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Impact Of pH Of L-threonine Single Crystals On Optical Parameters And Laser Damage Threshold Energy

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Abstract: The organic nonlinear optical crystal L-threonine was grown from aqueous solution at various pH values and subjected to optical and laser damage characterization. Optical band gap at all pH values has been determined by Uv-Vis-NIR spectra in the range of 190 to 1100 nm using Tauc's method. Measuring transmittance permitted the calculation of extinction coefficient K, refractive index *n*, and both the real ϵ_r and imaginary ϵ_i components of the dielectric constant as functions of photon energy. The refractive index of the crystals has been estimated using Abbe's refractometer. The laser damage threshold energy has been measured by irradiating laser beam using a Q-switched Nd: YAG laser (1064nm).L-threonine shows good transmission and high laser damage threshold at isoelectric pH. The results have been discussed in detail.

Keywords: Optical materials and properties, recrystallization, Refractive index, band gap.

1.Introduction

The fast development in the field of optoelectronics has stimulated the search for novel non linear optical materials for efficient signal processing, optical storage, optical communication, photonics, electro-optic modulation, optical parametric amplifiers, optical image processing etc., A molecular crystal suitable for non linear optical devices are required for sufficient crystal quality and high optical damage threshold [1].Organic molecules contain π electron conjugation systems asymmetrized by the electron donor and acceptor groups are highly polarizable entities for NLO applications [2]. The crystal L-threonine belongs to well known non-centrosymmetric orthorhombic system with space group $P2_12_12_1$. A few studies have been reported so far on the influence of pH on L-threonine single crystals [3,4]. To our knowledge no systematic studies on the impact of pH on optical and laser damage threshold studies have been made. In this investigation we report the studies on the impact of pH on optical and laser damage characterization.

2. Materials and methods

Commercially available L-threonine (Sigma Aldrich) was used for the growth procedure and successive recrystallization. Three different pH values are at pH 4.40, 5.87 and 6.80 were chosen for the studies .The pH adjustment procedure is followed as shown in [3].Good quality single crystals were harvested in the period of 12 days. Good transparency of the crystal is observed at isoelectric pH as mentioned in Ref. [3].

3.Results and discussion

3.1 Linear and nonlinear optical studies

The grown crystals at all pH were subjected to spectral analysis for studying the linear optical properties. The optical absorption spectrum of L-threonine at all pH of 2 mm thickness was recorded in the range of 190-1100nm using SL-218 Double beam Uv-Vis spectrophotometer (Fig. 1).

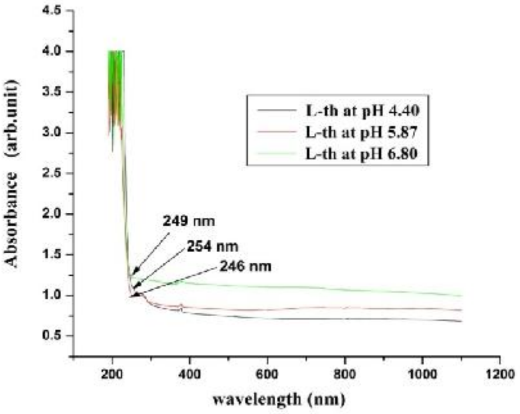

Fig. 1 UV absorption spectrum of L-threonine crystals at pH 4.40, 5.87 and 6.80

The cutoff wavelength of L-threonine crystals at pH 4.40, 5.87 and 6.80 was found to be 254, 246 and 249 nm respectively. The lower cutoff wavelength was observed to be at 246nm at isoelectric pH (5.87).

3.2 Determination of optical bang gap and optical constants

For optical device fabrications, the crystal should have high transparency in a considerable region of wavelength [5, 6]. The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of the electron. The absorption coefficient (*α*) and the optical constant (*k*) are determines from the following relations [7].

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

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

The optical band gap (E_g) has been evaluated from the transmission spectra and the optical absorption coefficient (*α*) near the absorption edge is given by

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

Where A is a constant, E_g the optical band gap, h the plank's constant and ν the frequency of incident photons.

The band gap of L-threonine crystals at pH 4.40, 5.87 and 6.80 were estimated by plotting $(\alpha h\nu)^2$ vs. $h\nu$ as shown in (Fig.2) while the linear portion of the plot is extrapolated near the onset of absorption edge to the energy axis.

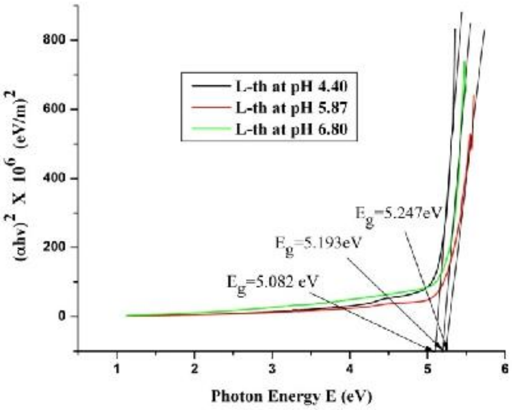

Fig.2 Plot of $(\alpha h\nu)^2$ vs. photon energy for L-threonine crystals at pH 4.40, 5.87 and 6.80

In this manner, the band gap for all the crystals of L-threonine at pH 4.40.5.87 and 6.80 was estimated to be 5.082, 5.247 and 5.193 eV respectively. At all pH, L-threonine at isoelectric pH (5.87) shows higher band gap indicates higher transparency. Thus this higher transparency is sufficient for the crystal to provide higher SHG efficiencies for L-threonine single crystals [3].

The extinction coefficient (*K)* can be obtained from the following relation

$$K = \frac{\lambda\alpha}{4\pi} \qquad (3)$$

The extinction coefficient as a function of wavelength is presented in (Fig.3.). The extinction coefficient increases with energy in addition, it shows inverse dependence with E in low energy range at all pH.

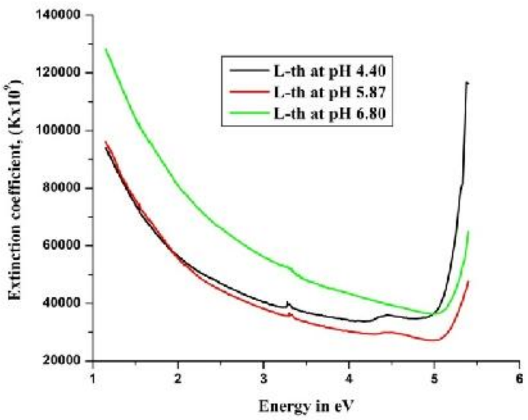

Fig.3 Plot of photon energy vs. extinction coefficient for L-threonine crystals at pH 4.40, 5.87 and 6.80.

The reflectance (R) in terms of the absorption coefficient and refractive index (n) can be derived from the relations:

$$R = \frac{1 \pm \sqrt{\left(1-\exp(-\alpha t)+\exp[(\alpha t)\right)]}}{1+\exp(-\alpha t)} \qquad (4)$$

$$n = \frac{-\left(R+1\right) \pm \sqrt{-3R^2+10R-3}}{2\,(R-1)} \qquad (5)$$

The dependence of Reflectance (R), and Refractive index (n) as a function of energy is shown in Fig.4 and Fig.5. From the Figure.5 it is observed that refractive index increases with increasing energy. The increase is very slow up to an energy of 5eV.There is a rapid increase in refractive index is observed at higher energies after 5eV.

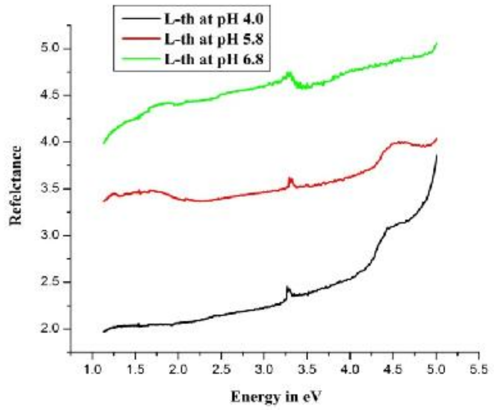

Fig.4 Plot of photon energy vs. Reflectance for L-threonine crystals at pH 4.40, 5.87 and 6.80.

From the optical constants, the electric susceptibility χ_e can be calculated according to the relation [8]

$$\epsilon_r = \epsilon_o + 4\pi\chi_c = n^2 - K^2,$$

$$\chi_e = \frac{n^2 - K^2 - \epsilon_o}{4\pi} \qquad (6)$$

where ϵ_o is the dielectric constant. The value of electric susceptibility χ_e at

λ = 1000nm at all pH is shown in **Table.1.**

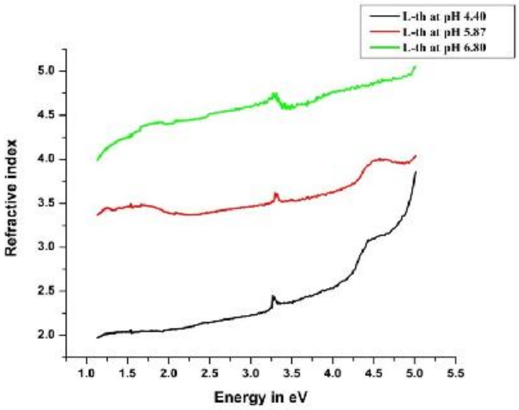

Fig.5 Plot of photon energy vs. Refractive index for L-threonine crystals at pH 4.40, 5.87 and 6.80.

Table.1 Values of electric susceptibility(χ_e), real dielectric constant(ϵ_r) and imaginary dielectric constant(ϵ_i) for L-threonine single crystals at all pH calculated at λ = 1000 nm.

S.no	Sample	χ_e	ϵ_r	ϵ_i
1	L-th at pH 4.40	0.08	1.01	1.78×10^{-4}
2	L-th at pH 5.87	0.39	8.51	5.30×10^{-4}
3	L-th at pH 6.80	1.15	14.51	9.22×10^{-4}

χ_e – electric susceptibility; ϵ_r – real dielectric constant ; ϵ_i – imaginary dielectric constant.

The real part dielectric constant ϵ_r and imaginary part dielectric constant ϵ_i can be calculated following the relations [9]:

$$\epsilon_r = n^2 - K^2 \text{ and } \epsilon_i = 2nK \qquad (7)$$

Figure.6 and Figure.7 show the variation of real and imaginary parts of the dielectric constant as a function of photon energy for L-threonine samples of different pH.It can be seen clearly from the figures that real part of dielectric constant increase and imaginary part decrease with increase in photon energy up to ~ 5eV.

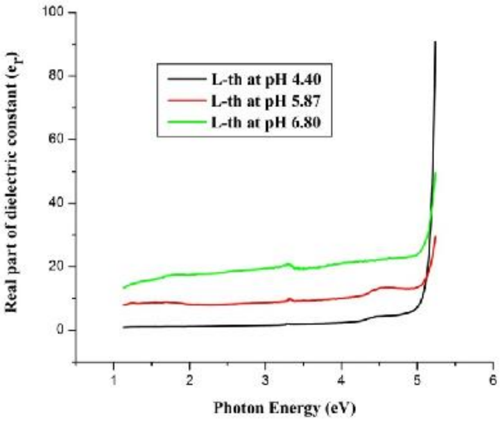

Fig.6 Variation of real part of dielectric constant as a function of photon energy for L-threonine samples at pH: 4.40, 5.86 and 6.80.

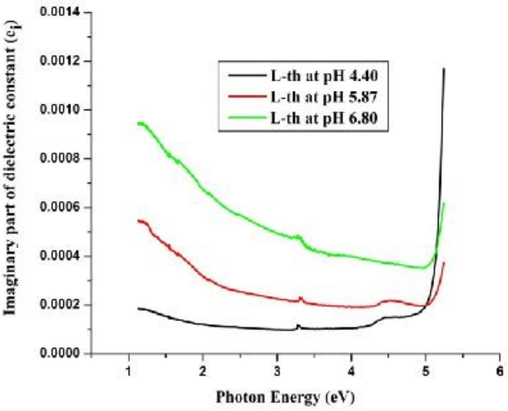

Fig.7 Variation of imaginary part of dielectric constant as a function of photon energy for L-threonine samples at pH: 4.40, 5.86 and 6.80.

The complex dielectric constant is given by the relation,

$$\epsilon_c = \epsilon_r + \epsilon_i \qquad (8)$$

ϵ_r and ϵ_i are the real and imaginary parts of dielectric constant respectively.

Fig.8 shows the variation of complex dielectric constant with photon energy.

The optical conductivity (σ_{op}) is a measure of the frequency response of the material when irradiated by light

$$\sigma_{op} = \frac{\alpha n c}{4\pi} \qquad (9)$$

where c is the velocity of light, α is the absorption coefficient and n is the refractive index.

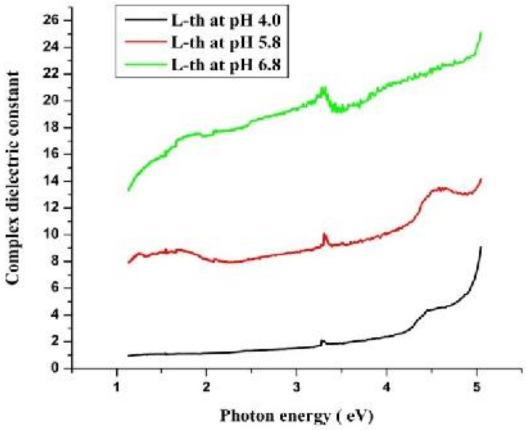

Fig.8 Dielectric constant as a function of photon energy for L-threonine samples at pH: 4.40, 5.86 and 6.80.

Fig.9 shows the variation of the optical conductivity as a function of photon energy for the L-threonine samples at pH 4.40, 5.86 and 6.80.It can be seen clearly that the optical conductivity directly depends on absorption coefficient and the refractive index of the material. It is observed from the figure that optical conductivity increases abruptly after ~5eV for all samples under investigation. The sudden increase in optical conductivity can be attributed to the increase in absorption coefficient.

L-threonine at all mentioned pH shows high magnitude of optical conductivity confirms the presence of very high photo response nature of the material. This makes the material more prominent for device applications in information processing and computing.

3.3. Refractive index analysis

Refractive index measurements of L-threonine single crystals at all pH was measured using Abbe refractometer model (ATAGO, NAR-4T, Japan) connected by digital thermometer using Thermistor cable connector jack. The experimental setup is shown in Fig.10 without digital thermometer. Polished samples of dimensions 9x2x2mm were chosen for the study. Each sample independently contact with the main prism with the contact liquid (Methylene iodide) which makes the sample to make close contact between sample and the prism. Open the secondary prism completely and stand a milky white reflector against the opposite side of secondary prism so that external light (sodium lamp) reflects on the reflector and it horizontally penetrates the sample. While observing to the eyepiece, gently turn the measurement knob to set the scale indication approximately to the refractive index shown on the test piece.

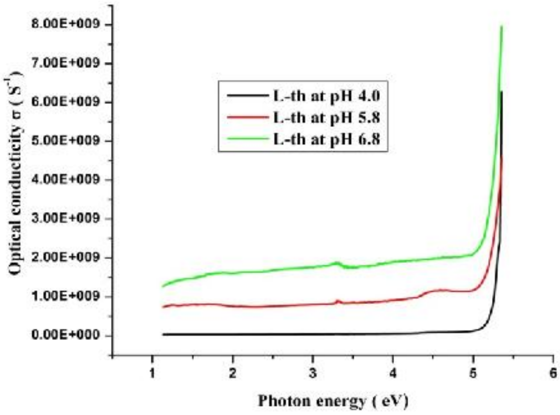

Fig.9 Optical conductivity as a function of photon energy for L-threonine samples at pH: 4.40, 5.86 and 6.80.

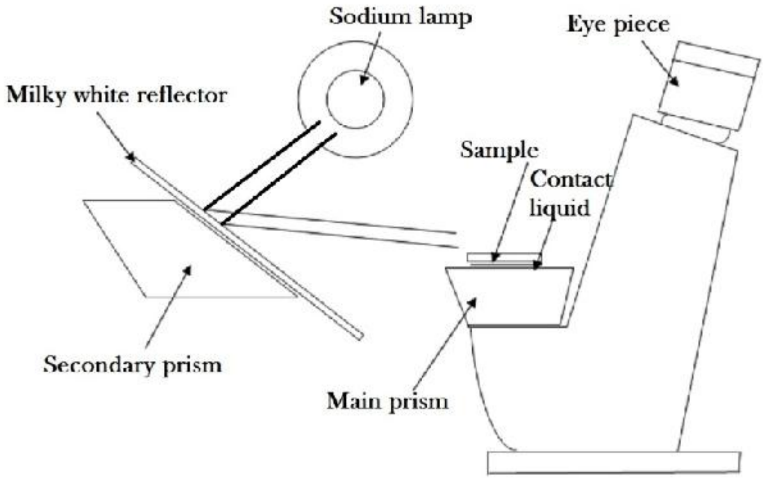

Fig.10 Experimental set-up of Abbe's refractometer.

The refractive index measured at ambient temperature (28.5^{o}C) of L-threonine single crystals at pH 4.40, 5.85 and 6.80 was measured to be 1.630, 1.654 and 1.595 respectively.

3.4 Measurement of laser damage threshold

In case of non linear optical crystals the harmonic conversion efficiency is proportional to the power per unit area of the fundamental beam. Hence a convenient way to increase the efficiency is to focus the beam in to the crystal. But this often leads to the breakdown of the materials catastrophically damaging the maximum permissible power for a particular crystal defined as damage threshold. The laser damage threshold of an optical crystal is an important factor affecting its applications. If the material has a low laser damage threshold it severely limits its applications, even though it has many excellent properties like high optical transmittance and high SHG efficiency [10, 11].

The energy density of the material was calculated using the formula, energy density =E/A, where E is the input energy measured in mJ and A is the area of the circular spot. Good quality crystals was mounted on the crystal holder in the path of Nd: YAG laser which generate pulses at 1064nm fundamental radiation at a frequency of 10Hz and pulse duration of 10 ns and the energy of the beam was increased from 5mJ in steps of 5.The crystal was exposed to the laser for a time period of 30 s for all measurements. The damage was observed and the energy of the laser beam was measured by Coherent energy/power meter (Model No .EPM 200). The laser damage threshold of L-threonine at pH 4.40, 5.87 and 6.80 was measured to be 2.22, 2.54 and 1.97 GW/cm^2 respectively which is higher than that of urea (1.5) crystals [12].

4. Conclusion

Single crystals of L-threonine have been grown in various pH values. The crystals grown at various pH values were subjected to optical transmission studies and laser damage threshold characterization. Crystals at isoelectric pH shows good transparency, wide band gap and higher laser damage threshold. Hence it is concluded that the crystal L-threonine grown at isoelectric pH can withstand higher laser energy than grown at other pH values. The optical band gap (Eg), absorption coefficient (α), extinction coefficient (K), refractive index (n), electric susceptibility (χ_e) and dielectric constants at all pH were also calculated as a function of energy.

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