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# Investigation of the Optical and Dielectric Properties of the Urea L-malic Acid NLO Single Crystal

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## **Author's contribution**

*This work was carried out only by author SS. The author SS read and approved the final manuscript.*

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## **ABSTRACT**

Single crystals of urea L-malic acid were grown by the slow evaporation technique. The single crystal X-ray diffraction analysis reveals that the crystal belongs to the monoclinic system. The optical transmission study reveals the transparency of the crystal in the entire visible region and the cut off wavelength has been found to be 210 nm. The optical band gap is found to be 5.90 eV. Optical constants such as the band gap, refractive index, reflectance, extinction coefficient and the real ( $\epsilon_r$ ) and imaginary ( $\epsilon_i$ ) components of the dielectric constant and electric susceptibility were determined from the UV-VIS-NIR spectrum. Dielectric constant and dielectric loss of urea L-malic acid are measured in the frequency range from 50 Hz to 5 MHz at different temperatures. The relative second harmonic generation efficiency of urea L-malic acid crystal has been tested by Kurtz-Perry powder technique.

**Keywords:** *Optical transmission spectrum; optical bandgap; refractive index (n); reflectance (R); extinction coefficient (k).*

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## 1. INTRODUCTION

The recent tremendous advances in the area of solid state lasers and nonlinear optics have been mainly driven by the development of new materials, having better properties than the standard ones. A very important group of these new materials is single crystals, which possess excellent properties, such as a high damage threshold for laser radiation, high coefficients of second harmonics generation, transparency far into ultraviolet, high optical quality, and good chemical and mechanical stability. The nonlinear crystals have proved to be interesting candidates for a number of applications, such as second harmonic generation, frequency mixing, electro-optic modulation, optical parametric oscillation etc. [1]. Due to the technological importance of these nonlinear crystals the needs for high quality organic crystals have grown drastically in the last decade. With rapid progress in the crystal growth technology, crystals having attractive nonlinear properties are being discovered. This has enabled the commercial development of single crystals with promising nonlinear optical properties. In recent years, an intense world wide effort has been focused on the design and development of highly efficient organic nonlinear optical (NLO) materials [2]. The nonlinearity of the organic compounds having a p-electron conjugated system is caused by nonlinear polarization that occurs, due to the interaction between the laser light which comprises a strong electromagnetic wave and the delocalized p-electrons in the organic molecules of interest. In order to increase the magnitude of the nonlinear polarization of the molecule, an electron donating group (donor) or an electron with a drawing group (acceptor) is introduced into the  $\pi$ -electron conjugated system, as a common technique for molecular design. Organic nonlinear materials have the advantage that they are less costly and can be synthesized fairly easily. In the present investigation we report the optical and electrical properties of the urea L-malic acid crystal.

## 2. MATERIALS AND METHODS

The urea L-malic acid single crystal was synthesized from urea and L-malic acid. The solution was agitated with a magnetic stirring device for 10 h continuously and filtered after the complete dissolution of the starting materials. The obtained salt was filtered and dried at room temperature. The solution thus prepared was allowed to evaporate at room temperature and crystals of good optical qualities were harvested from the solution in 35 days. Single crystals were extracted and subjected to single crystal XRD studies. The unit cell parameters were determined by using the single crystal X-ray diffraction. The unit cell parameters are  $a = 9.04 \text{ \AA}$ ,  $b = 6.92 \text{ \AA}$ ,  $c = 6.81 \text{ \AA}$  and  $\alpha = \gamma = 90^\circ$ ,  $\beta = 95.66^\circ$ . From the data, it is observed that the grown crystal belongs to the monoclinic system. The transmission spectrum of urea L-malic acid was recorded with a Varian Cary 5E spectrophotometer in the range of 200–800 nm. UV-Vis-NIR spectroscopy might be defined as the measurement of the absorption or emission of radiation associated with changes in the spatial distribution of electrons in atoms and molecules. In practice, the electrons involved are usually the outer valence or bonding electrons, which can be excited by the absorption of UV or visible or near IR radiation.

## 3. THEORY OF OPTICAL PROPERTIES

In most cases, crystals are transparent to visible and/or infrared light. The interaction of the electromagnetic radiation with these crystals is treated, by applying the boundary conditions to the solutions of the Maxwell equations at the boundary between the different media. In the field of optical crystals, the wavelength of the light is always much larger than the inter

atomic dimensions. Thus the interaction of light and matter is averaged over many unit cells. As a consequence, the optical properties within each layer can be described macroscopically in terms of phenomenological parameters, the so-called optical constants or optical parameters. As shown below, these are the real and imaginary parts of a complex index of refraction  $\tilde{n}$ . The real part,  $n(\lambda)$ , is the ratio of the velocity of light in vacuum to the velocity of the light of the wavelength ( $\lambda$ ) in the material. The imaginary part,  $-\kappa(\lambda)$ , is an attenuation coefficient measuring the absorption of light with distance. Using the Maxwell equations, it is possible to relate these frequency-dependent “constants” to other optical parameters such as the dielectric constant and conductivity. The crystals are composed of charged particles: bound and conduction electrons, ionic cores, impurities, etc. These particles move differently with oscillating electric fields, giving rise to polarization effects. At visible and infrared light frequencies, the only contribution to polarization comes from the displacement of the electron cloud, which produces an induced dipole moment. The parameters describing these optical effects, that is, the dielectric constant  $\epsilon$ , the dielectric susceptibility  $\chi$ , and the conductivity  $\sigma$ , can be treated as scalars for isotropic materials.

To find out what kind of electromagnetic waves exist inside the dielectric films, we take  $\rho = -\nabla \cdot \mathbf{P}$  and  $\mathbf{j} = \partial \mathbf{P} / \partial t$ , where  $\rho$  is an effective charge,  $\mathbf{P}$  is the polarization induced by the electromagnetic wave, assumed to be proportional to the electric field, and  $\mathbf{j}$  is the corresponding current density averaged over a small volume. Under these conditions, the average field Maxwell equations in MKS units read:

$$\nabla \cdot \mathbf{E} = -\frac{\nabla \cdot \mathbf{P}}{\epsilon_0} \quad (1)$$

$$\nabla \times \mathbf{E} = -\frac{\partial \mathbf{B}}{\partial t} \quad (2)$$

$$\nabla \cdot \mathbf{B} = 0 \quad (3)$$

$$c^2 \nabla \times \mathbf{B} = \frac{\partial}{\partial t} \left( \frac{\mathbf{P}}{\epsilon_0} + \mathbf{E} \right) \quad (4)$$

where the symbols have their usual meaning. Note that the normal component of the electric field  $\mathbf{E}$  is not conserved at the interface between materials of different polarizability. Instead,  $\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P}$ , called electrical displacement, is conserved across such interfaces. The solutions to these equations have the form of harmonic plane waves with the wave vector  $k$ :

$$\mathbf{E} = E_0 \exp[i(\omega t - k \cdot r)] \quad (5)$$

$$\mathbf{H} = H_0 \exp[i(\omega t - k \cdot r)] \quad (6)$$

and represent a wave travelling with a phase velocity  $\omega/k = c/n$ , where  $c$  is the speed of light in vacuum and  $n$  is the index of refraction. When optical absorption is present, the wave vector and the index are complex quantities. From the Maxwell equations, a dispersion

relation  $k_2 = \varepsilon(\omega/c)^2$  is obtained relating the time variation with the spatial variation of the perturbation. In general, then, the wave vector  $k$  and the dielectric constant  $\varepsilon$  are complex quantities, that is,  $k = k_1 - ik_2$  and  $\varepsilon = \varepsilon_1 - i\varepsilon_2$ . It is useful to define a complex index of refraction:

$$\tilde{n} \equiv \tilde{k} \left( \frac{c}{\omega} \right) = n - ik \quad (7)$$

For isotropic materials,  $k_1$  and  $k_2$  are parallel and

$$\varepsilon_1 = n^2 - k^2 \quad \& \quad \varepsilon_2 = 2nk \quad (8)$$

$$n^2 = \frac{1}{2} \left[ \varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} \right] \quad \& \quad k^2 = \frac{1}{2} \left[ -\varepsilon_1 + (\varepsilon_1^2 + \varepsilon_2^2)^{1/2} \right] \quad (9)$$

In the photon energy region where  $\varepsilon$  is real,  $n = \varepsilon^{1/2}$  is also real and the phase ( $\omega/k$ ) and group ( $\partial\omega/\partial k$ ) velocities are equal to  $c/n$ . In general, the velocity is reduced to  $v(\lambda) = 1/\sqrt{\varepsilon_c(\lambda)}$  in a medium of a complex dielectric constant  $\varepsilon_c$ . The real part of  $n$  determines the phase velocity of the light wave, the imaginary part determining the spatial decay of its amplitude. The absorption coefficient  $\alpha$  measures the intensity loss of the wave. For a beam travelling in the  $z$  direction,  $I(x) = I(0) \exp(-\alpha z)$ , which means  $\alpha = 2\omega k/c = 4k/\lambda$ .

#### 4. UV-VISIBLE SPECTROSCOPY

The transmission spectrum of urea L-malic acid was recorded with a Varian Cary 5E spectrophotometer in the range of 200–800 nm. The optical transmittance range and transparency cut off wavelength of the crystal are important factors for optical applications. Fig. 1 shows that there is no transmission up to 210 nm and it reveals that the crystal absorbs the entire UV region and transmits the visible and NIR region. The optical band gap energy of the grown crystal was calculated using the formula  $E_g = 1240/\lambda$  (nm) in eV, where  $\lambda$  is the lower cut off wavelength (210 nm). The band gap of the urea L-malic acid crystal is found to be 5.90 eV. As this crystal exhibits a wide transmission range, starting from 210 nm onwards, it can be used for optical applications, including the second harmonic generation of Nd: YAG laser of fundamental wavelength  $\lambda = 1064$  nm. The measured transmittance ( $T$ ) data was used to calculate the absorption coefficient ( $\alpha$ ) from the following relation,

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t} \quad (10)$$

where  $t$  is the thickness of the crystal. The dependence of the absorption coefficient on photon energy was analyzed in the absorption regions to obtain the detailed information about the energy bandgap of the crystal. Fig. 2 shows the variation of the absorption coefficient ( $\alpha$ ) as a function of the photon energy at room temperature. The optical band gap ( $E_g$ ) was evaluated from the transmission spectrum and the optical absorption coefficient ( $\alpha$ ) near the absorption edge using relation [3],

$$\alpha h\nu = A(h\nu - E_g)^{1/2} \tag{11}$$

where  $A$  is a constant,  $E_g$  the optical band gap,  $h$  the Planck constant and  $\nu$  the frequency of the incident photons. The band gap of the urea L-malic acid crystal was estimated by plotting  $(\alpha h\nu)^{1/2}$  versus  $h\nu$  as shown in Fig. 2.  $E_g$  is evaluated by the extrapolation of the linear part [4]. The band gap is found to be 5.90 eV. As a consequence of the wide band gap, the grown crystal has a large transmittance in the visible region [5].

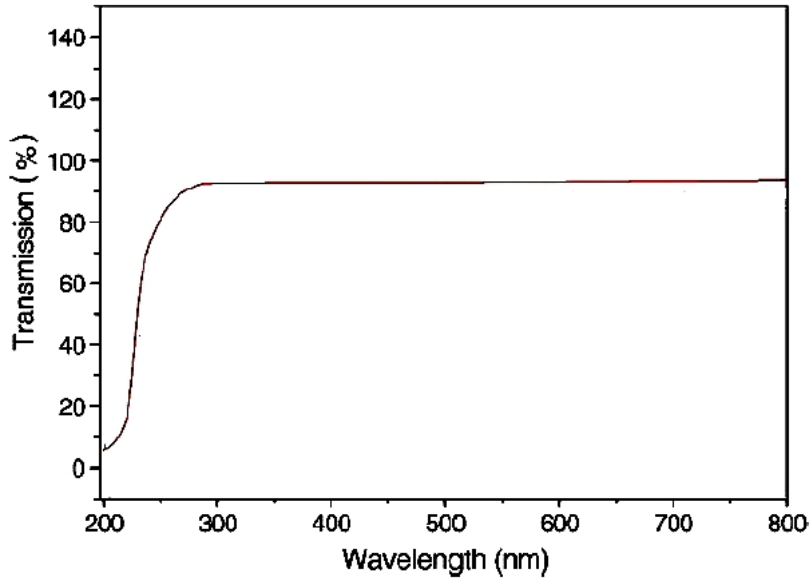


Fig. 1. UV transmission spectrum of urea L-malic acid single crystal

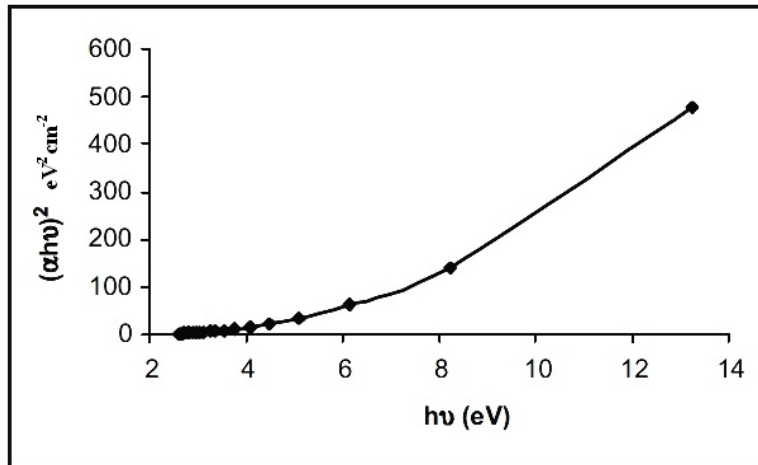


Fig. 2. Plot of  $(\alpha h\nu)^2$  versus photon energy of the title crystal

## 5. DETERMINATION OF OPTICAL CONSTANTS

The optical behaviour of a material is important to determine its usage in optoelectronic devices [6]. A knowledge of the optical constants of a material, such as the optical band gap and extinction coefficient is quite essential, to examine the material's potential optoelectronic applications [7]. Further, the optical properties may also be closely related to the material's atomic structure, electronic band structure and electrical properties. An accurate measurement of the optical constant can be easily performed on inorganic crystals. In such crystals, the photonic density of states and photonic mode spatial distribution can be tailored with great accuracy. The optical constants ( $n$ ,  $k$ ) are determined from the transmission ( $T$ ) and reflection ( $R$ ) spectrum following relations [8]. The transmittance ( $T$ ) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)} \quad (12)$$

where  $t$  is the thickness and  $\alpha$  is related to the extinction coefficient ( $k$ ) and is determined by

$$K = \frac{\lambda \alpha}{4\pi} \quad (13)$$

The refractive index ( $n$ ) can be determined from the reflectance ( $R$ ) [3]

$$R = \frac{(n-1)^2}{(n+1)^2} \quad (14)$$

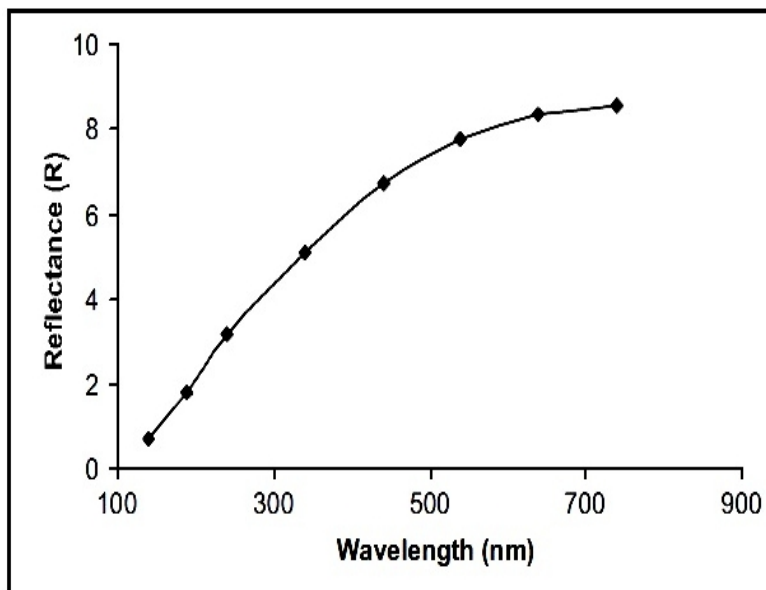


Fig. 3. Variation of reflectance with wavelength

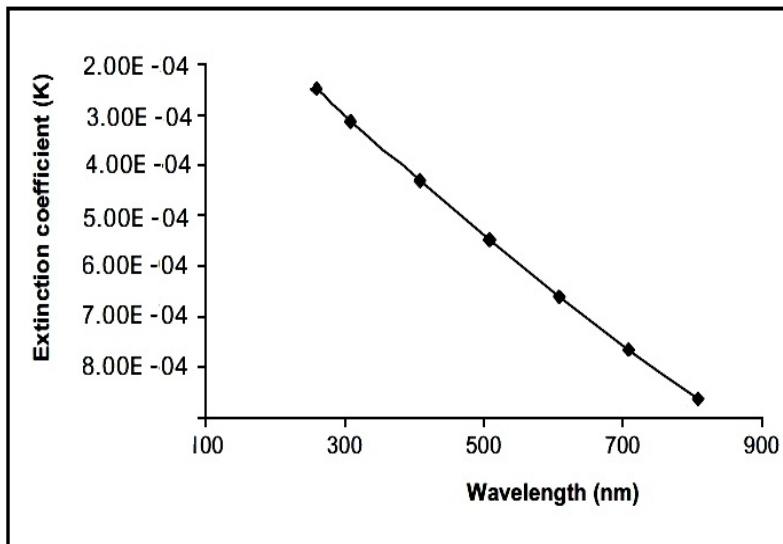


Fig. 4. Extinction coefficient versus wavelength

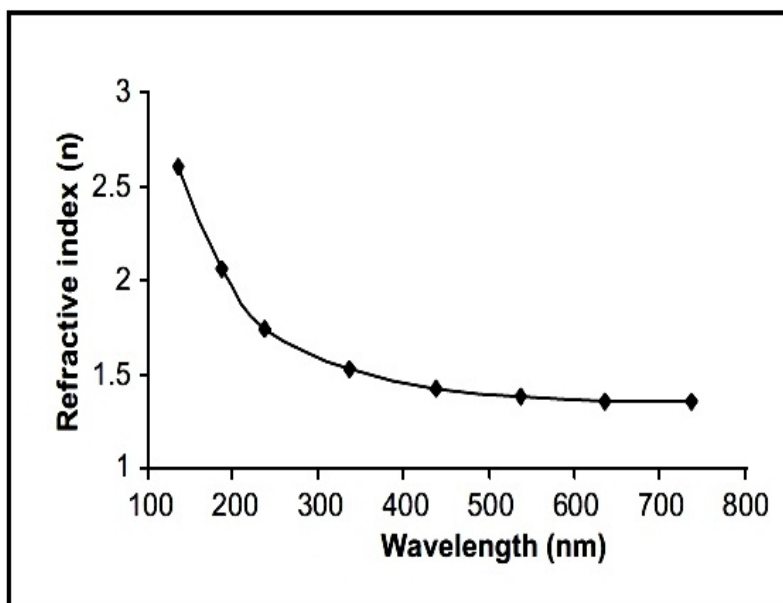


Fig. 5. Variation of refractive index with wavelength

The optical constants such as the refractive index ( $n$ ) extinction coefficient ( $k$ ) and reflectance have also been estimated. Fig. 3 shows the plot of the refractive index as a function of the wavelength and it could be noticed that the refractive index decreases abruptly as the wavelength increases. Figs. 4 and 5 show the variation of both the reflectance ( $R$ ) and extinction coefficient ( $K$ ) as a function of the wavelength, respectively. From the graphs, it is clear that both the reflectance and extinction coefficients decrease as the wavelength increases. This means that the absorbance is low in the visible and near IR

region. This prediction is also confirmed by the UV-VIS-NIR spectrum. The internal efficiency of the device also depends on wavelength. Hence, by tailoring the wavelength, one can achieve the desired material for the fabrication of electro-optic and optoelectronic devices. The reflectance (R) in terms of the absorption coefficient can be obtained from the above equation. Hence,

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T} \quad (15)$$

The refractive index (n) can be determined from the reflectance data using the following equation,

$$n = \frac{-(R+1) \pm 2\sqrt{nR}}{R-1} \quad (16)$$

From the optical constants, the electric susceptibility ( $\chi_c$ ) can be calculated according to the following relation [9]

$$\epsilon_r = \epsilon_0 + 4\pi\chi_c = n^2 - k^2 \quad (17)$$

Hence,

$$\chi_c = \frac{n^2 - k^2 - \epsilon_0}{4\pi} \quad (18)$$

The value of the electric susceptibility  $\chi_c$  is 0.137 at  $\lambda = 800$  nm. The real part dielectric constant  $\epsilon_r$  and imaginary part dielectric constant  $\epsilon_i$  can be calculated from the following relations [10],

$$\epsilon_r = n^2 - k^2 \quad \& \quad \epsilon_i = 2nk \quad (19)$$

The value of real  $\epsilon_r$  and imaginary  $\epsilon_i$  dielectric constants at  $\lambda = 800$  nm are 1.201 and  $6.023 \times 10^{-5}$  respectively. From the calculated values of the real and imaginary constants, the functions of the dielectrics were also determined. The real and imaginary parts of the dielectric constant of the grown crystal were determined. The lower value of the dielectric constant with a wide band gap of the urea L-malic acid crystal suggests its suitability for optoelectronic devices.

## 6. DIELECTRIC PROPERTIES

The study of dielectric constant of a material gives an outline about the nature of atoms, ions and their bonding in the material. From the analysis of dielectric constant and dielectric loss as a function of frequency and temperature, the different polarization mechanism in solids can be understood. The dielectric constant and the dielectric loss of the crystals were



studied at different temperatures using HIOKI 3532 LCR HITESTER in the frequency region 50 Hz to 5 MHz. The dielectric constant was measured as a function of frequency at different temperatures ranging from 30°C, 60°C and 90°C and is shown in Fig. 6, while the corresponding dielectric losses are depicted in Fig. 7. The dielectric constant is evaluated using the relation,

$$\epsilon_r = \frac{Cd}{\epsilon_0 A} \tag{20}$$

where  $d$  is the thickness of the sample,  $A$ , the area of the sample. The Fig. 6 shows the plot of dielectric constant ( $\epsilon$ ) versus log frequency for 30°C, 60°C and 90°C. It is seen that the value of dielectric constant is high in the lower frequency region for all the temperatures and then it decreases with increase in frequency. The high value of dielectric constant at low frequency region is attributed to space charge polarization due to charged lattice defects [11]. A graph is drawn between dielectric loss and log frequency for different temperatures (30°C, 60°C and 90°C) and is shown in Fig. 7. The low value of dielectric loss at high frequency suggests that the materials possess good optical quality.

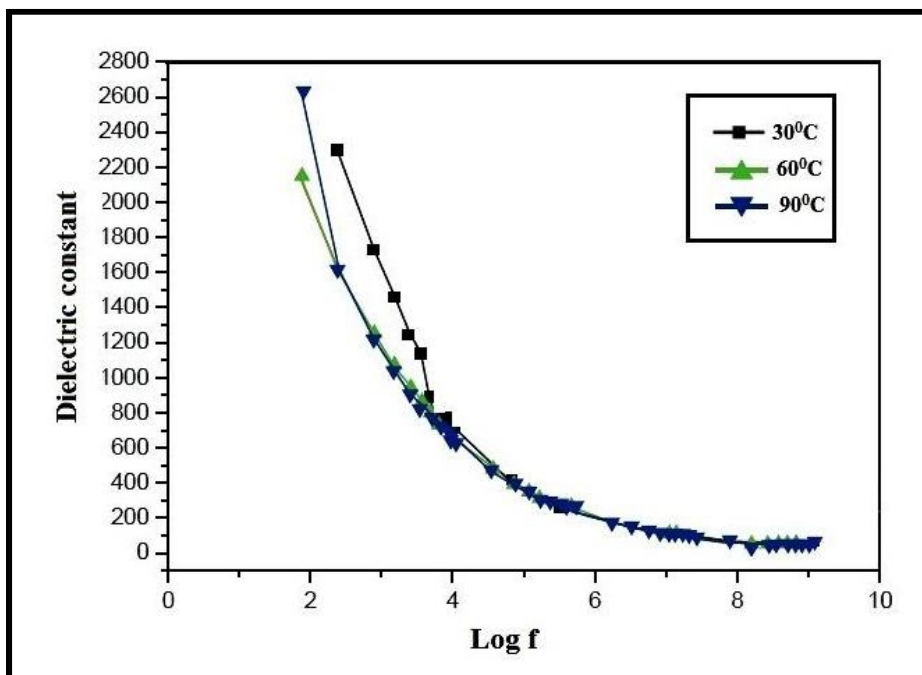


Fig. 6. Variation of dielectric constant with frequency for all temperatures

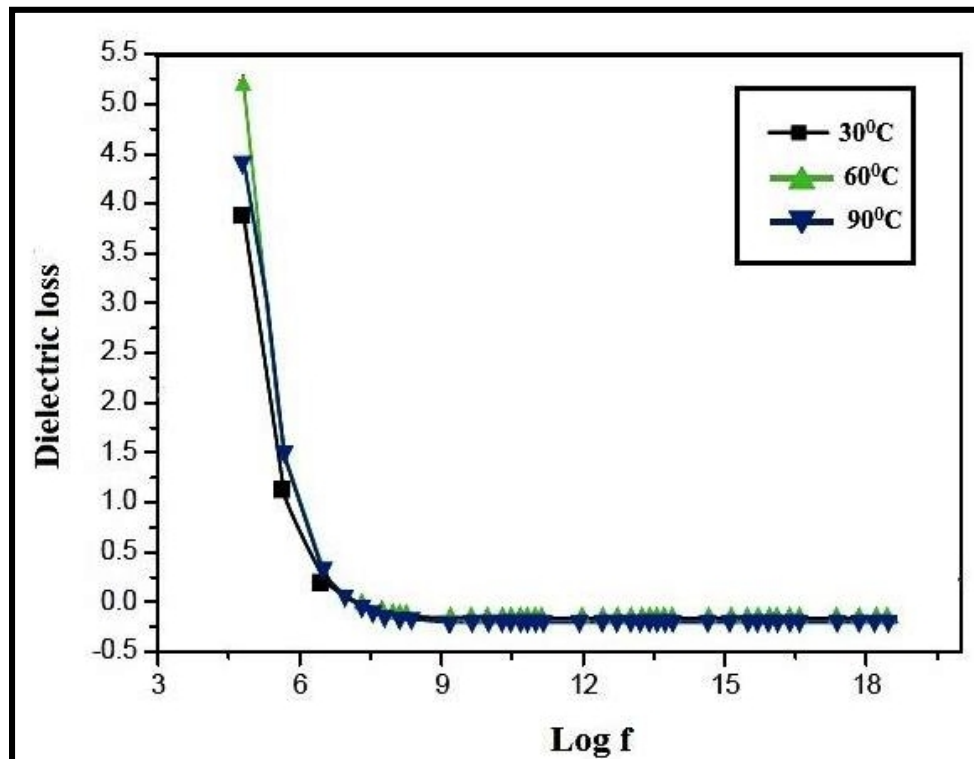


Fig. 7. Variation of dielectric loss with frequency for all temperatures

## 7. AC ELECTRICAL CONDUCTIVITY STUDIES

The AC conductivity has been calculated for the urea L-malic acid crystal using HIOKI 3532 LCR HITESTER in the frequency range 50 Hz to 5 MHz. Fig. 8 shows the variation of AC conductivity with various temperatures. It is seen that the value of ac conductivity increases with increase in frequency. The electronic exchange of the number of ions in the crystal gives local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization. The slope of the plot of ac conductivity versus temperature (Fig. 9) gives the activation energy required for the conduction process of the charge carriers. The value is found to be 0.138 eV and the lower value of activation energy establishes that the crystal contains less number of defects. The material is therefore useful for various microelectronic and nonlinear optical applications.

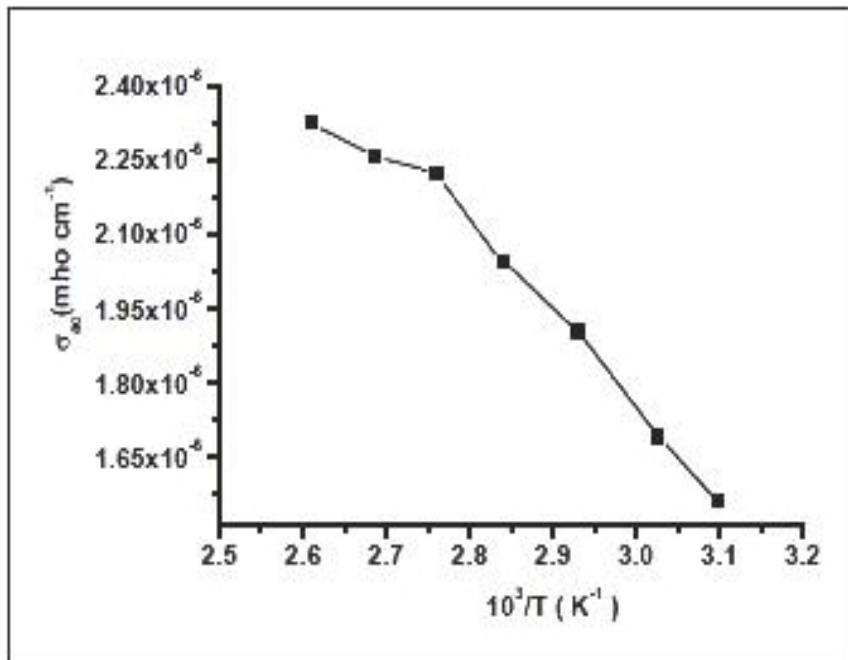


Fig. 8. Variation of ac conductivity with  $1000/T$

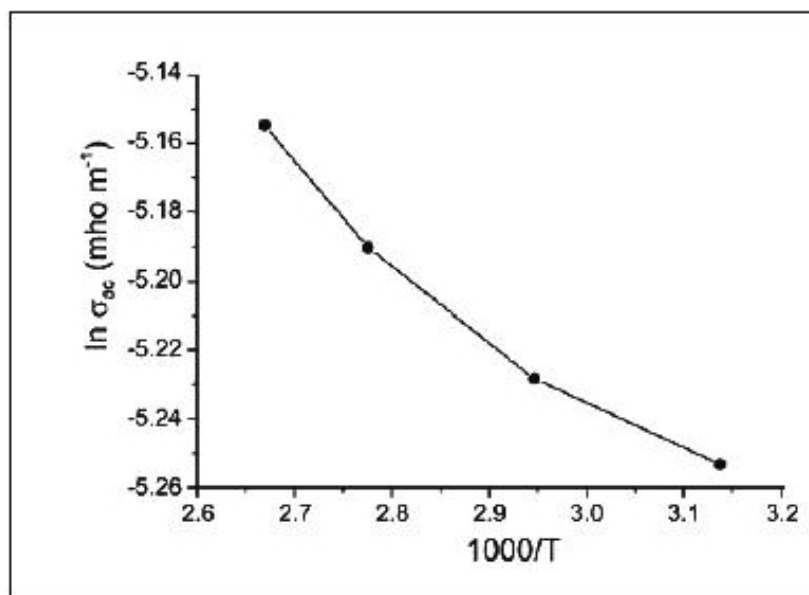


Fig. 9. Activation energy of urea L-malic acid crystal

## 8. KURTZ POWDER TECHNIQUE

Nonlinear optical property of the sample was tested by Kurtz and Perry technique and the efficiency of the sample was compared with microcrystalline powder of KDP and urea as the reference material [12]. A Q-switched mode locked Nd:YAG laser operates at the fundamental wavelength of 1064 nm, generating 6mJ/pulse. In the present investigation the laser pulse of 8ns with spot radius of 1mm was used. The input laser beam was passed through the Infrared reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of 0.154 mm. The second harmonic signal of 341.1 mW was obtained for urea L-malic acid with reference to KDP (87.62 mW). The experimental data shows that the second harmonic efficiency of the sample was nearly 3.8 times than that of KDP crystal. The SHG results are thus found to be in good agreement with the reported values of 3.76.

## 9. CONCLUSION

Single crystals of the urea L-malic acid were grown by the slow evaporation technique. The grown crystals were characterized by the single crystal XRD and it is confirmed that the crystal belongs to the monoclinic system. The optical constants, such as the optical band gap ( $E_g$ ), absorption coefficient ( $\alpha$ ), extinction coefficient ( $K$ ), refractive index ( $n$ ), electric susceptibility  $\chi_c$  and the real and imaginary dielectric constants were calculated to analyse the optical property of the crystal. Dielectric studies have been carried out to examine the dielectric constant and dielectric loss at different frequencies and different temperatures. The activation energy is determined from the plots of AC conductivity. The second harmonic generation efficiency by Kurtz-Perry powder technique reveals that the crystal was 3.8 times that of KDP.

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## COMPETING INTERESTS

Author has declared that no competing interests exist.

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