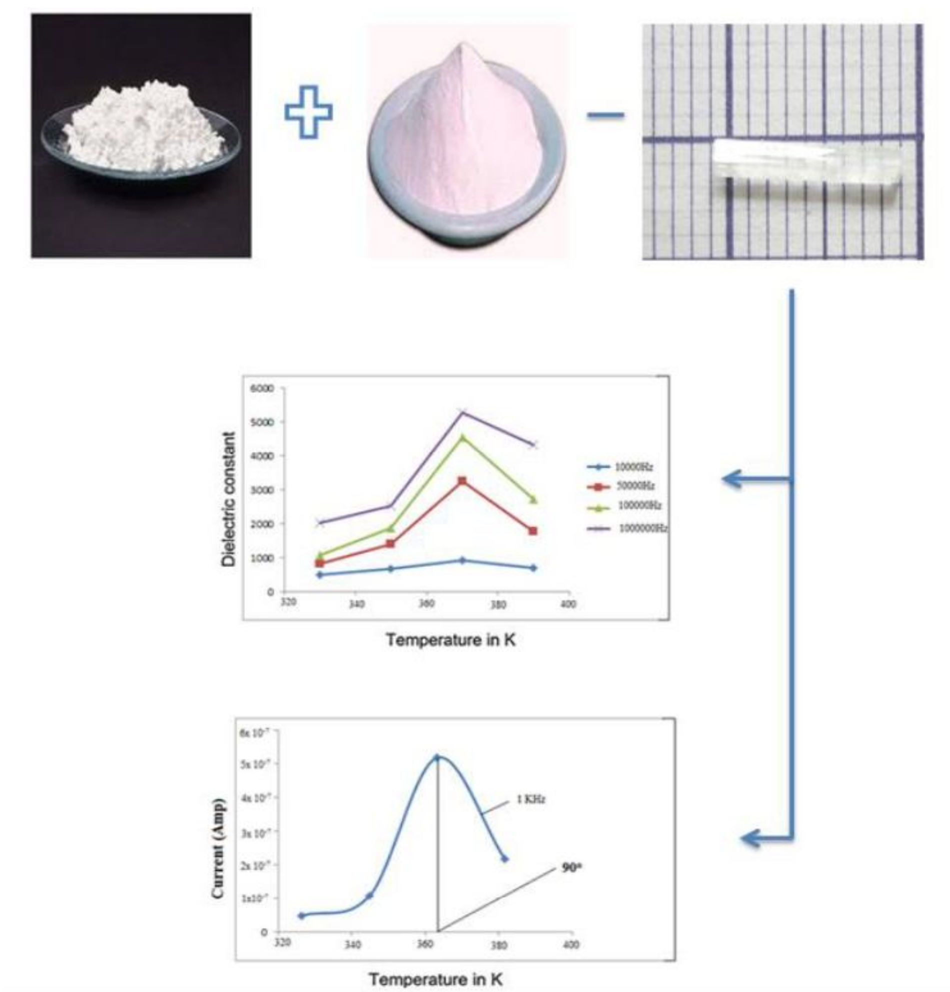
CHAPTER 7

GROWTH, SPECTROSCOPIC, DIELECTRIC & ELECTRICAL STUDIES OF GLYCINE MANGANOUS ACETATE SINGLE CRYSTAL (GMNAC)

7.1 GRAPHICAL ABSTRACT OF GLYCINE MANGANOUS ACETATE



7.2 INTRODUCTION

The search for new materials with high optical nonlinearity is a potential area for both academic and industrial purpose. These materials have attracted the interests of many theoretical and experimental researchers. Complexes of amino acids with inorganic acids and salts are promising materials for optical second harmonic generation (SHG), as they tend to combine the advantages of the organic amino acid with that of the inorganic acid salt. 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 (M.D. Aggarwal et al. ., 1999, T. E. Manjulavalli and A. G. Kannan 2015). Purely inorganic NLO materials have excellent mechanical and thermal properties but possess relatively moderate optical nonlinearity. The present fascinating field of research is to synthesize, grow and characterize semi organic NLO crystals. Here an attempt has been made to synthesize and grow NLO semi organic crystals. 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(Nalini Jayanthiet al.2015). These crystals have higher mechanical strength, chemical stability, and large non linearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness.

Amino acids are interesting materials, as they contain a proton donor carboxyl acid (-COOH) group and proton acceptor amino (-NH2) group which provide the ground state charge asymmetry of the molecule required for second order nonlinearity(Praveena et al. 2015, Abu El-Fadl et al. 2007). Recently a large number of amino acid based crystals has been reported for successful nonlinear optical applications such as L-alanine acetate, L-alanine cadmium chloride, L-glutamic acid hydro bromide, and L-Valine hydro bromide(Jai Pio Deva Sahaya Das & Helen Merina Albert 2016, Roshan et al. 2001) in the literature. Glycine is an organic compoundwith the formula NH_2CH_2COOH. Having a hydrogen substituent as its side-chain, glycine is the smallest of the 20 amino acids commonly found in proteins.Glycine is the simplest amino acid. Unlike other amino acids, it has no asymmetric carbon atom and is optically inactive. It has three polymeric crystalline forms α, β and γ. Glycine and its methylated analogues form complexes with mineral acids exhibiting interesting physical properties like ferro elastic, ferro electric or antiferro electric behaviour often associated with transitions. According to the structural analysis of ferroelectric triglycine sulfate, there are two kinds of glycine group's glycinium and zwitterions. Such conFigurerations of glycine ions interconnected by short O-H-O hydrogen bonds are regarded as significant for the ferroelectric behaviour of this crystal.

In the present work we, report on growth of new semi-organic crystal Glycine Manganous Acetate (GMnAc) from amino acid family and its characterization. To have a full understanding about the structure and its properties for the grown crystal single crystal XRD structure analyses, PXRD, UV- Vis absorption, Thermal analyses (TG/DTA), and SHG measurements were also been carried out. Dielectric studies are also taken for the grown crystal.

7.3 EXPERIMENTAL PROCEDURE

Commercially available Glycine Manganous Acetate was used for the growth. The solution was prepared by dissolving equimolar amounts of Glycine and Manganous Acetate in double distilled water. The reaction takes place according to the equation given below.

$$C_2H_5NO_2 + C_4H_6O_4Mn \rightarrow C_2H_5NO_2.C_4H_6O_4Mn \qquad (7.1)$$

The material was purified by repeated recrystallization.

7.3.1 Crystal Growth

Glycine, an amino acid was mixed with inorganic salt Manganous Acetate in aqueous solution in the ratio of (1:1) stirred continuously to get a uniform solution.The solution was then filtered twice to remove the suspended impurities and allowed to crystalline by slow evaporation technique at room temperature in a dust-free atmosphere.

The grown crystals are bright, transparent and white in colour. The grown crystals were collected from the mother liquid by using well cleaned forceps. Good transparent crystals were obtained in a period of about 3 weeks as shown in Figure7.1.

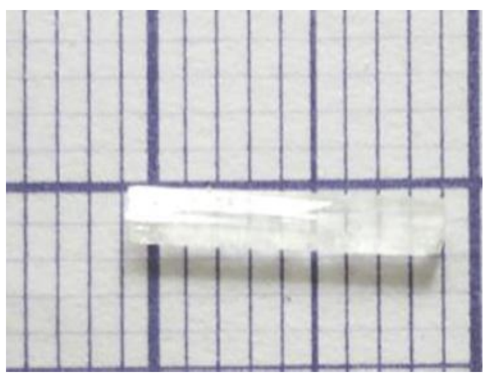


Figure7.1As grown crystal of GMnAc

7.3.2 Characterization Techniques

Single crystal XRD was recorded by Enraf Nonius CAD/MACH3 single crystal X-ray diffractometer to find the molecular structure, atomic coordinates, bond lengths, bond angles and molecular orientation. The powder XRD pattern of crystal was obtained using a BRUKER AXS D8 Advance X-ray diffractometer with CuKα radiation (λ = 1.54060˚A) at room temperature. The electronic absorption and transmittance spectra of the compound were recorded using Lambda 35 UV–visible spectrophotometer in the wavelength range from 190 to 800 nm. DSC analysis of GMnAc was carried out between 30 and 50 ^{o}C in nitrogen atmosphere at a heating rate of 10 ^{o}C using Perkin Elmer model. Mechanical properties of the grown GMnAc crystals were studied using MH–5 hardness testers. The dielectric studies of the compound were recorded at room temperature using a TH 2816 A DIGITAL LCRZ METER in the frequency region50 Hz–2MHz. The second harmonic generation (SHG) efficiency of the material was carried out by Kurtz–Perry powder technique using Nd: YAG laser beam.

7.4 RESULTS AND DISCUSSION

7.4.1 Single Crystal XRay Diffraction Analysis

GMnAc was subjected to Single crystal X-ray diffraction and powder X-ray diffraction studies. The X-ray data were collected using an Enraf Nonius CAD/MACH3 single crystal diffractometer instrument for grown Glycine Manganous Acetate crystal. The calculated lattice parameter values are a = 9.11 Å, b =17.54Å and c = 10.41Å, $\alpha = \gamma = 90^{o}$ and β = 11.08^{o}Volume of the unit cell =1552Å^{3}. The XRD data prove that the crystal is monoclinic crystal system. The XRD results are in good agreement with the reported values and thus confirm the grown crystal.

7.4.2 Powder X-Ray Diffraction

Powder X-ray diffraction study was used for the identification of crystallinity of the grown crystal. The Kα radiations (λ = 1.5418 Å) from a copper target were used. The sample was scanned in the range between 10 and 100^{o}C. Figure7.2 represents the indexed powder diffractogram for the grown crystal of GMnAc. The sharp intensity peaks found in spectra shows good crystalline nature and purity of the grown crystal.

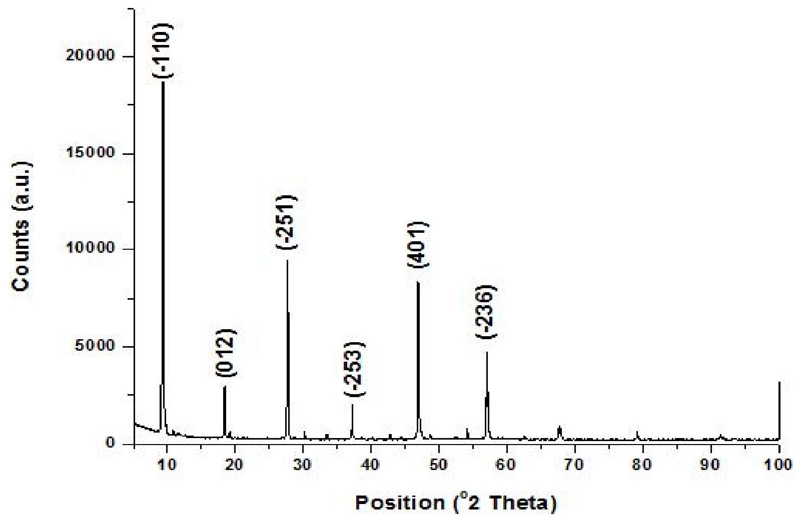


Figure 7.2 Powder XRD pattern of GMnAc

7.4.3 Thermal Studies

DSC was performed using Perkin Elmer (model DSC 7) in the temperature range 20–280° C at a heat rate of 10 K/min. The measurement was recorded at Nitrogen atmosphere. The sharp endothermic peak upwards at 71.9° C shown in Figure7.3 confirms the melting point of GMnAc crystal.

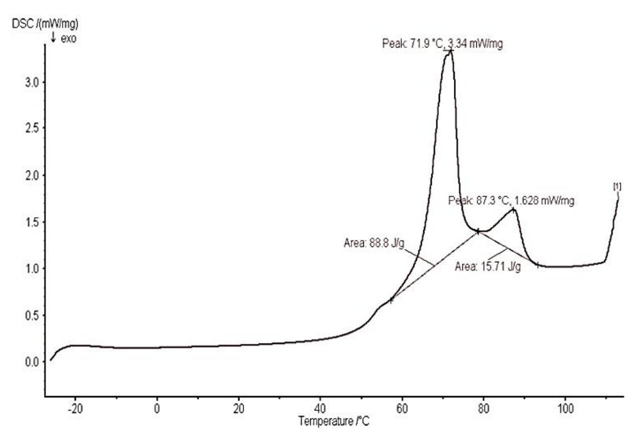


Figure7.3 DSC curve of GMnAc

7.4.4 Optical Studies

The crystal GMnAc is well polished and the sample is dissolved in water to measure the absorption and transmission spectrum in the spectral region shown in Figure7.4& 7.5using LAMBDA-35 UV–Vis spectrometer 190 – 1100 nm with Data interval 1.0000 nm and Scan Speed 960.00 nm/min. For optical fabrication, the crystal should be highly transparent over a considerable region of wavelength (Bagavathi et al. 2015, Wooster 1953). In the UV Vis spectrometer the lower cut off wavelength as recorded from the absorption spectrum is 276 nm. From the absorption spectrum the crystal is transparent in the range 381nm-1100nm without any absorption peak, which is an essential parameter of NLO crystals. Absence of absorption in the region 400–1100 nm is an advantage and it is the key requirement for materials exhibiting NLO property. Using the relation,

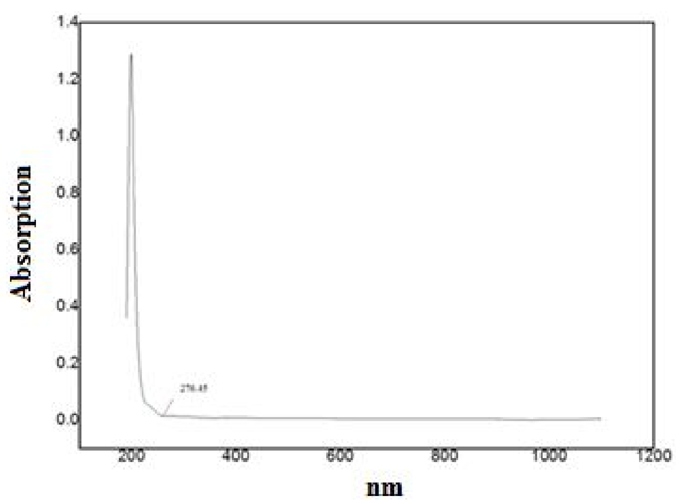


Figure 7.4 Absorption spectra of GMnAc

$$E_g = 1240/\lambda \qquad (7.2)$$

The band gap energy was found to be 4.5 eV. The optical absorption spectrum shows that absorption was very less in the entire visible region and part of IR region. The optical absorption coefficient (α) was calculated using the following relation

$$\alpha = (2.303/d) \log (1/T) \qquad (7.3)$$

Where T is the transmittance and d is the thickness of the crystal.

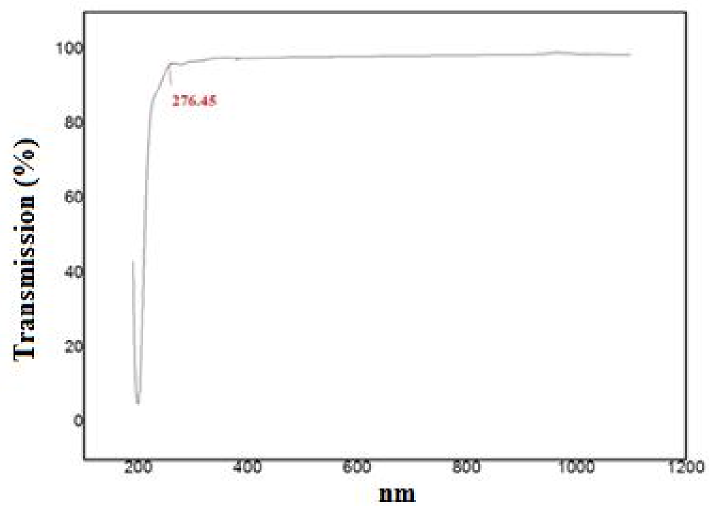


Figure 7.5 Transmission spectra of GMnAc

Using the Tauc's relation, a graph (Figure 7.6) has been plotted between hυ and $(\alpha h\upsilon)^2$ to estimate the direct band gap value, where α is absorption coefficient and hυ is the energy of the incident photon (E = hυ). The energy gap (E_g) is determined by extrapolating the straight line portion of the curve to $(\alpha h\upsilon)^2 = 0$. From the plot, the band gap of GMnAc is found to be 4.2 eV.

Transmission spectra are very important for any NLO material because a nonlinear optical material can be of practical use only if it has wide transparency window. The optical transmission spectrum for the wavelengths between 190 and 1100 nm were recorded. From the transmittance spectra, it is observed that GMnAc crystal have high transmittance in the entire visible and near IR region. The UV cut-off wavelength of the crystal is found to be at 276 nm. It is found that the maximum transmittance of the grown GMnAc single crystal is 52% and it has almost more than 45% transmittance from 276 to 1100 nm. The advantage of using amino acids shows the absence of strongly conjugated bonds leads to wide transparency range in the visible and UV spectral regions. The transparency is an added advantage for this crystal to be utilized in the field of optoelectronic devices.

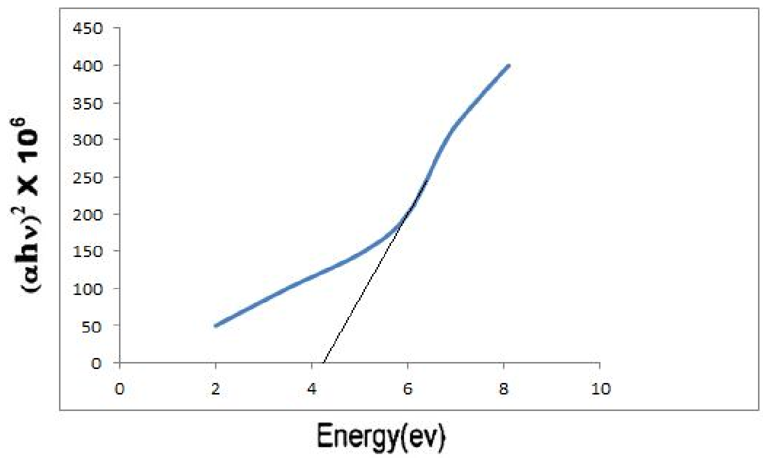


Figure 7.6 Plot of $(\alpha h\upsilon)^2$vs Photon energy of GMnAc

7.4.5 Mechanical Studies

One of the methods to determine the mechanical behaviour of the grown crystal is micro hardness test**.** The hardness of a material is a measure of its resistance to local deformation. It is correlated with other mechanical properties like elastic constants, yield strength, brittleness index and temperature of cracking. The indentation marks were made on the surface of GMnAc single crystal at room temperature by applying load of 25, 50 and 100 g. The distance between two indentation points has been maintained to more than three times the diagonal length so as to avoid the mutual interference of indentations. The Hv is found to increase with increase in the load from 25 to 100 g and crack occurs at higher loads. Mechanical properties of the grown GMnAc crystal were studied using M H–5 hardness testers.The diagonal lengths of the indented impression were measured using calibrated micrometre attached to the eyepiece of the microscope.

The Vickers micro hardness values were calculated from the standard formula (Wooster 1953)

$$Hv = 1.8544 (P/d^2) \text{ kg/mm}^2 \qquad (7.4)$$

Where, P is the applied load and d is the mean diagonal length of the indentation. The corresponding trace is shown in the Figure7.7, from which it is observed that the hardness increases with the increase of load up to 100g and crack occurs at that load. The Micro hardness value was taken as the average of the several impressions made. According to the normal indentation size effect (ISE), micro hardness of crystals decreases with increasing load and in reverse indentation size effect (RISE) hardness increases with applied load. In our case, Hv increases with applied load.

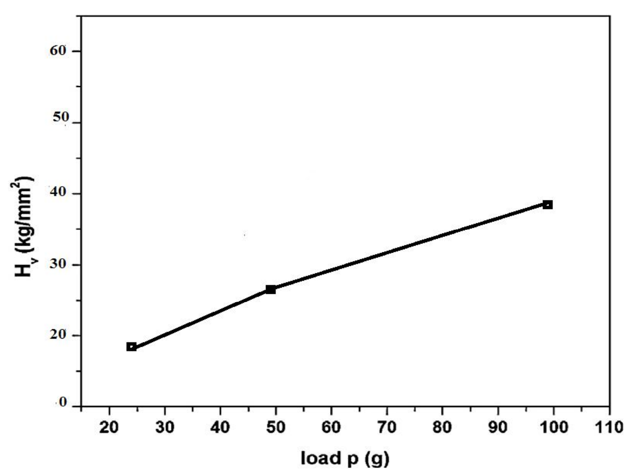


Figure7.7 Plotof load p vs. hardness number

To find the work hardening coefficient (n) of the grown crystal, another graph (Figure7.8) was drawn between logarithmic values of load and diagonal length of indentation.

From Meyer's law (Devasenan et al. 2016)

$$P = ad^n \qquad (7.5)$$

Here, a is the constant for the given material. It connecting the relationship between applied load and diagonal length of the indentation, work hardening coefficient or the Meyer index was calculated. The work hardening coefficient ''n'' was calculated as 3.49 from the Figure7.8. According to Onitsch (Rosker et al. 1996), if n lies between 1 and 1.6, then the grown crystal will be a harder material and it is more than 1.6 for soft materials (Bamzai &Kotru 2000).Since the calculated work hardening coefficient 'n' is more than 1.6, the grown crystal is suggested that it comes under the category of soft material.

Yield strength of the grown GMnAc crystalline material was also calculated using the formula,

$$\sigma_y = (Hv/3)(0.1)^{n-2} \qquad (7.5)$$

Where, σ_y is the yield strength, Hv is Vicker's hardness and n is the logarithmic exponent. It was found to be 3MP from the relation and hence the grown GMnAc single crystal has low mechanical strength.

The elastic stiffness constant (C_{11}) for different loads calculated using Wooster's (Webster 1999) empirical formula C_{11}= Hv $^{(7/4)}$ is given in Table 7.1 which gives an idea about tightness of bonding between neighbouring atoms.

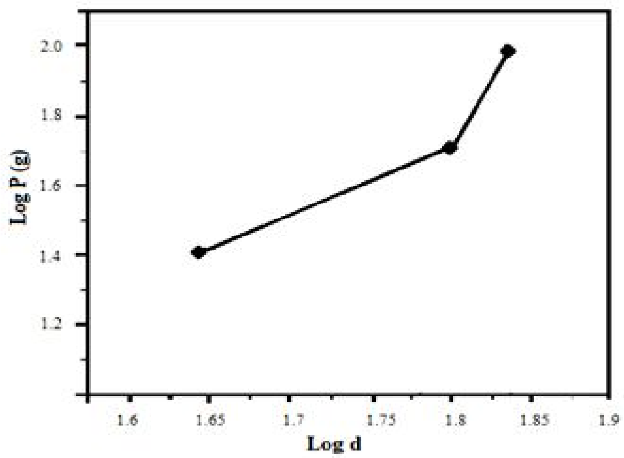


Figure7.8 Plot of Log d Vs. Log P (g)

Table 7.1 Stiffness constant

Load P	C_{11} ($x10^{14}$ Pa)
25	171.32
50	299.36
100	595.05

7.4.6 Dielectric Studies

Dielectric materials are used in the fabrication of capacitors, thin film transistors, resistors, insulators, tunneling devices. Good quality single crystal of GMnAc was selected for the dielectric measurements using TH 2816 A DIGITAL LCRZ METER in the frequency from 50 Hz to 2 MHz. The increase in dielectric constant at low frequency is attributed to the space charge polarization. The sample was polished by soft tissue paper. Silver paste was applied on both opposite faces to make a capacitor with the crystal as a dielectric medium. The sample was placed between two cooper electrodes, which act as a parallel plate capacitor. Dielectric studies give useful information about charge transport mechanism inside the crystal. In normal dielectric behaviour, the dielectric constant decreases with increasing frequency reaching a constant value, depending on the fact that beyond certain frequency of the electric field (Lin et al. 1999, Prasad &Williams 1991) and the dipole does not follow the alternating field. This type of dielectric response may be of great interest in electrical applications. The presence of dielectric between the capacitor plates increases the capacitance of the capacitor. The capacitance and dielectric loss were measured for different frequencies. Variation of dielectric loss vs. log frequency of GMnAc crystal is shown in Figure7.9. The dielectric constant was calculated using the following relation.

$$C_p d = \frac{\varepsilon_r}{A\varepsilon_0} \qquad (7.6)$$

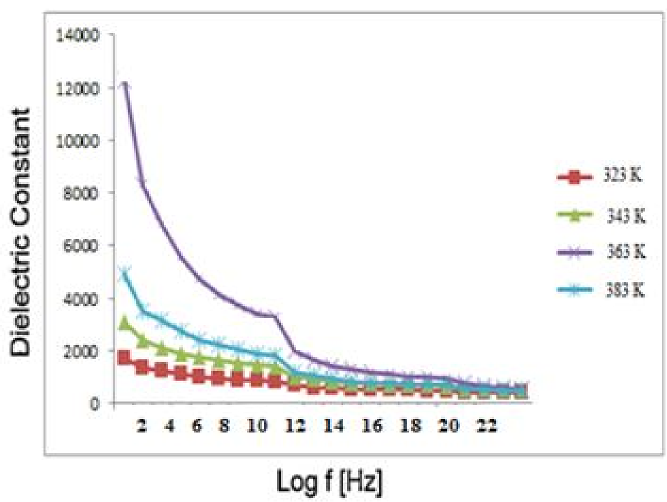


Figure 7.9 Variation of dielectric constant vs. Log frequency

Where 'Cp' is the capacitance of parallel plate capacitor, 'A' is the area of overlap of the two plates and'd' is the separation between the plates. As the frequency increases, the dipoles do not comply with the external field resulting in the decrease of polarization and hence the dielectric constant decreases as frequency increases. In accordance with Miller rule, the lower value of dielectric constant at higher frequencies is a suitable parameter for the enhancement of SHG coefficient. The variation of dielectric loss with frequency is shown in Figure7.10.

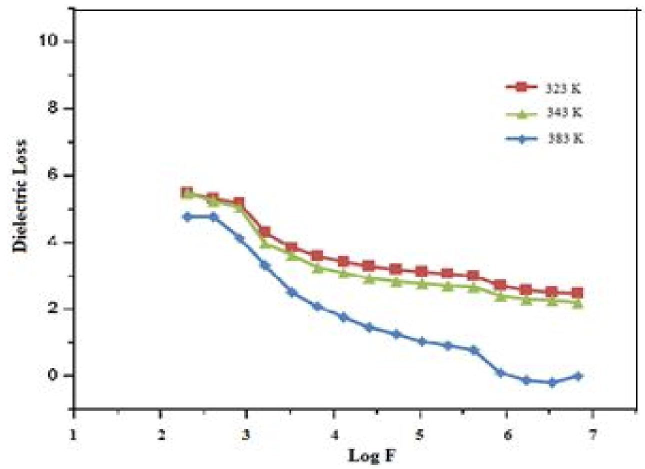


Figure 7.10 Variation of dielectric loss vs. Log frequency

The characteristic of low dielectric loss with high frequency for the sample suggests that the crystal possess enhanced optical quality with lesser defects and this plays a vital role for the fabrication of ferroelectric devices. The variation of Dielectric constant with temperature for GMnAc crystal is shown in Figure7.11.

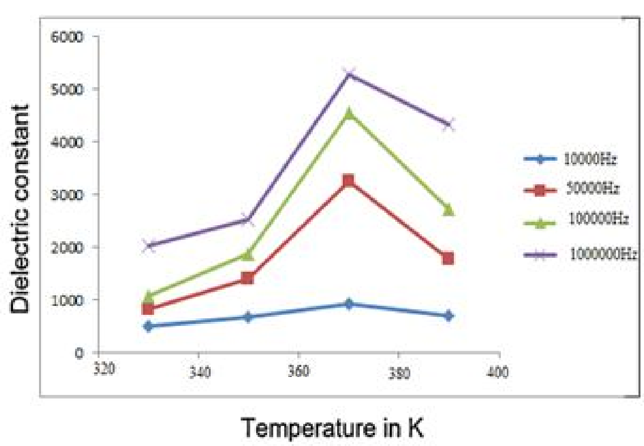


Figure 7.11 Variation of dielectric constant vs. Temperature

7.4.7 AC Conductivity Studies

The a.c. conductivity (σ_{ac}) was calculated from dielectric data using the empirical relation

$$\sigma_{ac} = \varepsilon_0 \varepsilon_r \omega \tan \delta \quad (7.7)$$

Where ε_0 is the permittivity of free space, ε_r relative permittivity, ω is the angular frequency (2Πf) and tan δ is the dielectric loss. From the graph (7.12) it is clear that conductivity decreases with temperature. The plot (7.14) of $\ln\sigma_{ac}T$ versus 1000/T obeys Arrhenius relationship

$$\sigma_{ac} = \sigma_o \exp(-E_a/kT). \quad (7.8)$$

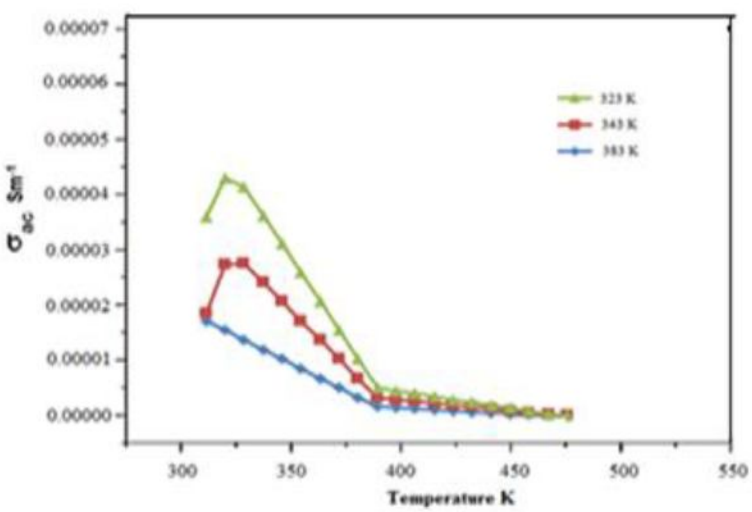


Figure 7.12Temperature variation of A.c. conductivity

Where, Ea is the activation energy, k is the Boltzmann constant and T is the temperature (in Kelvin). Therefore, the sample exhibits Arrhenius type conductivity. The sudden increase of ac conductivity is due to the good response of the charge carriers with the applied field. Activation energy was calculated using the slopes of the above line plots (E = - (slope) k × 1000).

The activation energy of GMnAc, calculated from the plot is found to be 0.239eV.

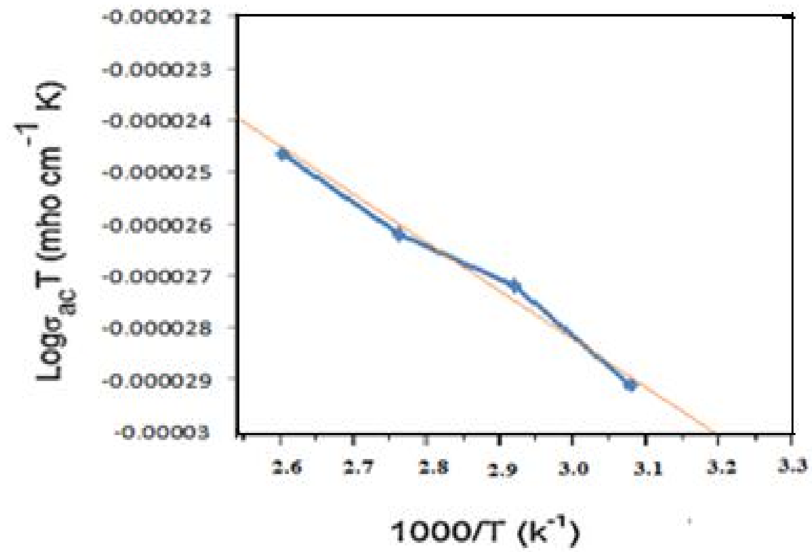


Figure 7.13Plot of Log σ_{ac}TVs. 1000/T

At high temperatures, the curve indicates a frequency independent d.c. conduction phenomenon. On the low temperature side, the conductivity curves branch out with weak dependence on temperature for lower frequencies.

7.4.8 D.C. Conductivity Studies

The current voltage plots of crystal are shown in Figure7.14. The DC conductivity of the material was calculated using the relation

σ= d/RA

d =thickness of sample crystal,

A= area of the face of the crystal in contact with electrode.

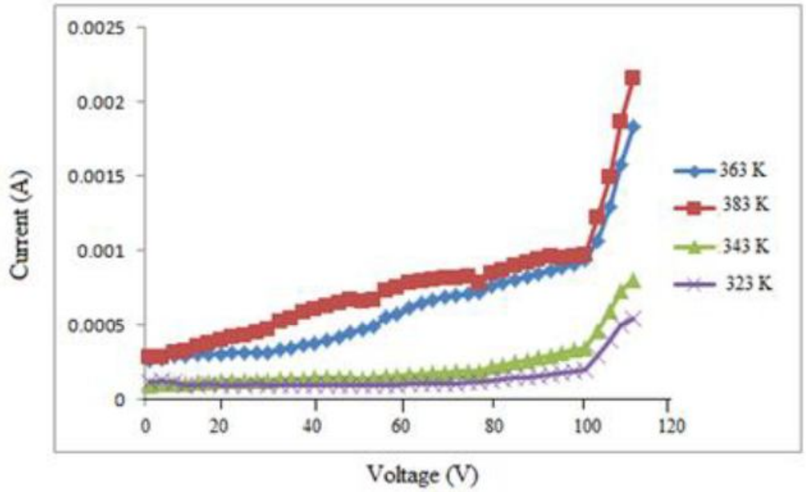


Figure 7.14 Plot of Voltage (V) Vs Current (A)

The Arrhenius plot can be drawn by taking ln (σ) along x-axis and (1000/T) along y-axis. The conductivity values can be fitted to the relation $\sigma = \sigma_0 \exp(-E/KT)$, where E is the activation energy, K is the Boltzmann constant, T represent absolute temperature and σ_0 is the parameter depending on the material. Activation energy can be estimated from the slope of above graph using the formulaE =-(slope) K x 1000.

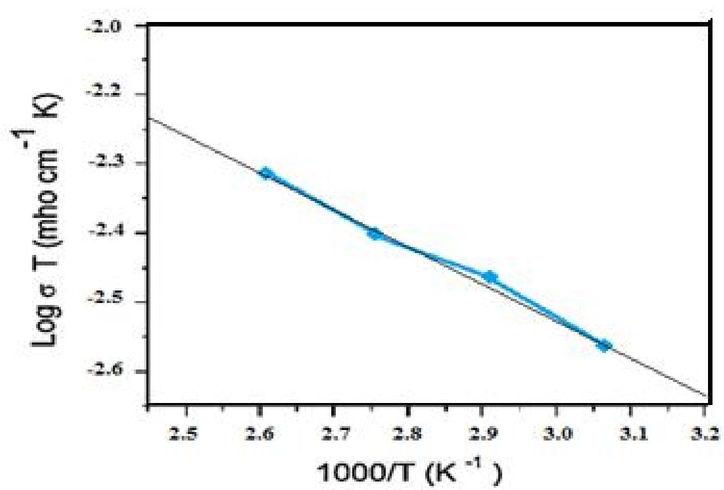


Figure 7.15 Variation of ln (σ) T vs. (1000/T)

The plot of ln (σ) T vs. (1000/T) is given in the Figure 7.15. The value of activation energy was found to be 0.286eV. The crystal GMnAc has the activation energy value which is more than reported value of KDP (0.22eV). The value of the activation energy provides the information that GMnAc crystal is non-semiconducting in nature.

7.4.9 a.c Resistivity and Conductivity

The a.c resistivity and a.c conductivity were calculated using the following relation

$$P = A/2\Pi\, fCd \quad (7.9)$$

$$\sigma_\rho = 1/\rho \quad (7.10)$$

Where C is the capacitance, d is the thickness, A is the area of the crystal, and f is the frequency of the applied field. As shown in Figure7.16, a.c resistivity decreased rapidly as frequency increased.

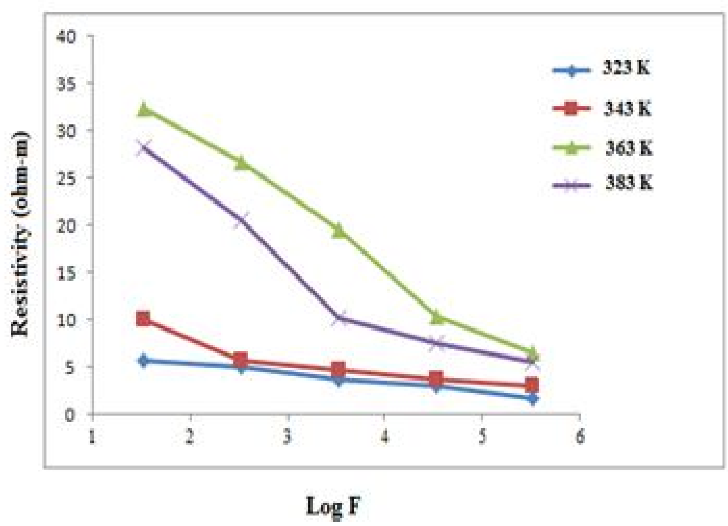


Figure 7.16 Variation of Frequency with resistivity

Obviously reverse trend was observed for a.c conductivity Figure 7.17and Figure 7.18 of the grown crystals (Iwai et al. 2000). Pyro electricity is the ability of certain materials to generate temporary voltage when they are heated or cooled (Wang et al. 2003). The pyro electric material shows change in the direction of spontaneous polarization when electric field is applied on them.

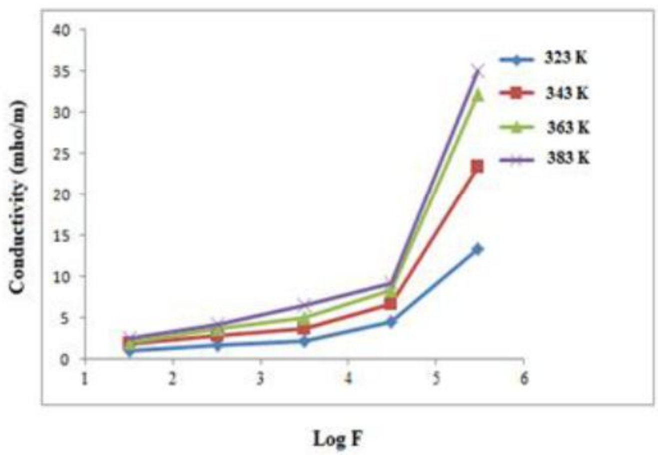


Figure 7.17 Variation of Conductivity with Frequency

In GMnAc crystal, the critical temperature is found to be 90°C which closely agrees with the literature (Bright & Freeda 2010).

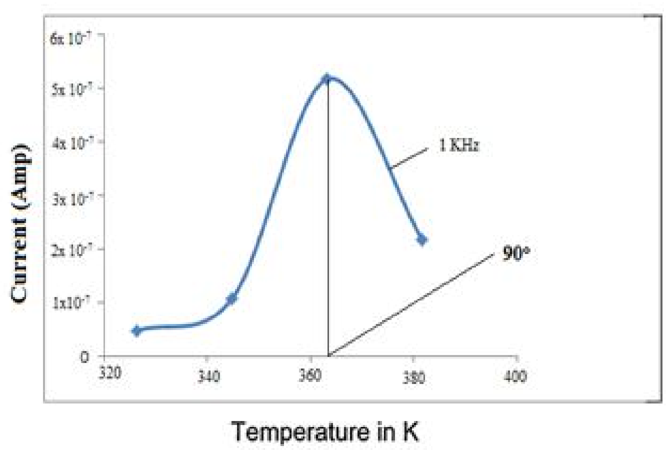


Figure 7.18 Variation incurrent with Temperature

7.5 CONCLUSION

Glycine Manganous Acetate optical quality single crystal have been grown by slow evaporation technique. The grown crystals are colourless and transparent in appearance. Single crystal X-ray diffraction study of the crystal revealed that the crystal belongs to non-Centro symmetric mono clinic system with space group P and crystalline nature was confirmed by powder X-ray diffraction study. Its thermal behaviour was examined by DSC. The optical transmission study confirms that the GMnAc had good transparency in the entire visible region and there was no absorption of light to any appreciable extent in the visible range and the lower cut-off wavelength was found to be 276 nm. Vickers micro hardness was calculated in order to understand the mechanical stability of the grown crystal.Dielectric measurements indicate that the dielectric constant of the crystal decreases with increasing frequency significantly to make the crystal a more interesting material in the microelectronics industry. The ac/dc conductivity studies are measured and the activation energy is determined. GMnAc is an electrically non conducting material at room temperature. Hence GMnAc crystal is found to be more beneficial from an application point of view.