GROWTH, THEORETICAL, OPTICAL AND DIELECTRIC PROPERTIES OF L-TARTARIC ACID NLO SINGLE CRYSTALS

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Single crystals of L-Tartaric Acid with good degree of transparency were grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic system with the space group $P2_1$. Some fundamental data such as valance electron plasma energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal were calculated. The optical transmission study reveals the transparency of the crystal in the entire visible region and the cut off wave length has been found to be 220 nm. The optical band gap is found to be 3.65eV. The transmittance of L-Tartaric Acid crystal has been used to calculate the refractive index (n), the extinction coefficient (K) and both the real ε_r and imaginary ε_i components of the dielectric constant as functions of wavelength. Dielectric constant and dielectric loss measurements were carried out at different temperatures and frequencies.

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1. Introduction

The search for new materials with high optical nonlinearities is an important area due to their practical applications such as optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reactions, laser remote sensing, colour display, medical diagnostics, etc. In semiorganic materials, the organic ligand is ionically bonded with inorganic host. Organic nonlinear materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra-fast response times and high optical thresholds for laser power as compared with inorganic materials [1]. In the present investigation we report bulk growth, theoretical, optical, and dielectric properties of L-Tartaric acid single crystals.

2. Experimental

Single crystals of L-Tartaric acid were grown from aqueous solution by slow evaporation method. The solution was stirred continuously using magnetic stirrer for 3 days. The prepared solution was filtered and kept undisturbed at room temperature. Tiny seed crystals with good transparency were obtained due to the spontaneous nucleation. Among them, defect free seed crystal was suspended in the mother solution, which was allowed to evaporate at room temperature. Large size single crystals were obtained due to collection of monomers at the seed crystal sites from the mother solution. Fig.1 shows single crystals of L-tartaric acid.

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Fig. 1. Photograph of L-Tartaric acid single crystal

3. Results and Discussion

3.1 Single-crystal X-ray diffraction and fundamental parameters

Single crystal data collection was performed by using ENRAF NONIUS CAD-4 X-ray diffractometer. The XRD study reveals that the crystal belongs to monoclinic system with lattice parameters a = 6.203 Å, b = 6.018 Å and c = 7.720 Å, and space group is $P2_1$, which is in agreement with those of reported values [2].
The molecular weight of the grown crystal is M=150 and total number of valance electron Z=70**.** The density of the grown crystal was found to be ρ=1.76 g.cm^{-3} and dielectric constant at 1 MHz is ε_∞ =87.6. The valence electron plasma energy, $\hbar\omega_P$ is given by

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{\frac{1}{2}} \tag{1}$$

where Z is the total number of valence electrons, ρ is the density and M is the molecular weight of the L-Tartaric acid. Fermi energy in terms of Plasma energy [3] is given as

$$E_P = \frac{\hbar\omega_P}{\left(\varepsilon_\infty - 1\right)^{1/2}} \tag{2}$$

and

$$E_\mathrm{F} = 0.2948\left(\hbar\omega_P\right)^{4/3} \tag{3}$$

Polarizability, α is obtained using the relation [4]

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^{-3} \tag{4}$$

where S_0 is a constant for a particular material, and is given by

$$S_0 = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2 \tag{5}$$

The value of α so obtained agrees well with that of Clausius-Mossotti equation, which is given by,

$$\alpha = \frac{3M}{4\pi N_a \rho}\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \tag{6}$$

where the symbols have their usual significance. N_A is Avagadro number and the calculated fundamental data on the grown crystal of L-Tartaric acid are listed in Table2.

Table 1 Some theoretical data for L-Tartaric acid single crystal

Parameters	Values
Plasma energy (eV)	19.60
Penn gap (eV)	2.11
Fermi gap (eV)	15.43
Polarizability (cm^{-3}) using Penn analysis	3.24 x 10^{-23}
Polarizability (cm^{-3}) using Clausius-Mossotti Equation	3.27 x 10^{-23}

3.2 Optical Studies

The UV–vis–NIR transmission spectrum of the crystal was recorded in the wavelength range of 190–800nm and is shown in Fig.2. It is seen that the UV transparency cutoff occurs around 220 nm and there is no remarkable absorption in the entire region of the spectrum. It is an important requirement for NLO materials for possible applications.

The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula

$$\alpha = \frac{2.3026 \log\left(\frac{1}{T}\right)}{t} \tag{7}$$

where t is the thickness of the sample. Optical band gap (E_g) was evaluated from the transmission spectra and optical absorption coefficient (α) near the absorption edge is given by [5]

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \tag{8}$$

where A is a constant, E_g the optical band gap, h the Planck constant and n the frequency of the incident photons. The band gap of L-Tartaric acid crystal was estimated by plotting $(\alpha h\nu)^2$ versus $h\nu$ as shown in Fig. 3 and extrapolating the linear portion near the onset of absorption edge to the energy axis. From the figure, the value of band gap was found to be 3.65 eV.

Extinction coefficient (K) can be obtained from the following equation:

$$K = \frac{\lambda\alpha}{4\pi} \tag{9}$$

The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)} \tag{10}$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation. Hence,

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T} \tag{11}$$

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

$$n = -(R+1) \pm 2\frac{\sqrt{R}}{(R-1)} \tag{12}$$

The refractive index (n) is 1.52 at λ =800 nm.

From the optical constants, electric susceptibility (χ_c) can be calculated according to the following relation [6].

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \tag{13}$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \quad (14)$$

where ε_0 is the dielectric constant. The value of electric susceptibility χ_C is 0.123 at λ =800 nm. The real part dielectric constant ε_r and imaginary part dielectric constant ε_i can be calculated from the following relations [7]

$$\varepsilon_r = n^2 - k^2 \quad \& \quad \varepsilon_i = 2nk \quad (15)$$

The value of real ε_r and ε_i imaginary dielectric constants at λ = 800 nm are 1.41 and 6.564 x 10^{-5} respectively.

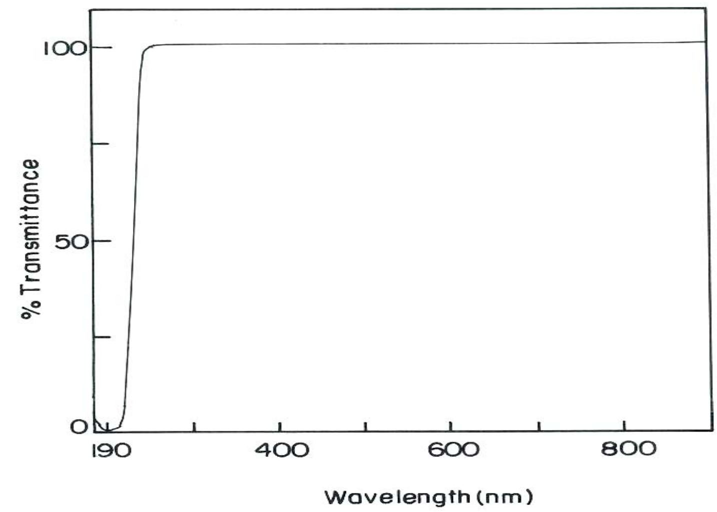

Fig.2. Optical transmittance spectrum

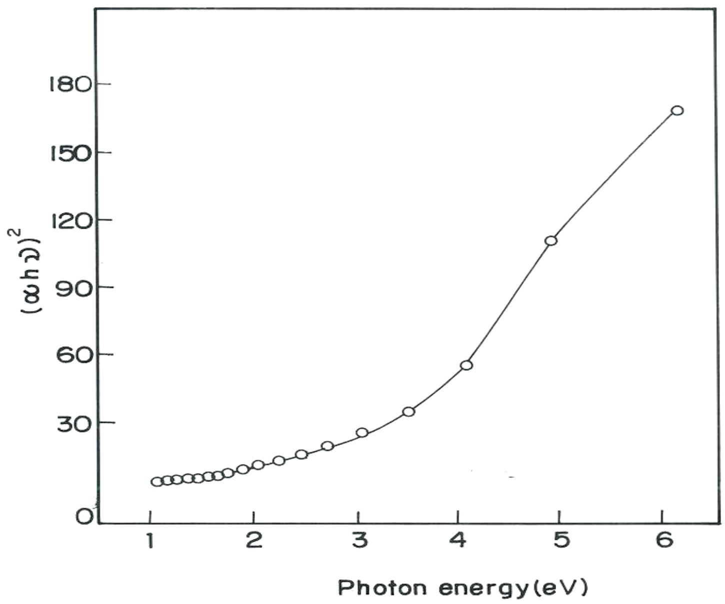

Fig.3. $(\alpha h\nu)^2$ *versus* $h\nu$

3.3 Dielectric studies

The dielectric constant and the dielectric loss of the L-Tartaric acid crystals were studied at different temperatures using HIOKI 3532 LCR HITESTER in the frequency region 50 Hz to 5 MHz. The variation of dielectric constant was measured as a function of frequency at different temperatures ranging from 30 to 90 ^{0}C and is shown in Fig.4, while the corresponding dielectric losses are depicted in Fig.5. . It is observed from the plot (Fig. 4) that the dielectric constant decreases exponentially with increasing frequency and then attains almost a constant value in the high frequency region. It is also observed that as the temperature increases, the value of the dielectric constant also increases. The same trend is observed in the case of dielectric loss versus frequency. At relatively lower frequency, the higher the temperature, the larger is the dielectric constant. The contributions of all the four polarizations such as electronic and space charge are predominant in the low-frequency region [8, 9]. The characteristics of low dielectric constant and dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with less defects and this parameter is of vital importance for various nonlinear optical materials and their applications [10].

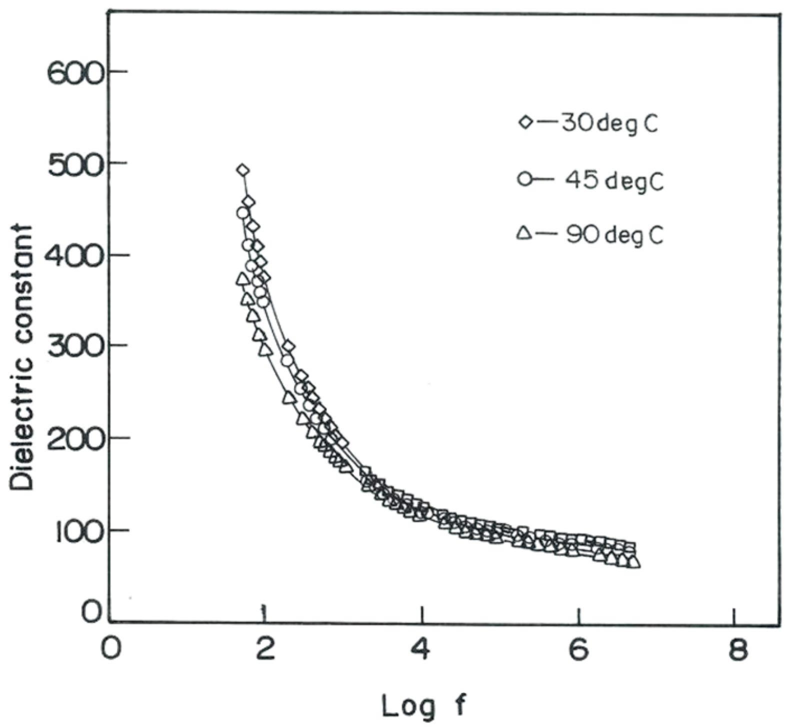

Fig.4.Dielectric constant vs log f

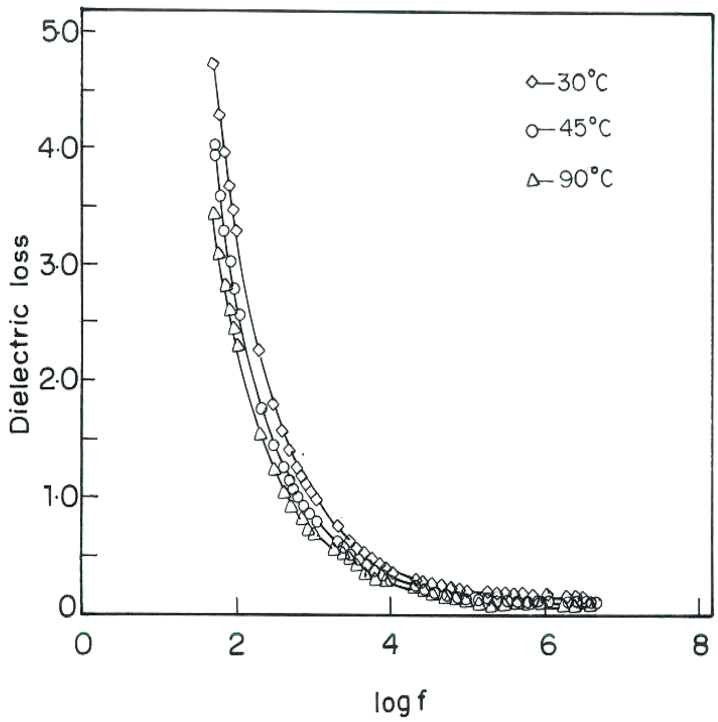

Fig.5.Dielectric loss vs log f

4. Conclusion

Good quality single crystals of L-Tartaric acid were grown by slow evaporation technique. Single-crystal XRD analysis confirmed that the crystals belong to monoclinic system. Fundamental parameters like plasma energy, Penn gap, Fermi energy and electronic polarizability of the crystal have been calculated. Optical band gap (E_g), absorption coefficient (α), extinction coefficient (K), refractive index (n), electric susceptibility χ_c and dielectric constants were calculated as a function of wavelength. The frequency dependence of dielectric constant decreases with increasing frequency at different temperatures.

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