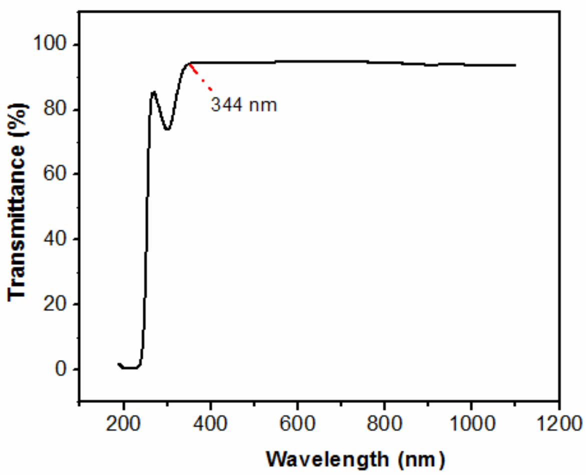

Figure 4: Transmittance graph of Zn-GM crystal.

The transparency of Zn-GM crystals is more than 90 % in the entire visible region and the lower cut-off wavelength around 344 nm is sufficient for application in the blue green region.

The transmittance graph of Zn-GM was shown in Fig.4. From the transmittance (T) value the absorption coefficient (α) value can be found using the following relation [8]

$$\alpha = \{2.303 \log (1/T)\}/d$$

Where "d" is the thickness of the sample and "T" is the transmittance, from the observed transmittance data. In a crystalline and polycrystalline material both direct or indirect optical transitions are possible depending on the band structure of the material.

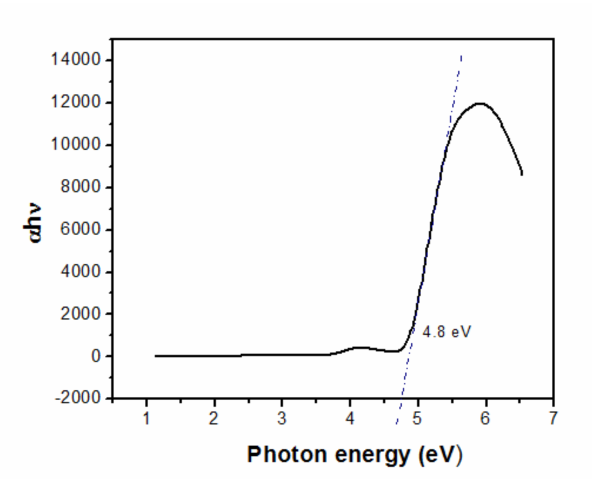

Figure 5: Graph of αhν and photon energy for Zn-GM crystal.

For direct transition n = 1/2 or 3/2 depending on the transition whether is allowed or forbidden in quantum mechanical sense. Similarly, n = 2 or 3 for indirect allowed and forbidden transitions respectively. There will be single linear region in direct transition and two liner regions in the indirect transition [9]. In the present study of band gap plot, it has single linear region and corresponds to direct optical transition. Tauc's graph [10] (band gap) was plotted between $\alpha h\nu$ and photon energy ($h\nu$) is shown in the Fig.5. By extrapolating the linear portion near the onset of absorption edge [11] the band gap (Eg) was found to be 4.8 eV for the Zn-GM single crystals as shown in the Fig.5.

Refractive index (n) can be determined from the reflectance (R) data using

$$R = (n-1)^2 / (n+1)^2$$

and transmittance (T) is given by

$$T = [(1-R)^2 \exp(-\alpha t)] / [1-R^2 \exp(-2\alpha t)]$$

Reflectance in terms of absorption coefficient (α) can be derived from the above equation.

$$R = [1 \pm \sqrt{(1 - \exp(-\alpha t) + \exp(\alpha t))}] / [1+\exp(-\alpha t)]$$

And from the above data the refractive index "n" can be derived as

$$n = [-(R+1) \pm \sqrt{(-3R^2 + 10R - 3)}] / [2(R-1)]$$

The extinction coefficient (k) is found using the formula $k = \lambda\alpha/4\pi$, where λ and α are the wavelength and absorption coefficient of the material. The value of refractive index (n) for Zn-GM crystal is calculated to be -0.015638246 at 1100 nm.

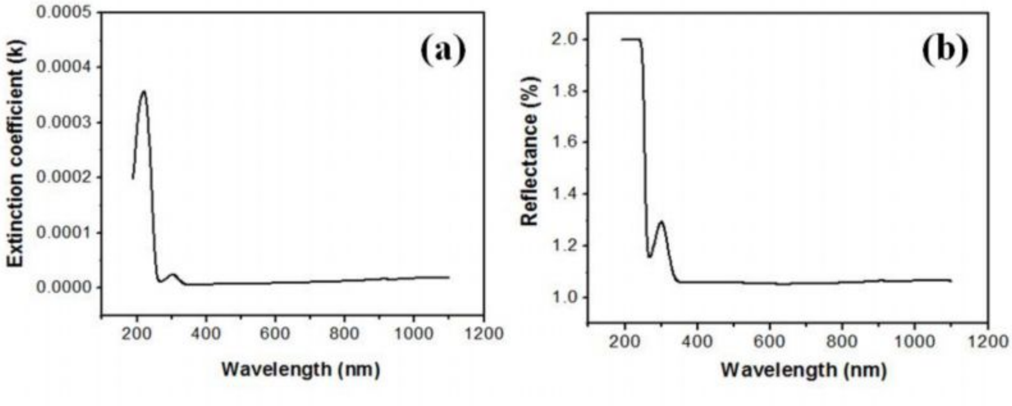

Figure 6: (a) Extinction coefficient and (b) Reflectance graph of Zn-GM crystal.

Fig. 6(a) and (b) shows the extinction coefficient and reflectance graph of Zn-GM crystal. The decay or damping of the amplitude of the incident electric and magnetic field is known as the extinction coefficient [12]. From these optical constant values, the real (ε_r) and imaginary (ε_i) part of dielectric constant can be calculated using the equation[13].

$\varepsilon_r = n^2 - k^2$ and $\varepsilon_i = 2nk$

The value of real (ε_r) dielectric constant is calculated to be 0.000244554 and -0.000000590259 for imaginary (ε_i) dielectric constant at λ = 1100 nm respectively.

The dielectric measurement for the Zn-GM crystal was taken using the Numeric Q (Model N4L) Phase Sensitive Multimeter 1735. Good quality transparent crystals were selected and both sides are coated with silver paste to have good ohmic contact with the electrodes. It is observed from the Fig. 7(a) that the dielectric constant value decreases with increase in frequency due to the space charge polarization.

As the frequency increases the temperature does not make much change in the dielectric behavior of the compound, Figure 7(a) shows the plot of dielectric constant versus frequency and Figure 7(b) shows the plot of dielectric loss verses frequency for various temperatures.

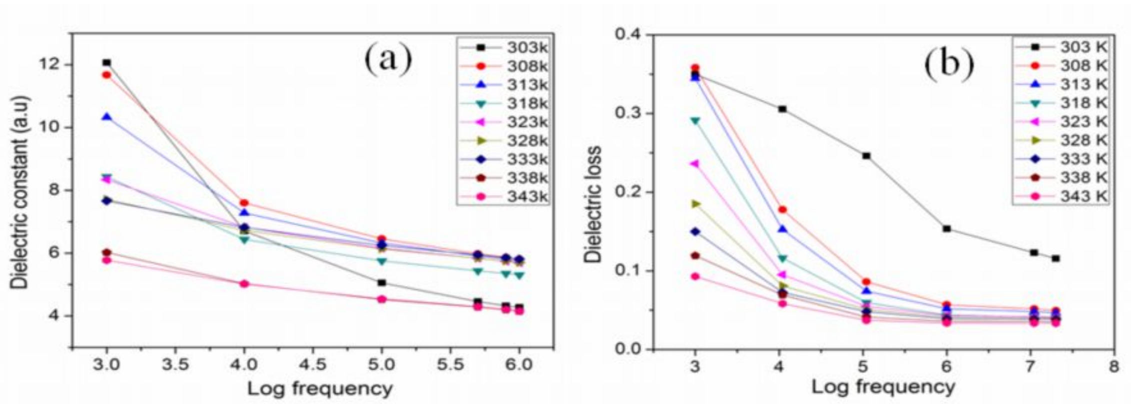

Figure 7: (a) Graph of dielectric constant and (b) dielectric loss vs frequency for Zn-GM crystal.

It is expected that the power dissipation will be more at high dielectric constant, hence the dissipation will be less at higher frequency region for the grown crystal [14]. The high value of dielectric loss at lower frequency region indicates the purity of the crystal with lesser defects and improved optical quality. The low value of dielectric constant at high frequency region indicates the less dissipation of charges at high frequency region. Therefore, both doped and undoped GM crystal gives normal dielectric behavior for various temperatures [3]. The dielectric measurements show that the crystal is capable for practical applications in the microelectronic industries respectively.

The AAS analysis was carried out using Perkin Elmer Spectrophotometer to determine the percentage of the zinc metal in the grown GM crystal. For the doping process 5 g of Zn metal was made to dissolve in 40 ml of aqua regia solution. From the grown Zn-GM crystal 0.1 g was dissolved in 25 ml of distilled water and it is used for the study. Air and acetylene (C_2H_2) was used for ignition of blue flame, height of the flame was measured to be 7 mm. Absorption peak of 0.5608 was absorbed for the solution concentration of 1.157 mg/L. Using the concentration value, percentage of Zn metal present in the Zn-GM crystal was found to be 0.0289 wt. %.

Attempt was made with higher concentration of doping Zn of around 0.5 ml from the 40 ml aqua regia but the higher concentration let to precipitation. The reason was not clear at this moment and so this method is suitable for minimum amount of metal doping.

The TG/DTA measurement of the Zn-GM crystal was observed using the Q600 SDT instrument under nitrogen atmosphere from room temperature to 800 ^oC at the heating rate of 10 ^oC/min. Gradual weight loss was observed for the crystal, as shown in the Fig.8. The first stage of weight loss around 137 ^oC may be due to the evaporation of observed water molecules. The sharp endothermic peak at 152 ^oC may be associated to the thermal energy utilized to overcome the valance bonding between the glycine cation and the maleate anion, mostly happens at the initial stage of decomposition [3]. The endothermic peak around 328 ^oC may be due to the formation of peptide [6].

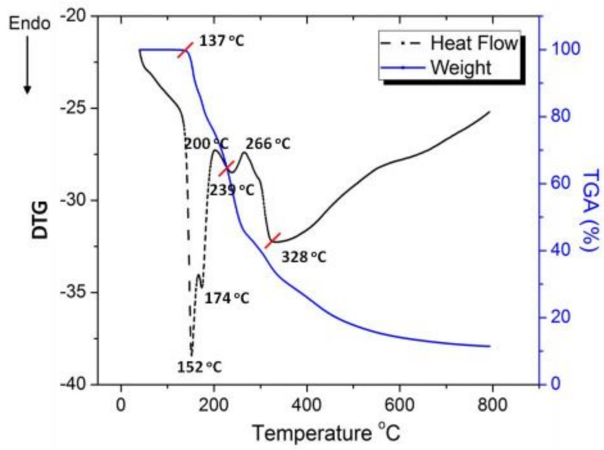

Figure 8: TG/DTG graph of Zn-GM crystal.

4. Conclusion:

Zinc doped organic crystal of glycinium maleate (Zn-GM) was grown under constant temperature by restricted evaporation method. Novel attempt for doping of Zn metal in GM crystal was achieved in the study. By using this doping method other metal may be doped with crystal in a minimal amount. The zinc metal when doped with GM crystal suppresses the FT-IR peak intensities. High intense Raman peaks shows the presence of Zn metal in the GM crystal.

Optical constants like absorption coefficient (α), reflectance (R), refractive index (n), extinction coefficient (k), band gap (E_g), real (ε_r) and imaginary (ε_i) part of dielectric constants of Zn-GM crystal was evaluated from the transmission spectrum. The percentage of zinc metal present in the grown crystal was calculated to be 0.028 weight percentage. The crystal shows a normal dielectric behavior for various temperatures. Thermal measurements show that the Zn-GM crystal can withstand upto 152 ^oC. High value of dielectric loss at lower frequency region confirms the crystal is capable of fabricating optoelectronic devices.

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