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Growth, Optical, Theoretical and Dielectric Studies on L-valine Single Crystals

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Abstract: Single crystals of L-valine with very high 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, Fermienergy 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 was found to be 240 nm. The optical band gap is found to be 3.75 eV. The dielectric studied was carried out by room temperature.
Key words: Solution growth; Single crystal XRD; Optical transmission; Dielectric studies.

1. Introduction

The search for new materials with high optical nonlinearities is an important task because of their practical applications in harmonic generation, amplitude and phase modulation, laser technology, switching and other signal processing devices. Nonlinear optical (NLO) crystals find wide range of applications in the field of telecommunication for efficient signal processing and optical information storage devices. NLO crystals with high conversion efficiencies for second harmonic generation (SHG) and transparent in visible and ultraviolet ranges are required for various devices in the field of optoelectronics and photonics [1-3]. Within the last decade much progress has been made in the development of these NLO organic materials having large nonlinear optical coefficients. However, weak Van der Walls and hydrogen bonds with conjugated electrons constitute most of the organic NLO crystals. So they are soft in nature and difficult to polish and these materials also have intense absorption in UV region. In view of these problems, new types of hybrid NLO materials have been explored from organic-inorganic complexes with stronger ionic bond. Recent interest is centered on semi organic crystals, which have the combined properties of both inorganic and organic crystals. The present paper deals with characterization by single-crystal X-ray diffraction (XRD), UV analysis, and dielectric studies. Fundamental parameters like plasma energy, Penngap, Fermi energy and electronic polarizability of the crystal were calculated for the first time

2 Experimental

L-valine single crystals were grown from aqueous solution by slow evaporation technique using water as

a solvent. The starting material was synthesized by dissolving high purity L-valine (AR grade) in triple distilled water. After a period of three weeks, optically transparent defect free crystals were obtained from the mother solution as shown in Fig. 1.

Fig .1. Photograph of as-grown crystal of L-valine

Results and Discussion

3. 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= 9.701Å, b = 5.261 Å and c = 11.953 Å, α = γ = 90, and β = 90.66°, which is in agreement with that of reported values [4-5]. The molecular weight of the grown crystal is *M*=116.0 g, and total number of valance electron *Z*=48. The density of the grown crystal was found to be ρ=1.26 g.cm^{-3} and dielectric constant at 1 MHz is ε_∞ =113.5. The valence electron plasma energy, $\hbar\omega_P$ is

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

where Z = ((5 x Z_C) + (11 x Z_H) + (1 x Z_N) + (2 x Z_O) = 48 is the total number of valence electrons, ρ is the density and M is the molecular weight of the L-valine single crystal. The Plasma energy is terms of Penn gap and Fermi energy [6] as,

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

and

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

Polarizability, α is obtained using the relation [7]

$$\alpha = \left[\frac{\left(\hbar\omega_P\right)^2 S_0}{\left(\hbar\omega_P\right)^2 S_0 + 3E_P^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} cm^{-1} \qquad (4)$$

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

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

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

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

where the symbols have their usual significance. *N*a is Avagadro number and the calculated fundamental data on the grown crystal of L-valine are listed in Table1.

Table 1 Some theoretical data for L-valine single crystal

Parameters	Values
Plasma energy (eV)	15.02
Penn gab (eV)	1.42
Fermi gap (eV)	10.83
Polarizability(cm^3) Penn analysis	4.481 x 10^{-23}
Clausius-Mossotti Equation	4.913 x 10^{-23}

4. Optical transmission

Fig.2 shows optical transmission spectrum of 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. The optical absorption coefficient (α) was calculated using the following relation,

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right) \qquad (7)$$

where T is the transmittance and d is 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 (hν)

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

where E_g is the optical band gap of the crystal and A is a constant. The plot of $(\alpha h\nu)^2$ versus hν is shown in Figure 3. E_g was evaluated by the extrapolation of the linear part [10]. 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 [11].

5. Dielectric studies

Single crystals of L-valine of thickness 1 mm were subjected to dielectric studies at room temperature for various frequencies ranging from 100 Hz to 5 MHz using HIOKI 3532-50 LCR HITESTER. The dielectric constant is evaluated using the relation

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \qquad (9)$$

where d is the thickness and A is the area of the cross section of the grown crystal. The variation of dielectric constant as a function of frequency at room temperature is shown in figure 4. From the graph, the dielectric constant is seen to decrease with increase in frequency. The very low value of dielectric constant at higher frequencies is important for the fabrication of materials towards ferroelectric, photonic and electro-optic devices. The dielectric loss is also studied as a function of frequency at room temperature and is shown in Fig.5. These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of dielectric constant.

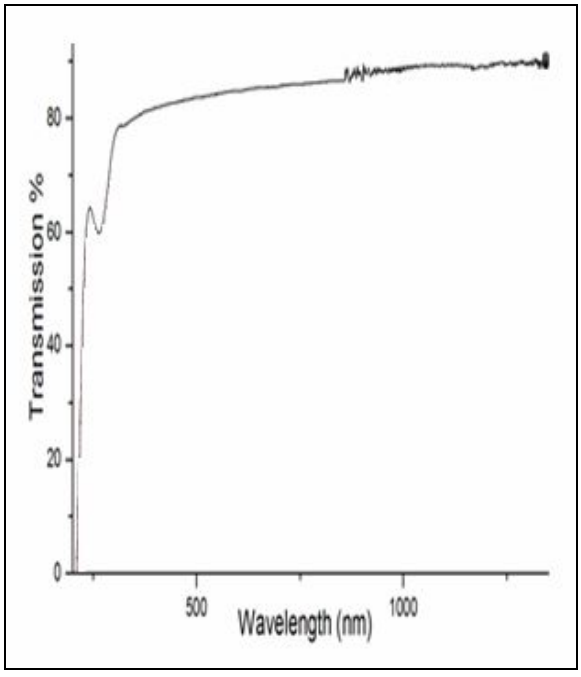

Fig.2. Optical transmittance spectrum of L-valine

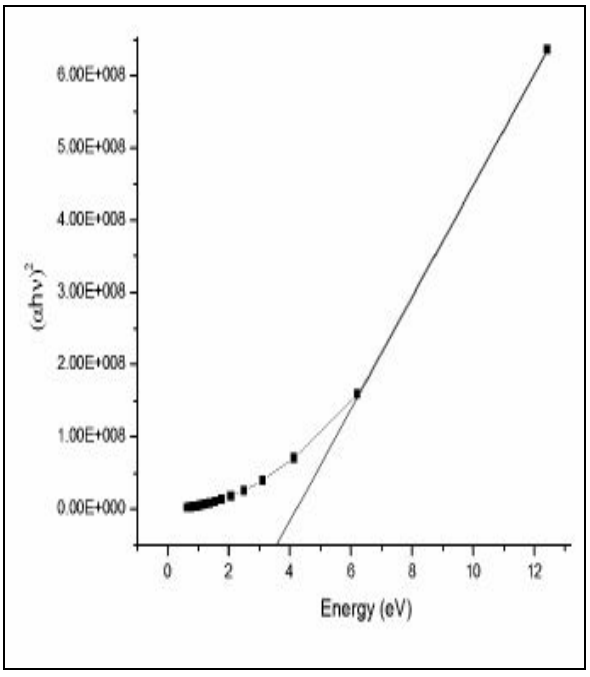

Fig.3. Spectral dependence hν vs $(\alpha h\nu)^2$

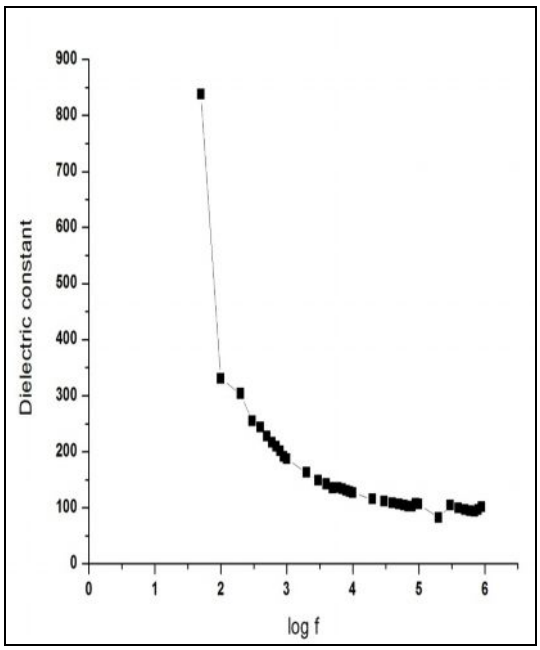

Fig.4. Dielectric constant vs log f

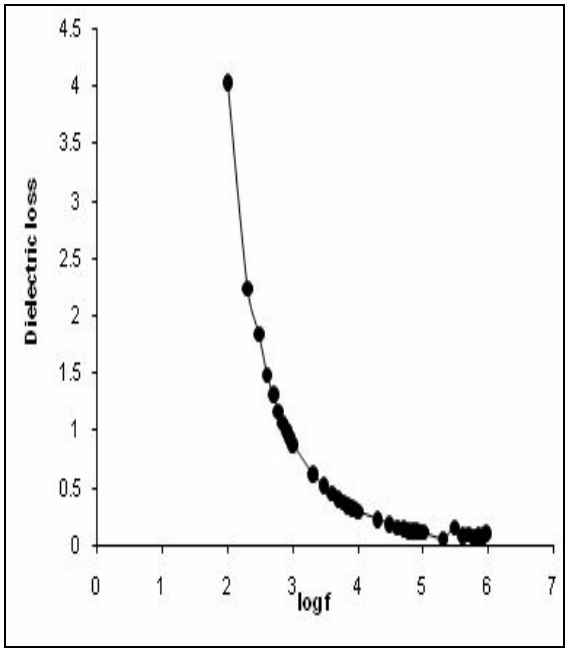

Fig.5. Dielectric loss vs log f

Conclusion

Good quality single crystals of L- valine were grown by slow evaporation technique. Single-crystal XRD analysis confirmed that the crystals belong to monoclinic system with the space group $P2_1$. The band gap energy for the grown crystal is found to be 3.75 eV. Fundamental parameters like plasma energy, Penn gap, Fermi energy and electronic polarizability of the crystal have been calculated. The variations of dielectric constant / dielectric loss of L-valine were studied with varying frequency at room temperature.

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