Growth and studies of L-tartaric acid crystals doped with glycine

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ABSTRACT *Glycine doped L-tartaric acid (GLTA) sample was synthesized and grown in the form of single crystals by aqueous solution growth method. Structural characterization of the grown crystal was carried out by XRD method. SHG measurement was carried out by Kurtz powder technique. Linear optical parameters such as optical transmittance, absorbance, reflectance, absorption coefficient, extinction coefficient, linear refractive index and optical conductivity of GLTA crystal were evaluated by UV-visible spectral method. The electrical parameters such as dielectric constant, dielectric loss, AC conductivity and activation energy of GLTA crystal were determined by parallel plate capacitor method.*

Keywords: *NLO; single crystal; solution growth; doping; XRD; SHG; optical transmittance; dielectric parameters; optical and electrical conductivity*

1. Introduction

Nonlinear optical (NLO) materials play a major role in nonlinear optics and in particular they have a great impact on information technology and industrial applications. The understanding of the nonlinear polarization mechanisms and their relations to the structural characteristics of the materials have been considerably improved during the last 10 years. Researchers are doing NLO research to develop novel materials having large NLO properties and satisfying at the same time all the technological requirements for applications such as wide transparency range, high thermal stability, high hardness and high damage threshold [1,2]. Some technologically important organic NLO crystals were grown and characterized by many researchers [3-6]. L-tartaric acid (LTA) crystal is an organic NLO crystal and it crystallizes in monoclinic system [7]. Growth and various studies of L-tartaric acid crystals are reported by many authors [8,9]. The literature shows that the dopants like organic and metal dopants have been added into many NLO crystals to alter their properties [10-13]. In this investigation, an organic dopant viz., glycine has been added as the dopant into L-tartaric acid crystals to change the various properties and the results of structural, optical, mechanical, electrical and NLO studies of the grown doped crystals are reported.

2. Experimental

2.1 Synthesis and crystal growth

AR grade chemicals like L-tartaric acid and glycine were purchased commercially from Merck India. The single crystals of glycine doped L-tartaric acid were grown by solution method with slow evaporation technique. 2 mole% of glycine was added into L-tartaic acid and the aqueous saturated solution was prepared. This solution was heated at 50 ^{o}C to synthesize the salt of glycine doped L-tartaric acid. Using the synthesized salt and double distilled water, the saturated solution was prepared and it was stirred well and this solution was filtered using the Whatman filter paper. This solution was taken in a growth vessel for the crystal growth and for slow evaporation the growth vessel was covered with a perforated paper. Due to evaporation, the saturated solution was converted into supersaturated solution and tiny crystal nuclei were formed. After the growth period of one month, the crystal nuclei are grown into big-sized crystals of glycine doped L-tartaric acid (GLTA). The grown crystal of GLTA is shown in the figure 1.

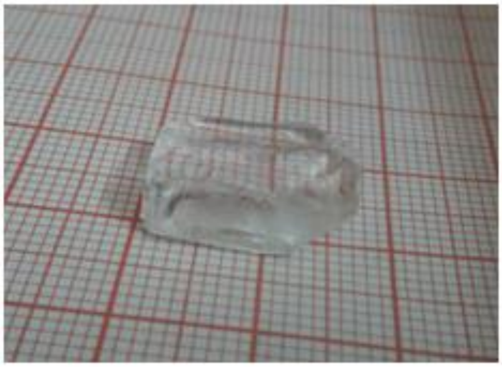


Fig.1. A grown crystal of glycine doped L-tartaric acid (GLTA)

2.2 Characterization techniques

The grown crystal of GLTA was subjected to single crystal X-ray diffraction studies using an ENRAF NONIUS CAD-4 X-ray Diffractometer with MoK_{α} radiation (λ = 0.7107 Å) to obtain the unit cell dimensions. The optical transmission spectrum of GLTA crystal has been recorded in the region 190-1100 nm using a Perkin Elmer (Model:Lambda 35) UV-vis spectrometer. The NLO conversion efficiency was tested using a modified setup of Kurtz and Perry. The dielectric constant and the dielectric loss of sample were measured using HIOKI 3532-50 LCR HITESTER in the frequency region 100 Hz to 1 MHz.

3.Results and discussion

3.1 Measurement of SHG efficiency

The process of second harmonic generation (SHG) by an incident wave of frequency ω is a two step process. In the first step, a polarization wave at the second harmonic frequency 2ω is produced and in the second step, the transfer of energy from the polarization wave to laser wave of 2ω will take place. For getting high value of SHG efficiency, the refractive index for polarization wave must be matched with that for output laser beam. For obtaining high conversion efficiency, the phase vectors of input beam and generated beam have to be matched. Hence phase matching condition is necessary to obtain high conversion efficiency. GLTA crystal was tested using Q-switched and Nd: YAG laser (1064 nm, Quanta ray series). The crystal was ground into powder and densely packed between two transparent glass slides. The incident laser beam falls normally on the sample and sample converts the 1064 nm radiation into green light of wavelength 532 nm. The emission of green radiation from the crystal confirms the second harmonic generation. The second harmonic signal was detected by a photomultiplier tube and displayed on the storage oscilloscope. Here KDP was used as the reference sample and it is to be mentioned that the particle size (150-200 μm) of both KDP and GLTA samples is maintained almost the same. The data in connection with the SHG measurement are given in the table 1. The data shows that the relative SHG efficiency of GLTA crystal is 1.12 times that of the reference sample viz., KDP.

Table 1: SHG data for glycine doped L-tartaric acid crystal

Sl. No.	Sample Code / Name of the Sample	Output Energy (milli joule)	Input Energy (joule)	Relative SHG efficiency
1	Glycine doped L-tartaric acid	9.98	0.70	1.12
2	KDP (Reference)	8.91	0.70	1

3.2 Linear optical parameters

Linear optical parameters like transmittance, reflectance and refractive index of GLTA crystal have been calculated using the optical transmittance spectrum. A UV-visible spectrophotometer was used to record the UV-visible transmittance spectrum of the sample in the wavelength range 190-1100 nm and the recorded spectrum of GLTA crystal is shown in the figure 2. The result shows that this crystal has high optical transmittance in the UV-NIR region and hence this sample is suited for SHG. At 244 nm, there is a sudden decrease of transmittance is observed for GLTA crystal and the wavelength at which a sharp fall of transmittance and high absorbance observed in the UV region is called the UV cut-off wavelength or the fundamental absorbance. It is reported that the UV cut-off wavelength of undoped L-tartaric acid (LTA) crystal is 253 nm [14] and in comparison with the undoped LTA crystal, the cut-off wavelength of GLTA crystal is slightly less. Using the relation $E_g = 1242/\lambda$ (nm), the optical band gap value was calculated to be 5.091 eV. The transmittance of about 80% in the entire visible region and low UV cut-off wavelength are the interesting parameters for the grown crystal of GLTA and hence it is the suitable for the NLO and opto-electronic applications. The linear optical absorption coefficient of the sample was calculated using the formula $\alpha = (2.303/d)^* \log(1/T)$ where d is thickness and T is the transmittance of the crystal. The calculated values of absorption coefficient of GLTA crystal are presented in the form of a plot (Fig.3) and the results indicates that the absorption coefficient is low in the visible-NIR region and it is high at the wavelength of 244 nm. The plot of absorbance versus wavelength for GLTA crystal is presented in the figure 4 and this plot shows the same behaviour as the plot of absorption coefficient versus wavelength (Fig.3).

The reflectance (R) and linear refractive index (n) of the sample can be determined using the following equations [15]

$$\mathbf{R} = \frac{1 \pm \sqrt{1 - e^{(-\alpha d)} + e^{(\alpha d)}}}{1 + e^{(-\alpha d)}}$$

$$\mathbf{n} = \frac{-(R+1) \pm \sqrt{(-3R^2 + 10R - 3)}}{2\,(R-1)}$$

The variation of reflectance with wavelength for GLTA crystal is shown in the figure 5 and the reflectance is found to be decreasing with increase of wavelength region 244-800 nm and in the visible region the reflectance is low. In the wavelength region 80-1100 nm, the reflectance is observed to be increasing slightly with increase of wavelength. At cut-off wavelength, the reflectance is observed to be very high. The plot of linear refractive index versus wavelength for GLTA crystal is presented in the figure 6. The result shows that the refractive index decreases with increase of wavelength and it obeys the Cauchy's relation $n = A + B / \lambda^2$ where A and B are the constants. The linear refractive index of GLTA crystal at wavelength 632.8 nm is 1.78 and this value can be used to determine nonlinear susceptibility of the sample. The figure 7 shows the variation of refractive index with optical energy for GLTA crystal and it indicates that the refractive index is high at the cut-off wavelength at 244 nm. The extinction coefficient of GLTA crystal was calculated using the relation $K = \alpha\lambda/4\pi$ where α is the linear absorption coefficient and λ is the wavelength of the light and the plot of wavelength dependence of extinction coefficient for GLTA crystal is shown in the figure 8. The result depicts that the extinction coefficient increases with increase of wavelength in visible-NIR region and it is noticed to be high at the UV-region. Since the extinction coefficient of this sample is low of the order of 10^{-5}, it is a good optical material without having the optical energy loss. When a crystal is irradiated with light, the frequency response of the material is a measure of the optical conductivity (σ_{op}) and it can be determined using the relation $\sigma_{op}=(n\ \alpha\ c) / 4\pi$ where c is the velocity of light, α is the absorption coefficient and n is the refractive index. Here it can be seen that the optical conductivity is directly proportional to refractive index and absorption coefficient of the material. The wavelength dependence of optical conductivity for GLTA crystal is shown in the figure 9. The result indicates that the optical conductivity is high at the UV cut-off wavelength at 244 nm and it is low in the visible-NIR region. Hence, in the visible-NIR region, the interaction of ordinary light with GLTA crystal is low and the magnitude of optical conductivity confirms the presence of photo response nature of the material.

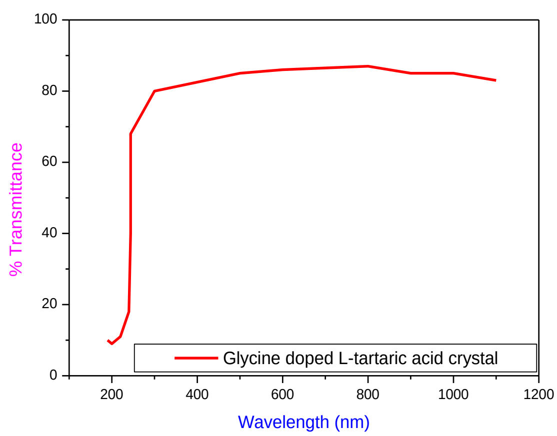


Fig.2. UV-visible transmittance spectrum of GLTA crystal

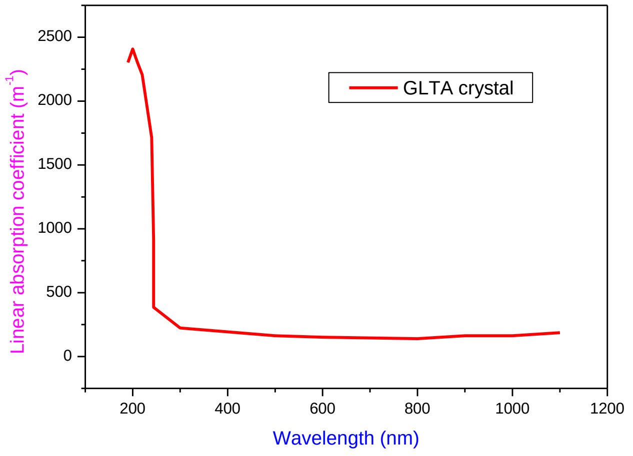


Fig.3. Plot of linear absorption coefficient versus wavelength for GLTA crystal

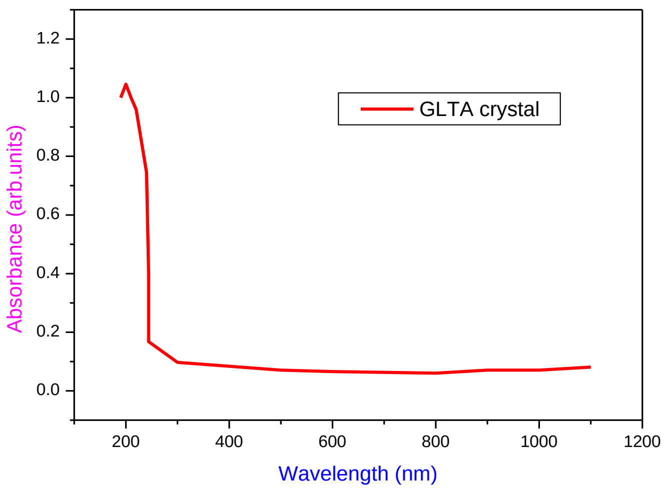


Fig.4. Plot of absorbance versus wavelength for GLTA crystal

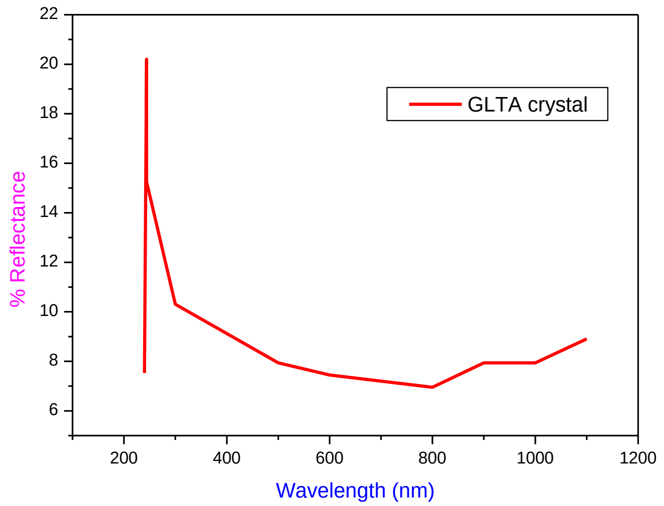


Fig.5. Plot of reflectance versus wavelength for GLTA crystal

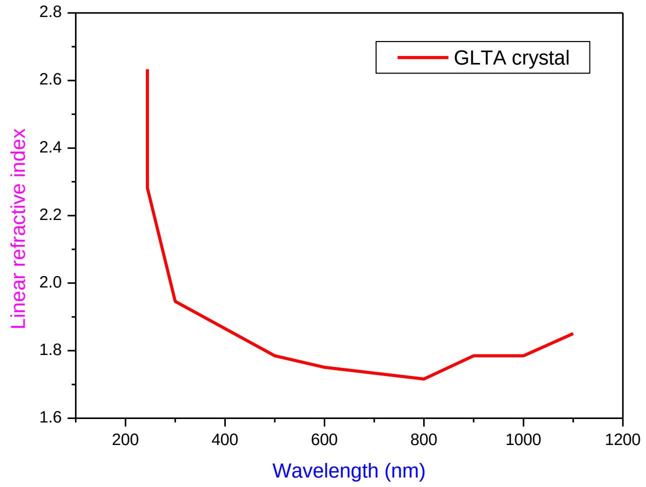


Fig.6: Variation of refractive index with wavelength for GLTA crystal

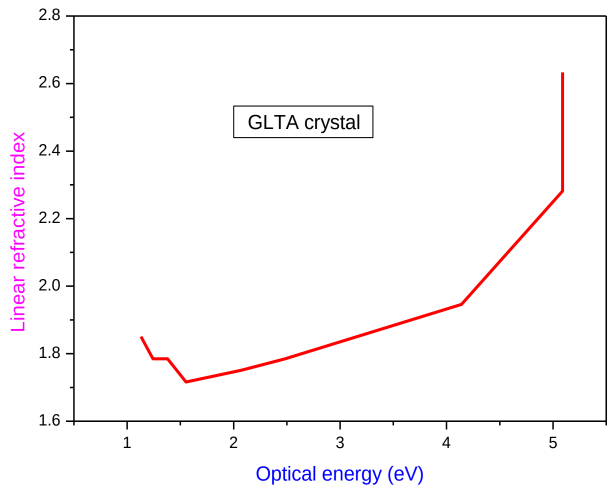


Fig.7: Variation of refractive index with optical energy for GLTA crystal

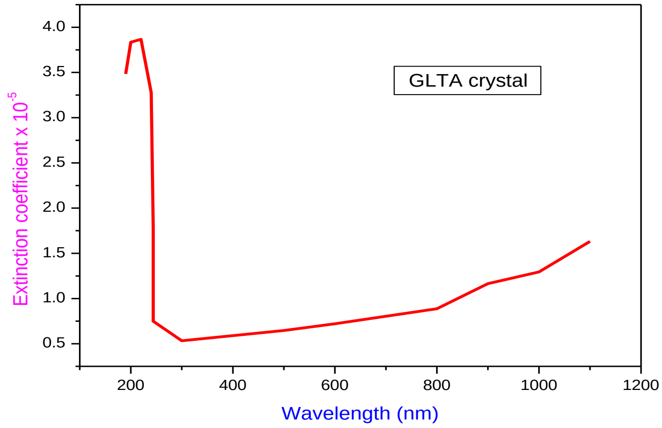


Fig.8: Wavelength dependence of extinction coefficient for GLTA crystal

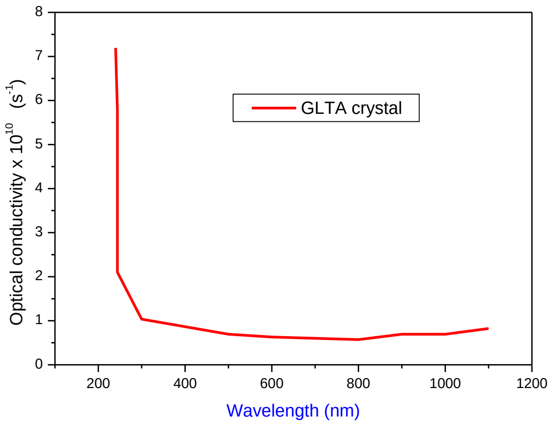


Fig.9: Variation of optical conductivity with wavelength for GLTA crystal

3.3 Identifying the crystal structure

XRD method is based on the principle of X-ray diffraction and Bragg's law and in this method X-rays are allowed to fall on a crystal and they are diffracted due to regular arrangement of atoms or molecules in the crystal. A single crystal X-ray diffractometer was used to identify the crystal structure of GLTA crystal. A small piece, good quality and transparent crystal of GLTA was used here. This work was carried out in STIC, Cochin University, Cochin and the obtained lattice parameters of GLTA crystal are a = 6.241 (2) Å, b = 6.025 (4) Å, c = 7.709 (6) Å, $\alpha = \gamma = 90^o$ and $\beta = 101.23^o$ (3) and volume of the unit cell is found to be 284.32 $Å^3$. From the data, the crystal structure of GLTA crystal is identified as monoclinic structure.

3.4 Dielectric studies

Dielectric properties of various materials are finding increasing application, as fast and new technology is adapted for use in their respective industries and research laboratories. Dielectric data were measured to measure the change in capacitance and suitable sample holding capacitors were used here. The complex permittivity (ε^*) is expressed as $\varepsilon^* = \varepsilon' - j\,\varepsilon''$ where ε' is real part of permittivity and it corresponds to dielectric constant and ε" is the imaginary part of permittivity and it corresponds to dielectric loss factor of the material. The absolute permittivity is given by $\varepsilon = \varepsilon_r \varepsilon_o$ where ε_r is the dielectric constant or relative permittivity and ε_o is the permittivity of vacuum or free space (8.85 x 10^{-12} F/m). A good quality crystal of GLTA was selected from the harvested crystals and its faces are polished and coated with silver paint to ensure good electrical contact between the crystal and the electrodes. The capacitance values of the parallel plate capacitor with sample and without sample are measured using a multi-frequency LCR meter and the dielectric constant was determined. The dielectric loss factor or dissipation factor (tan δ) of the sample was measured directly from the LCR meter. Both the dielectric parameters were measured at various frequencies and temperatures and the obtained values are given in the dielectric plots (Figs. 10 and 11). The results indicate that the dielectric parameters like dielectric constant and dielectric loss are increasing with increase of temperature and are decreasing with increase of frequency and hence this crystal shows the normal behaviour of dielectrics. AC conductivity (σ_{ac}) of GLTA crystal was determined using the relation $\sigma_{ac} = 2\,\pi\, f\, \varepsilon_o\, \varepsilon_r \tan\delta$ where f is the frequency of the AC supply, ε_o is the permittivity of free space or vacuum, ε_r is the dielectric constant and tan δ is the dielectric loss factor. The frequency and temperature dependence of AC conductivity for GLTA crystal are shown in the figure 12. From the results, it is observed that AC conductivity increases with increase of both frequency and temperature. When the temperature of GLTA crystal increases, there is an excitation of electrons from valence band to conduction band and these electrons are converted into conduction electrons and the conduction electrons are responsible for the increase of conductivity. The temperature dependence of AC conductivity of a dielectric material like GLTA crystal obeys the Arrhenius relation given by $\sigma_{ac} = \sigma \exp(-E_{ac}/kT)$ where k is the Boltzmann's constant, T is the absolute temperature, σ is the constant depending on the material and E_{ac} is the AC activation energy [16-18]. By drawing a plot of ln σ_{ac} versus 1000/T for GLTA crystal, the value of AC activation energy was calculated. The plots of σ_{ac} versus 1000/T for GLTA crystal at frequencies 10^2 Hz, 10^3 Hz 10^4 Hz 10^5 Hz and 10^6 Hz are drawn and they are presented in the figure 13. The obtained values AC activation energy of GLTA crystal are provided in the table 2 and as the frequency increases, the activation energy increases for GLTA crystal.

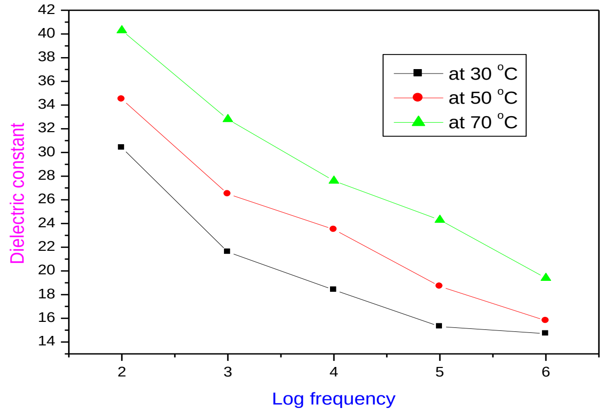


Fig.10. Frequency dependence of dielectric constant for GLTA crystal at different temperatures

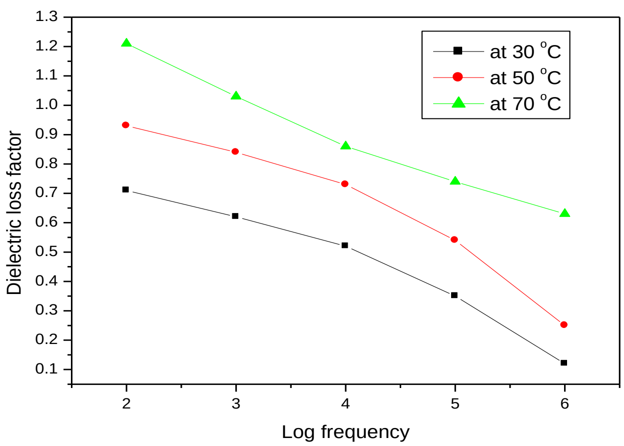


Fig.11. Frequency dependence of dielectric loss for GLTA crystal at different temperatures

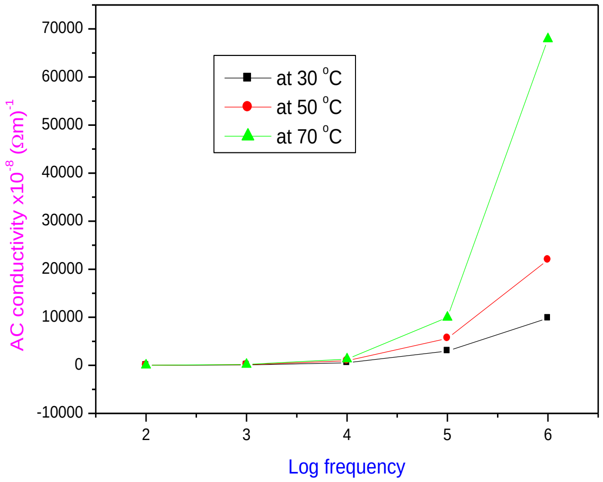
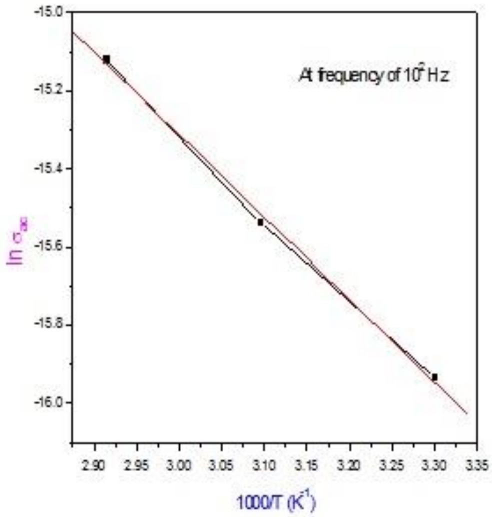
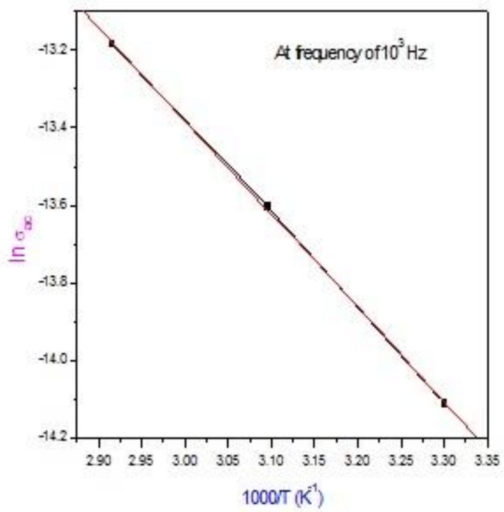


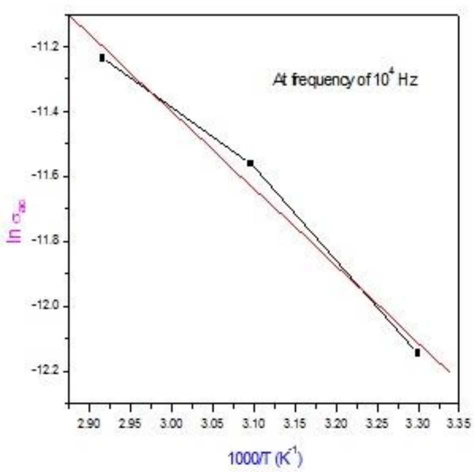
Fig.12. Frequency and temperature dependence of AC conductivity for GLTA crystal



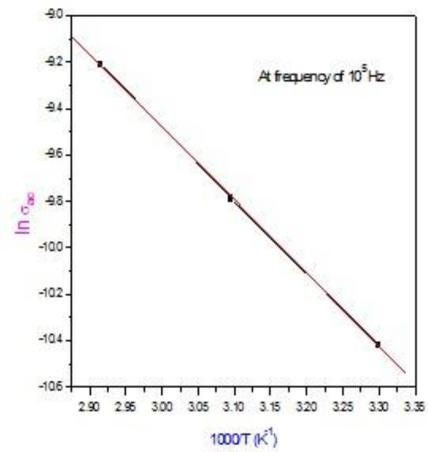
(a)



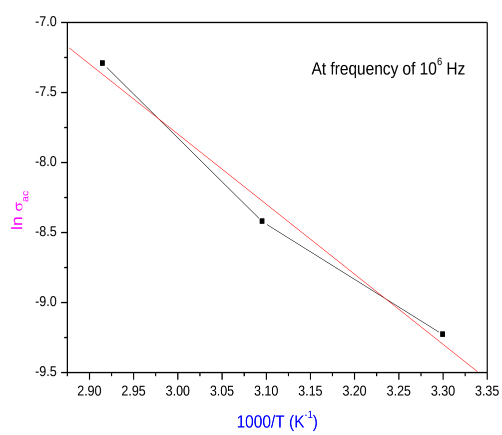
(b)



(c)



(d)



(e)

Fig.13. Plots of ln σ_{ac} versus 1000/T for GLTA crystal at frequency of (a) at 10^2 Hz, (b) at 10^3 Hz , (c) at 10^4 Hz, (d) at 10^5 Hz and (e) at 10^6 Hz

Table 2: Values of activation energy for GLTA crystal at different frequencies

S.No.	Frequency	Activation energy
1.	10^2 Hz	0.1823 eV
2.	10^3 Hz	0.2076 eV
3.	10^4 Hz	0.2092 eV
4.	10^5 Hz	0.2708 eV
5.	10^6 Hz	0.3842 eV

4.Conclusions of the work

Single crystals of glycine doped L-tartaric acid (GLTA) were grown by solution growth method with slow evaporation technique and the grown crystals are observed to be colourless and transparent. The crystal structure of GLTA crystal is found to be monoclinic. Kurtz powder technique was used to find the relative SHG efficiency and its value of GLTA crystal is 1.12 times that of the reference KDP sample. UV-visible spectrum of GLTA crystal was recorded using a UV-visible spectrophotometer in wavelength range 190-1100 nm and the various linear optical parameters were found out. High transmittance, low absorbance, low extinction coefficient, low reflectance of GLTA crystal are indicating that this crystal is suitable for NLO applications. The dielectric parameters such as dielectric constant and dielectric loss of GLTA crystal were measured using a multi-frequency LCR meter at different frequencies and temperatures. Using the dielectric data, AC conductivity and AC activation energy of the sample were determined and activation energy is found to be increasing with increase of frequency.

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