Optical and conductivity properties of L-Histidine Nitrate NLO single crystal

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Abstract

Single crystals of L-Histidine Nitrate (LHN) were grown from aqueous solution by slow evaporation technique. Single crystal X-ray diffraction analysis reveals that the crystal belongs to orthorhombic system with the space group $P2_12_12_1$. The optical transmission study reveals the transparency of the crystal in the region 230-1100nm and the cut off wave length has been found to be 230nm. The optical band gap is found to be 3.80eV. Dielectric studies were also carried out. Photoconductivity measurements carried out on the grown crystal reveal a negative photoconducting nature.

Keywords: Solution growth, Single crystal XRD, Optical transmission, Dielectric studies, Photoconductivity studies.

Resumen

Monocristales de Nitrato de L-Histidina (LHN) fueron cultivados en una solución acuosa mediante la técnica de evaporación lenta. El análisis de difracción de rayos X para un solo cristal revela que el cristal pertenece al sistema ortorrómbico con el grupo espacial P212121. El estudio revela la transmisión óptica de la transparencia del cristal en la región de 230-1100nm y la longitud de onda de corte se ha encontrado a 230nm. El ancho de banda óptico se encuentra a 3.80eV. Estudios dieléctricos fueron también llevados a cabo. Las mediciones de fotoconductividad realizadas en el cristal crecido revelan una naturaleza negativa de fotoconductores.

Palabras clave: Crecimiento de solución, cristal único XRD, transmisión óptica, estudios dieléctricos, estudios de fotoconductividad.

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I. INTRODUCTION

Nonlinear optical materials have attracted much attention because of their potential applications in emerging optoelectronic technologies [1] and [2]. In this respect, amino acids and their salts belong to a family of organic materials that have wider NLO applications [3, 4]. The importance of amino acid for NLO application lies on the fact that almost all amino acids contain an asymmetric carbon atom and crystallize in non-centrosymmetric space group. These applications depend upon the various properties of the materials, such as transparency, birefringence, refractive index, dielectric constant, thermal, photochemical and chemical stability. Organic crystals have large nonlinear susceptibilities compared to inorganic crystals. However, these crystals have certain limitations such as increased optical absorption, narrow transparency window and poor mechanical and thermal stability. Inorganic crystals have excellent mechanical and thermal properties but possess relatively low optical nonlinearities because of the lack of π^- electron delocalization. Combining the high optical nonlinearity and chemical flexibility of organics with thermal stability and excellent transmittance of inorganics, semiorganic materials have been proposed and are attracting a great deal of attention in the field of nonlinear optics [5]. In the present investigation, optical and conductivity properties of LHN have been reported.

II. EXPERIMENTAL PROCEDURE

Single crystals of LHN were grown from L-Histidine and nitric acid in equimolar proportion in aqueous solution by slow evaporation method. The solution was stirred continuously using magnetic stirrer. The prepared solution was filtered and kept undisturbed at room temperature. Tiny seed crystals with good transparency were obtained due to spontaneous nucleation. Among them, a defect-free seed crystal was chosen and 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.

III. SINGLE CRYSTAL X-RAY DIFFRACTION

Single crystal X-ray analysis was carried out for the grown crystals using ENRAF NONIUS CAD 4 automatic X-ray diffractometer. The lattice parameter values are found to be a = 5.23Å, b = 7.13Å and c = 25.02Å, $\alpha = \beta = \gamma = 90$. The XRD data prove that the crystal is orthorhombic in structure with the space group $P2_12_12_1$. The results are found to be in good agreement with the reported results [6].The single crystalline nature of the material is thus established from XRD studies.

IV. OPTICAL TRANSMISSION STUDIES

The optical transmission spectrum of L-histidine nitrate (LHN) single crystal was recorded in the wavelength region 200–1100nm and is shown in Fig. 1. For optical fabrications, the crystal should be highly transparent in the considered region of wavelength [7] and [8]. Favourable transmittance of the crystal in the entire visible region suggests its suitability for second harmonic generation [9]. The UV absorption edge for the grown crystal was observed to be around 230nm. The dependence of optical absorption coefficient on photon energy helps to study the band structure and type of transition of electrons [10].

Optical absorption coefficient (α) was calculated from transmittance using the following relation:

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right), \tag{1}$$

where T is the transmittance and t the thickness of the crystal. As a direct band gap material, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies (hv)

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

where E_g is the optical band gap of the crystal and A is a constant. A plot of variation of $(\alpha hv)^2$ versus hv is shown in Fig. 2. E_g is evaluated using extrapolation of the linear part [11]. The energy absorption gap is of direct type and the band gap energy is found to be 3.80eV. As a consequence of a wide band gap, the grown crystal has a large transmittance in the visible and near infrared region [12]. The transparency of the material in the required region is very useful for analyzing the induced polarization when powerful radiation is incident on the material.

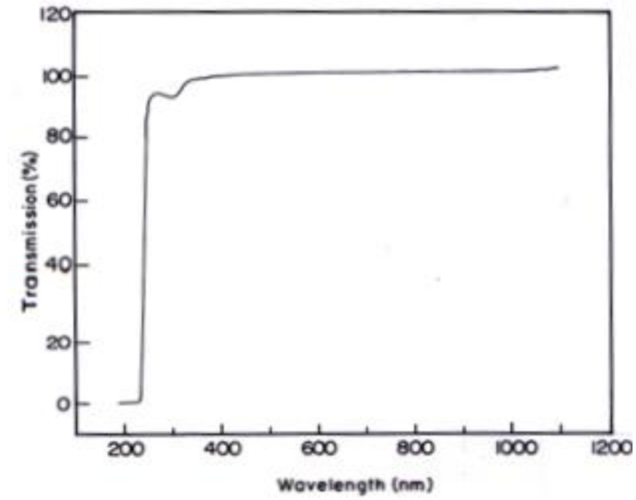

FIGURE 1. Transmittance spectrum of LHN.

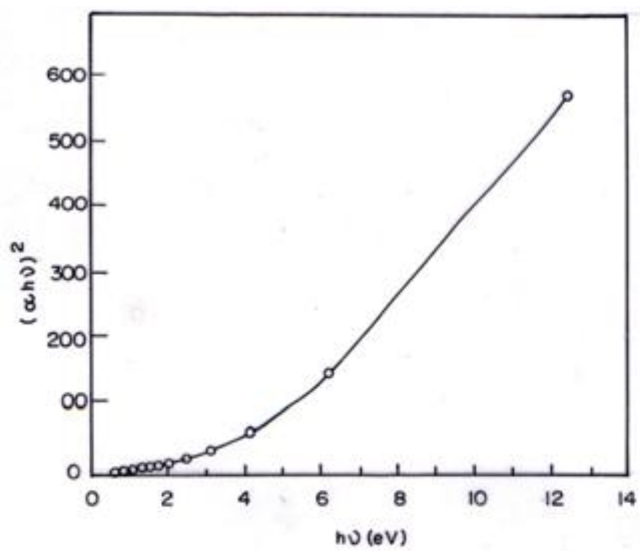

FIGURE 2. $(\alpha hv)^2$ versus hv.

A. Determination of Optical Constant

Optical behaviour of materials is important to determine its usage in optoelectronic devices [13]. Optical constant (n, K) are determined from the transmission (T) and reflection (R) spectra based on the following relations

$$T = \frac{(1-R)^2\exp(-\alpha t)}{1-\mathrm{R}^2\exp(-2\alpha t)}, \tag{3}$$

where t is the thickness and α is related to extinction coefficient K by

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

The refractive index (n) can be determined from the reflectance (R) data using the relation

$$R = \frac{\left(n-1\right)^2}{\left(n+1\right)^2}. \quad (5)$$

Reflectance can also be written in terms of absorption coefficient

$$R = \frac{1 \pm \sqrt{1-\exp(-\alpha t + \exp(\alpha t)}}{1+\exp(-\alpha t)}, \quad (6)$$

and from the above equation, refractive index n can also be derived as

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)}. \quad (7)$$

Figs. 3 and 4 show the variation of both reflectance (R) and extinction coefficient (K) as a function of absorption coefficient, respectively. From the graphs, it is clear that both reflectance and extinction coefficients depend on absorption coefficient. Internal efficiency of the device also depends on absorption coefficient. Hence, by tailoring absorption coefficient, one can achieve a desired material for the fabrication of electro-optic and optoelectronic devices.

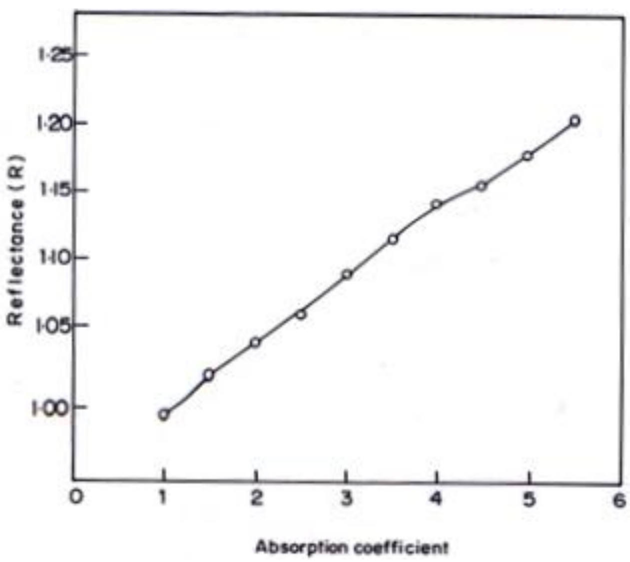

FIGURE 3. Plots reflectance vs absorption coefficient (α).

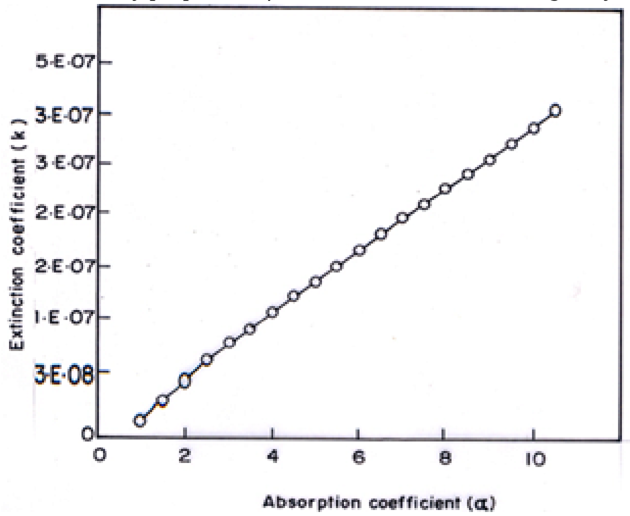

FIGURE 4. Plots of extinction coefficient (K) vs absorption coefficient (α).

V. DIELECTRIC STUDIES

The dielectric constant and the dielectric loss of LHN sample were measured in the frequency region from 50Hz to 5MHz. Figs. 5 and 6 show variations of dielectric constant and dielectric loss with log frequency under different temperatures from 40 to 150°C respectively. It is observed from the Plot (Fig. 5) 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 (Fig. 6). The low value of dielectric loss indicates that the grown crystals are good in quality. The larger values of dielectric loss at lower frequency may be attributed to space charge polarization owing to charge lattice defect [14]. The characteristic of low dielectric constant and dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is of vital importance for various nonlinear optical materials and their applications. The material is thus capable of producing dipoles when powerful radiation or electric field is applied to the material.

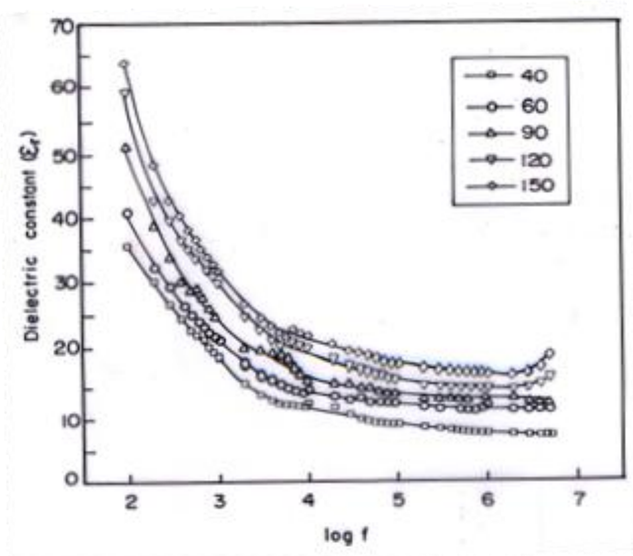

FIGURE 5. Dielectric constant vs log f.

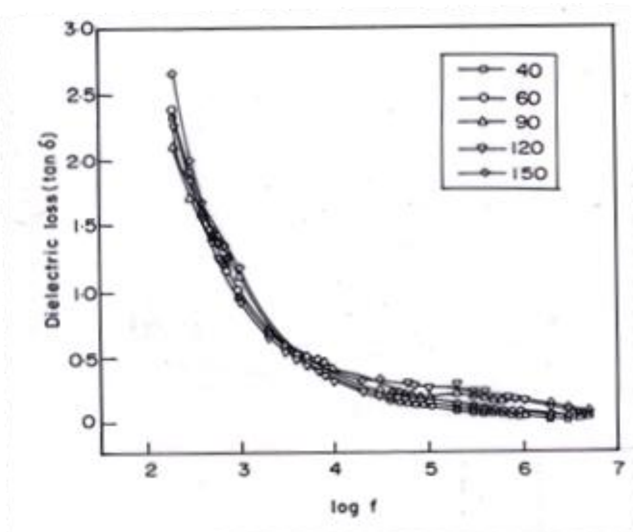

FIGURE 6. Dielectric loss vs log f.

VI. PHOTOCONDUCTIVITY STUDY

Photoconductivity study of the LHN single crystal was carried out by using Keithly 485 picoammeter. By not allowing any radiation to fall on the sample and by varying the applied field from 100 to 4000V/cm, the corresponding dark current values shown by the picoammeter were recorded. To measure the photo current, the sample was illuminated with a halogen lamp (100W) containing iodine vapour by focusing a spot of light on the sample with the help of a convex lens. The applied field was increased from 100 to 4000V/cm and the corresponding photo current was recorded. The photo current and dark current are plotted as a function of the applied field (Fig. 7). It is observed from the plot that the dark current is always greater than the photo current, hence it is concluded that LHN exhibits negative photoconductivity. The Stockmann model explains the phenomenon of negative photoconductivity successfully with specific references to semiconducting crystals [15]. However, the material can create more charges to produce appreciably larger photocurrent than dark current when it is subjected to powerful radiation in the transmission range predicted by UV spectral studies.

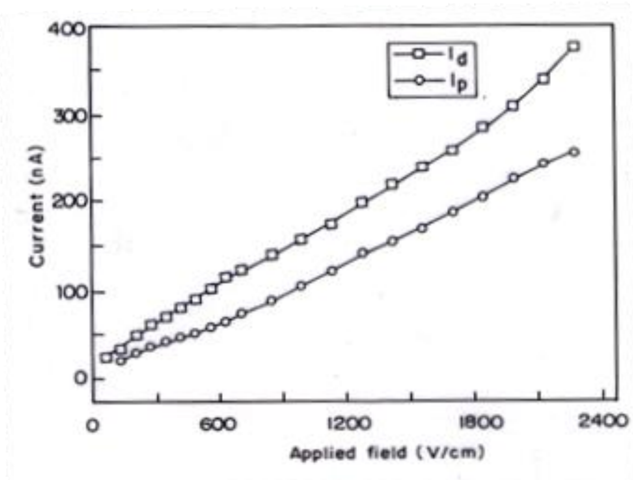

FIGURE 7. Field dependent photoconductivity of LHN single crystal.

VII. CONCLUSION

Single crystals of L-histidine nitrate were grown from aqueous solution by slow evaporation technique under room temperature. The grown crystals were characterized by single crystal XRD and it is confirmed that the crystal belongs to the orthorhombic system with space group $P2_12_12_1$. The band gap for the grown crystal is found to be 3.80eV. The optical investigations show a high value of both extinction coefficient (K) and reflectance (R) indicating high transparency of the crystal which confirms its suitability for optical switch device fabrications. Dielectric characterization shows low value of dielectric constant at higher frequencies for these crystals. The photoconductivity study ascertains the negative photoconducting nature of the crystal for the visible region.

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