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PHYSICS

GROWTH, OPTICAL, DIELECTRIC AND FUNDAMENTAL PROPERTIES OF L-ARGININE ACETATE NLO SINGLE CRYSTALS

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Abstract

Some organic materials exhibit exceeding by large amount of nonlinear property and they are found to be more suitable for device fabrications. Hence, in the present study L-Arginine Acetate (LAA) an organic material, has been extensively studied with regard to the growth and characterization. Single crystals of L-Arginine Acetate (LAA) 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 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 absorption studies show that the crystal is transparent in the entire visible region with a cut off wavelength of 240 nm. The optical band gap is found to be 3.75 eV. The dependence of extinction coefficient (K) and refractive index (n) on wavelength has also been reported. Dielectric constant measurements were carried out at different temperatures and frequencies.

Keywords: Single crystal, Growth from solution, Single crystal XRD, Optical absorption, Dielectric constant

Introduction

Nonlinear optics (NLO) is a frontier field in science and technology, which has found wide applications in the field of telecommunication, optical information and optical storage devices, etc. [1]. In the recent years, organic molecular nonlinear optical (NLO) materials have been intensively investigated due to their high nonlinearities, rapid response to electro-optic effect, as compared to inorganic NLO materials [2].Organic NLO materials play vital role in second-harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric oscillation, optical bi-stability, optical image processing, colour displays, underwater communications and medical diagnostics, etc. [3]. In the present investigation we report bulk growth, fundamental properties, optical, and dielectric properties of L-Arginine Acetate single crystals.

Experimental

L-Arginine Acetate (LAA) was synthesized by the reaction between L-arginine and acetic acid and by slow evaporation technique. The reactants were thoroughly dissolved in double distilled water and stirred well using a temperature controlled magnetic stirrer to yield a homogeneous mixture of solution. Then the solution was allowed to evaporate at room temperature, which results in the yield of colourless crystalline salt of LAA due to supersaturation followed by nucleation. The seed crystals were harvested from the solution after eight days and a suitable seed was selected. The selected seed was suspended in the freshly prepared solution. After a period of three weeks, optically transparent defect free crystals were obtained from the mother solution. Fig.1 shows single crystals of LAA with high degree of transparency.

Fig.1. As-grown single crystals of LAA

Results and Discussion

Density of LAA Crystal

The density of LAA crystal was calculated using the equation [4]

$$\rho = MZ / N_A abc \quad (1)$$

where M is molecular weight of LAA, molecular unit cell Z = 2, N_A is Avogadro's number and a, b and c are the lattice parameters of LAA crystal. The theoretical density is found to be 1.345 g/cm^3. The density of LAA crystal was measured experimentally by the floatation method at room temperature (32ºC), and the measured density can be obtained using the expression

$$\rho = M \rho_{solvent} / m - m' \quad (2)$$

where m is the mass of LAA crystal sample in the air, m´ is the mass when the LAA crystal sample was

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immersed in CCl_4 and $\rho_{solvent}$ is the density of solvent (CCl_4) used at measured temperature. The density was measured by floatation technique. From this measurement, the density of the crystal is found to be 1.346 g/cm^3, which is in good agreement with the theoretically found value.

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= 9.221 Å, b = 5.184 Å and c = 13.090 Å, and v=586.20Å^3, which are found to be in agreement with those of reported values [5]. The molecular weight of the grown crystal is *M*=246 g, and total number of valance electron *Z*=88. The density of the grown crystal was found to be ρ=1.345 g.cm^{-3} and dielectric constant at 1 MHz was calculated as ε_∞ = 41.5. The valence electron plasma energy, $\hbar\omega_P$ is given by

$$\hbar\omega_P = 28.8\left(\frac{Z\rho}{M}\right)^{\frac{1}{2}} \quad (3)$$

where Z is the total number of valence electrons, ρ is the density and M is the molecular weight of the LAA single crystal. The Plasma energy is terms of Penn gap and Fermi energy [6] is given as

$$E_P = \frac{\hbar\omega_P}{\left(\varepsilon_\infty - 1\right)^{1/2}} \quad (4)$$

and

$$E_F = 0.2948\left(\hbar\omega_P\right)^{4/3} \quad (5)$$

Polarizability, α is obtained using the relation [7]

$$\alpha = \left[\frac{\left(\hbar\omega_P\right)^2 S_0}{\left(\hbar\omega_P\right)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^{-1} \quad (6)$$

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

$$S_0 = 1 - \left[\frac{E_F}{4E_F}\right] + \frac{1}{3}\left[\frac{E_F}{4E_F}\right]^2 \quad (7)$$

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

$$\alpha = \frac{3M}{4\pi N_a \rho}\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \quad (8)$$

where the symbols have their usual meaning. N_A is Avagadro number and the calculated fundamental data on the grown crystal of LAA are listed in Table1.

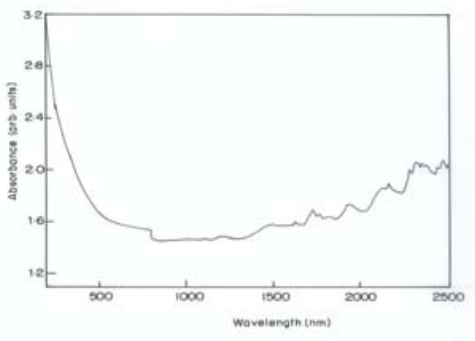
Table 1. Some theoretical data for LAA single crystal

Parameters	Values
Plasma energy (eV)	19.98
Penn gap (eV)	3.14
Fermi gap (eV)	15.82
Polarizability (cm^3) Penn analysis	9.03 x 10^{-23}
Polarizability (cm^3) Clausius-Mossotti Equation	9.08 x 10^{-23}

Optical absorption

Fig.2 shows optical absorption spectrum of LAA single crystal recorded in the wavelength region ranging from 200 nm to 800 nm using PERKIN-ELMER LAMBDA 25 spectrophotometer. For optical fabrication, the crystal should be highly transparent over a considerable region of wavelength [8-9].The UV cut off wavelength for the grown crystal was found to be 240 nm which makes it a potential material for optical device fabrications. LAA is likely to improve the nonlinear optical (NLO) property.

Fig.2. UV- absorption of LAA



Optical band gap and optical constants

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 constants (n, K) are determined from the transmission (T) and reflection (R) spectrum based on the following relations [10].

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

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

$$K = \frac{\alpha\lambda}{4\pi} \quad (2)$$

The reflectance (R) in terms of the absorption coefficient and refractive index (n) can be expressed

$$R = \frac{1 \pm \sqrt{1-\exp(-\alpha t + \exp(\alpha t)}}{1+\exp(-\alpha t)} \quad (3)$$

$$n = \frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \quad (4)$$

In the high photon energy region, the energy dependence of absorption coefficient suggests the occurrence of direct band gap of the crystal obeying the following equation for high photon energies (hν)

$$\alpha = \frac{A(h\upsilon - E_g)^{1/2}}{h\upsilon} \quad (5)$$

where E_g is the optical band gap of the crystal and A is a constant. The plot of $(\alpha h\nu)^2$ against hν is shown in Fig 3. E_g was evaluated by extrapolation of the linear part [11]. The band gap is found to be 3.75 eV. As a consequence of wide band gap, the grown crystal has large transmittance in the visible region [12]. Figs 4 and 5 represent the dependence of extinction coefficient and refractive index on the wave length [13].

Fig.3 $(\alpha hu)^2$ vs hu

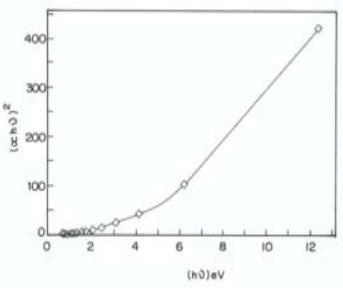


Fig.4 extinction coefficient vs wavelength

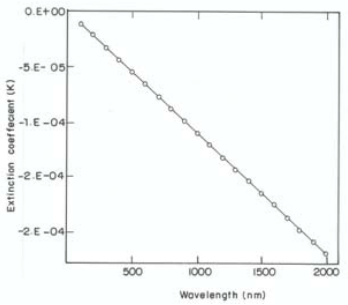
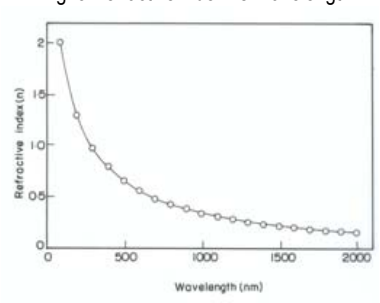


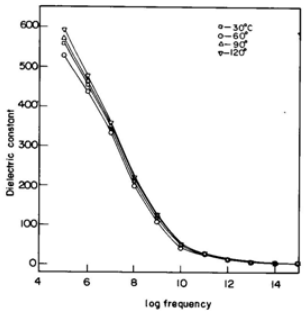
Fig. 5 Refractive index vs Wavelength



Dielectric studies

The dielectric constant of the LAA crystals was studied at different temperatures using HIOKI 3532 LCR HITESTER in the frequency region 50 Hz to 5 MHz. Fig.6 shows the plot of dielectric constant (ε_r) vs log frequency. The dielectric constant has high values in the lower frequency region and then decreases with the applied frequency. The very high value of ε_r at low frequencies may be due to the presence of all the four polarizations namely, space charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually. From the plot, it is also observed that dielectric constant increases with increasing temperature, attributed to space charge polarization near the grain boundary interfaces, which depends on the purity and perfection of the sample.

Fig.6.Dielectric constant vs. log f



Conclusion

Good quality single crystals of LAA were grown by slow evaporation technique. Single-crystal XRD analysis confirmed that the crystals belong to monoclinic system with the space group $P2_1$. Fundamental parameters like plasma energy, Penn gap, Fermi energy and electronic polarizability of the crystal have been calculated. The band gap energy for the grown crystal is found to be 3.75 eV. The optical investigations show a high value of both extinction coefficient (K) and refractive index (n) indicating high transparency of the crystal which confirms its suitability for optical switch device fabrications. The frequency dependence of dielectric constant decreases with increasing frequency at different temperatures.

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