

Growth, Optical, Mechanical, Dielectric and Photoconductivity Properties of L-Proline Succinate NLO Single Crystal

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Abstract Single crystals of L-Proline Succinate (LPS) were grown by slow evaporation technique. Single crystal X-ray diffraction analysis reveals that the crystal belongs to monoclinic crystal system. 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 210nm. The optical band gap is found to be 5.90eV. The transmittance of L-Proline succinate crystal has been used to calculate the refractive index (n), the extinction coefficient (K) and the real (ϵ_r) and imaginary (ϵ_i) components of the dielectric constant. Mechanical strength of the grown crystal was analyzed using Vickers microhardness tester. Nonlinear optical property of the crystal was confirmed by Kurtz Perry powder technique. Dielectric constant measurements were carried out at different temperatures. Some fundamental data such as valence electron plasma energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal have been estimated. Photoconductivity measurements carried out on the grown crystal reveal the negative photoconducting nature.

Keywords: solution growth, single crystal XRD, optical transmission, SHG, dielectric constant, photoconductivity studies

1. Introduction

Most of the nonlinear optical materials are currently used in the fabrication of passive and active photonic devices [1,2]. Nonlinear optical processes provide the key functions of frequency conversion and optical switching [3]. These applications depend upon the various properties of the materials, such as transparency, birefringence, refractive index, dielectric constant, thermal, photochemical and chemical stability. 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 [4]. Although the crystal growing technology for these materials is highly developed and their nonlinear optical susceptibilities are sufficient for most of the current photonic applications, they have features that are less than desirable. Hence, new nonlinear optical materials are needed to extend the range of photonic applications. For any device fabrication in the electronic industry pure and defect less single crystals are needed. In the present work, we have grown the L-Proline succinate single crystal by slow evaporation technique. The grown crystal was characterized using the studies of single crystal XRD, FTIR, UV-VIS-NIR spectral analysis,

microhardness and NLO test. Dielectric constant measurements were also carried out at different frequencies and temperatures. Some fundamental data such as valence electron plasma energy, Penn gap, Fermi energy and electronic polarizability of the grown crystal were calculated. Photoconductivity measurements also carried out on the grown crystal reveal the negative photoconducting nature.

2. Experimental Procedure

Single crystals of LPS were grown from L-Proline and succinic acid taken in equimolar ratio in aqueous solution by slow evaporation method. The solution was stirred continuously using a magnetic stirrer. 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 after the nucleation process was completed. Figure 1 shows as-grown crystals of LPS.

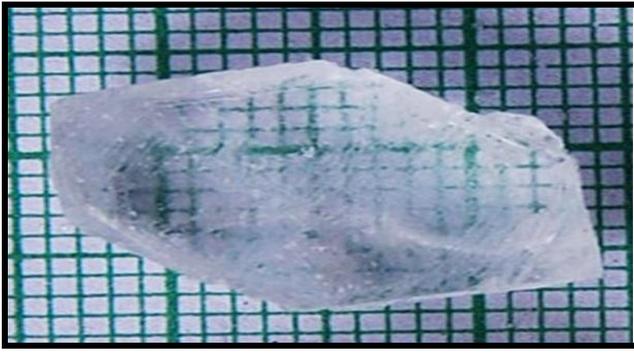


Figure 1. Photograph of LPS crystal

3. Single Crystal X-ray Diffraction Analysis

Single crystal X-ray diffraction analysis for the grown crystals has been carried out to identify the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray diffractometer. Calculated lattice parameters are $a = 5.06 \text{ \AA}$, $b = 8.83 \text{ \AA}$, $c = 5.47 \text{ \AA}$, $\beta = 92.60^\circ$ and the crystal belongs to monoclinic crystal system.

4. UV-visible Spectroscopy

The transmission spectrum of LPS was recorded with a Varian Cary 5E spectrophotometer in the range 200-1000 nm. From the spectrum (Figure 2), it is evident that LPS crystal has UV cut off wavelength at 210nm. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula.

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

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

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

where A is a constant, E_g the optical band gap, h the Planck constant and ν the frequency of the incident photons. The band gap of LPS crystal was estimated by plotting $(\alpha h\nu)^{1/2}$ versus $h\nu$ as shown in Figure 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 5.90eV. Extinction coefficient (K) can be obtained from the equation,

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

The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)} \quad (4)$$

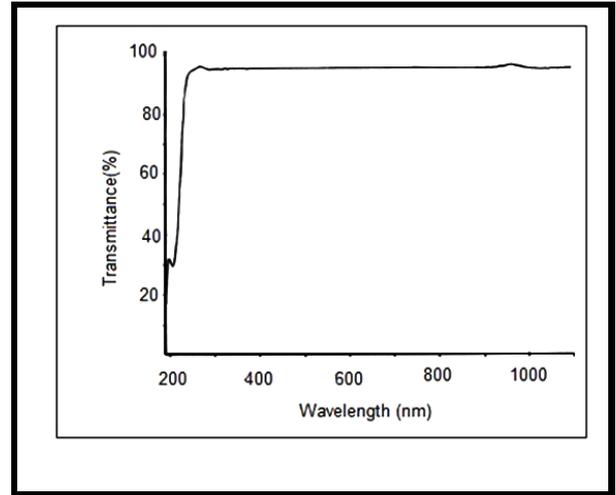


Figure 2. Transmission spectrum of LPS crystal

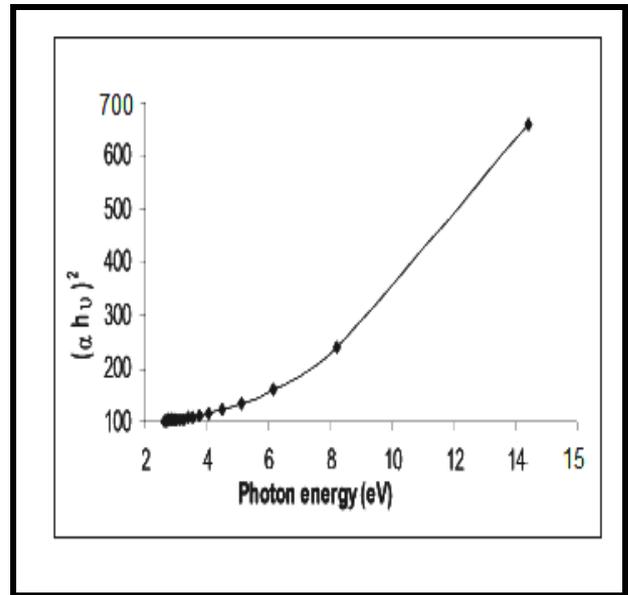


Figure 3. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for LPS single crystal

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

Hence,

$$R = \frac{\exp(-\alpha t) \pm \sqrt{\exp(-\alpha t)T - \exp(-3\alpha t)T + \exp(-2\alpha t)T^2}}{\exp(-\alpha t) + \exp(-2\alpha t)T} \quad (5)$$

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

$$n = -(R+1) \pm 2 \frac{\sqrt{R}}{(R-1)} \quad (6)$$

The refractive index (n) is 1.57 at $\lambda = 1100\text{nm}$. From the optical constants, electric susceptibility (χ_c) can be calculated according to the following relation [6],

$$\epsilon_r = \epsilon_0 + 4\pi\chi_c = n^2 - k^2 \quad (7)$$

Hence,

$$\chi_c = \frac{n^2 - k^2 - \epsilon_0}{4\pi} \quad (8)$$

The value of electric susceptibility χ_c is 0.143 at $\lambda = 1100\text{nm}$. The real part dielectric constant ϵ_r and imaginary part dielectric constant ϵ_i can be calculated from the following relations [7],

$$\epsilon_r = n^2 - k^2 \quad \& \quad \epsilon_i = 2nk \quad (9)$$

The value of real ϵ_r and ϵ_i imaginary dielectric constants at $\lambda = 1100\text{nm}$ are 1.37 and 7.214×10^{-5} respectively.

5. Second Harmonic Generation

Second harmonic generation of the grown crystal was confirmed using Kurtz and Perry powder technique [8]. A high intense beam of laser wavelength 1064nm was allowed to illuminate the sample with pulse width of 8 ns . The emission of green radiation 532nm from the sample confirms that the material exhibits nonlinear optical property. The power of incident laser beam was measured as 4.3 mJ/pulse . The output radiation from the crystal was allowed to fall on a photomultiplier tube which converts the light signal into electrical signal. The second harmonic generation is confirmed by the emission of green light and its efficiency is found to be 22% of that of KDP crystal. Moreover, the crystal has the advantage of combined thermal and mechanical robustness required for nonlinear optical device fabrications.

6. Vickers Microhardness Test

Analysis of mechanical property of the grown crystal is also important for the fabrication of electronic and optical devices. Microhardness studies have been carried out on a selected well transparent single crystal using microhardness tester, fitted with a Vickers diamond pyramidal indenter. To get accurate results of hardness of the grown crystal indentations were made on the LPS crystals with applied load ranging from 5g to 25g . The time of indentation was kept constant for 10s . Five indentations were made on each surface under examination for the same load and the mean diagonal length was measured. To avoid surface defects, the distance between consecutive indentations were kept more than five times the diagonal length of the indentation mark. The values of Vickers microhardness at different loads were calculated using the relation,

$$H_v = 1.8544 P / d^2 \text{ kg / mm}^2 \quad (10)$$

where, P is the applied load and d is the mean diagonal length of the indenter impression. Figure 4 shows the variation of hardness with the applied load. It is observed that the hardness of LPS increases by increasing load up to 25g which indicates the reverse indentation size effect [9,10,11]. The cracks start to occur after the load 25g . This may be due to the release of internal stress generated locally by indentation. The increasing trend of microhardness with the load up to 25g is well understood from Mayer law and Onitsch condition. According to Mayer law, the relationship between the load (P) and the size (d) of the indentation is given as

$$P = kd^n \quad (11)$$

where, n is called Mayer index or work hardening index. Hence the slope of the plot of $\log d$ versus $\log P$ will give the work hardening index. The slope of the plot for LPS (Figure 5) is found to be 3.6. According to Onitsch if n is greater than 2, the microhardness will increase with the increase of load. Hence, the material shows increasing trend for the hardness of the material up to a particular load 25g .

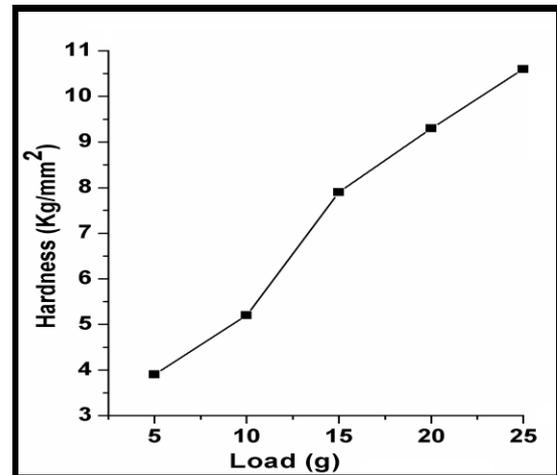


Figure 4. Vickers microhardness of LPS crystal

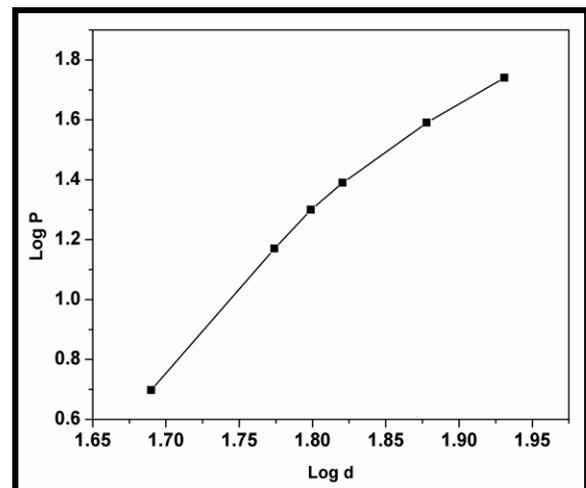


Figure 5. Plot of $\log d$ vs $\log P$

7. Dielectric Studies

The dielectric constant of the L-Proline Succinate crystal was studied using HIOKI 3532 LCR HITESTER. The experiment was carried out for the frequencies from 50Hz to 5MHz with the different temperatures $40\text{ }^\circ\text{C}$, $60\text{ }^\circ\text{C}$, $90\text{ }^\circ\text{C}$, $120\text{ }^\circ\text{C}$ and $150\text{ }^\circ\text{C}$ respectively. The variation of dielectric constant of the grown crystal as a function of frequency is shown in Figure 6. From the graph, the dielectric constant is seen to decrease with increase in frequency. The large value of dielectric constant at low frequency is due to the presence of space charge polarization [12]. The decrease in the value of dielectric constant with frequency is due to the fact that the frequency of electric charge carriers cannot follow the alternation of the ac electric field applied beyond a certain

critical frequency [13]. The very low value of dielectric constant at higher frequencies is important for the fabrication of materials for ferroelectric, photonic and electro-optic devices. The value of dielectric constant at higher frequencies can be used to calculate Penn gap, Fermi energy and polarisability of the grown crystals [14].

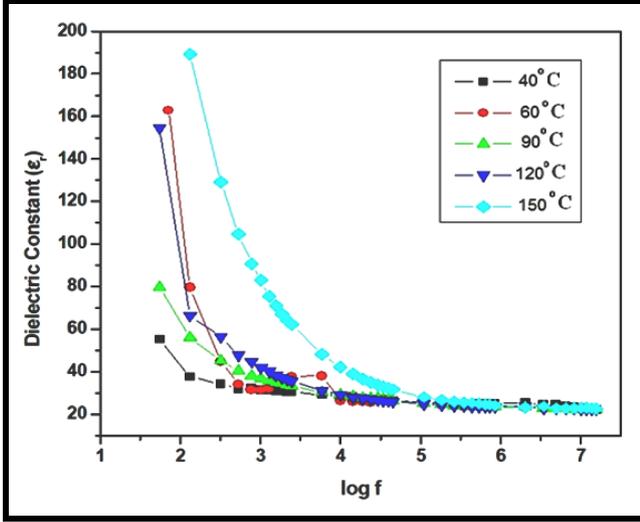


Figure 6. Dielectric constant vs log f

Theoretical calculations shows that the high frequency dielectric constant is explicitly dependent on the valence electron Plasmon energy, an average energy gap referred to as the Penn gap and the Fermi energy. The Penn gap is determined by fitting the dielectric constant with the Plasmon energy [15]. The valence electron plasma energy, $\hbar\omega_p$, is calculated using the relation,

$$\hbar\omega_p = 28.8 \left(\frac{Z\rho}{M} \right)^{1/2} \quad (12)$$

$$E_p = \frac{\hbar\omega_p}{(\epsilon_\infty - 1)^{1/2}} \quad (13)$$

Plasma energy are the Penn gap and the Fermi energy [15] given by

$$E_F = 0.2948(\hbar\omega_p)^{4/3} \quad (14)$$

Then we obtained electronic polarizability α using a relation [16,17],

$$\alpha = \left[\frac{(\hbar\omega_p)^2 S_0}{(\hbar\omega_p)^2 S_0 + 3E_p^2} \right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \text{ cm}^3 \quad (15)$$

where S_0 is a constant given by

$$S_0 = 1 - \left[\frac{E_p}{4E_F} \right] + \frac{1}{3} \left[\frac{E_p}{4E_F} \right]^2 \quad (16)$$

The value of α obtained from equation (15) closely matches with that obtained using Clausius-Mossotti relation,

$$\alpha = \frac{3}{4} \frac{M}{\pi N_a \rho} \left[\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2} \right] \quad (17)$$

All the above parameters as estimated are shown in Table 1.

Table 1. Important parameters of LPS Single crystal

Parameters	Value
Plasma energy ($\hbar\omega_p$)	17.62 eV
Penn gap (E_p)	3.46 eV
Fermi Energy (E_F)	13.39 eV
Electronic polarizability (Penn analysis)	$8.672 \times 10^{-25} \text{ cm}^3$
Electronic polarizability (using CM relation)	$8.746 \times 10^{-25} \text{ cm}^3$

8. Photoconductivity Studies

Photoconductivity measurements were made using Keithley 485 picoammeter. The dark current was recorded by keeping the sample unexposed to any radiation. Figure 7 shows the variation of both dark current (I_d) and photocurrent (I_p) with applied field. It is seen from the plots that both I_d and I_p of the sample increase linearly with applied field. It is observed from the plot that the dark current is always higher than the photo current, thus confirming the negative photoconductivity. The phenomenon of negative photoconductivity is explained by Stockmann model [18]. The negative photoconductivity in a solid is due to the decrease in the number of charge carriers or their lifetime, in the presence of radiation [19]. For a negative photoconductor, forbidden gap holds two energy levels in which one is placed between the Fermi level and the conduction band while the other is located close to the valence band. The second state has higher capture cross-section for electrons and holes. As it captures electrons from the conduction band and holes from the valence band, the number of charge carriers in the conduction band gets reduced and the current decreases in the presence of radiation.

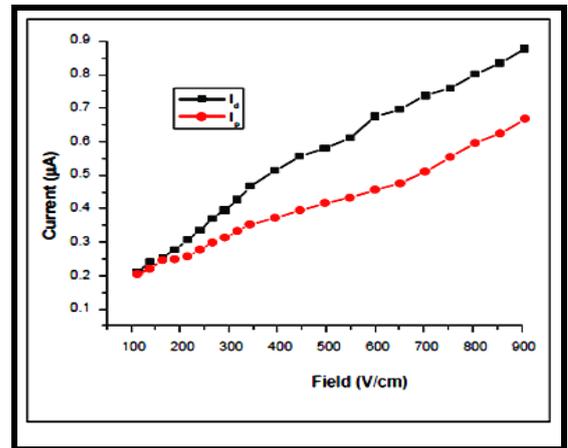


Figure 7. Field dependent photoconductivity of LPS

9. Conclusion

Single crystals of L-Proline Succinate were grown by slow evaporation technique. Single-crystal XRD analysis confirmed that the crystals belong to monoclinic crystal system. Optical band gap (E_g), absorption coefficient (α), extinction coefficient (K), refractive index (n), electric susceptibility χ_c and dielectric constants were calculated. Mechanical behaviour has been studied by Vickers

microhardness test. Kurtz Perry powder technique confirms that LPS is one of the promising nonlinear optical materials with appreciable SHG efficiency. The frequency dependence of dielectric constant decreases with increasing frequency at different temperatures. Fundamental parameters like plasma energy, Penn gap, Fermi energy and electronic polarizability of the crystal have been calculated. Photoconductivity investigations reveal the negative photoconducting nature of the grown single crystal.

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