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Growth, Optical, and Dielectric Properties of N, N-dimethyl anilinium picrate NLO Single Crystals

S.Suresh[1]*, A.Ramanand[1], and D.Jayaraman[2]

[1]Department of Physics, Loyola College, Chennai- 600 034, India.

[2]Department of Physics, Loyola Institute of Technology, Chennai-602 103, India.

*Corres. author: sureshsagadevan@yahoo.co.in,
Contact number-+91-9841646040

Abstract: Single crystals of N, N-dimethyl anilinium picrate (DMAP) with good degree of transparency were grown from aqueous solution by slow evaporation technique. The crystalline nature of the material has been confirmed by powder X-ray diffraction method. 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 410 nm. The optical band gap is found to be 2.60 eV. The transmittance of DMAP crystal has been used to calculate the refractive index n, the extinction coefficient K and both the real ε_r and imaginary ε_i components of the dielectric constant as functions of wavelength. Dielectric constant and dielectric loss measurements were carried out at different temperatures and frequencies.
Key words: Solution growth, Powder XRD, Optical transmission, Dielectric studies.

1. INTRODUCTION

The research in the field of organic NLO materials has gained momentum in the recent past on account of their interesting nonlinear optical effects extended to optical parametric amplifiers, optical parametric oscillators, Qswitched optical applications, etc [1-5]. However, most of the organic NLO crystals are associated with poor mechanical strength and thermal stability [6,7]. An organic molecule should have high second order hyperpolarizability (β) to exhibit large NLO properties. The hyperpolarizability can be enhanced by increasing intramolecular charge transfer interaction by extending π-conjugated system [8]. The increase in conjugation length decreases the energy gap and narrows down the optical transparency window.

In the present investigation we report bulk growth, optical, and dielectric properties of N, N-dimethyl anilinium picrate single crystals.

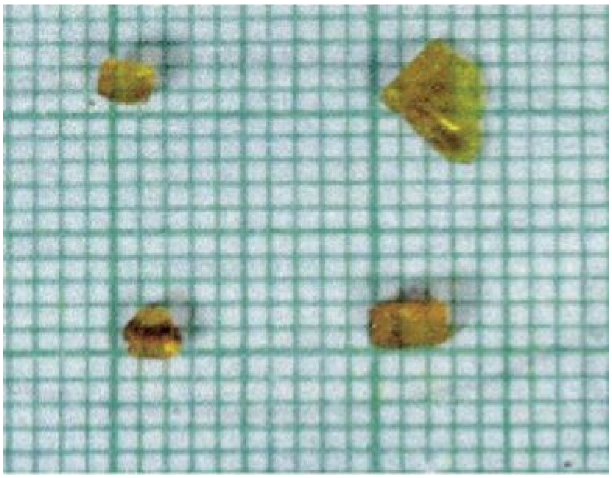

Fig. 1. As-grown single crystals of DMAP

2. EXPERIMENTAL PROCEDURE

A solution of DMAP in chloroform was prepared and stirred continuously using magnetic stirrer for homogenization and tiny seed crystals were obtained by spontaneous nucleation. Recrystallisation process was carried out two times and finally the crystals were obtained over a period of 35 days. DMAP with an average dimension 5 x 4 x 2 mm were obtained. The photograph of the crystals has been shown in figure 1.

3. RESULTS AND DISCUSSIONS

3.1 Powder X-ray diffraction

The recorded powder X-ray diffraction pattern of DMAP sample is shown in figure 2. The sharp and well defined Bragg peaks at specific 2θ angles testimonies the crystallinity of the material.

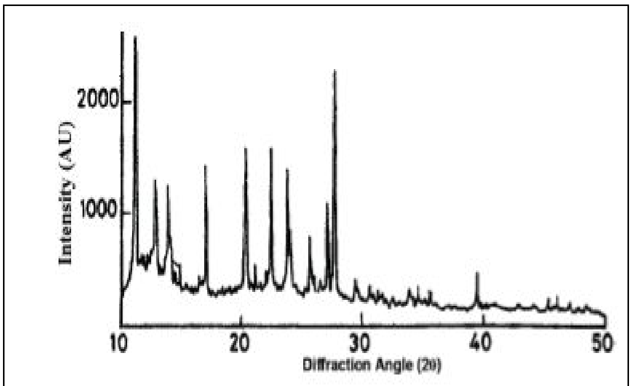

Fig.2 Powder XRD pattern of DMAP crystal

3.2 Optical Studies

The UV–Vis–NIR spectrum of DMAP was recorded with a Lambda 35 spectrophotometer in the range 300–1100 nm with a crystal of thickness 2 mm. From the spectra, it is evident that DMAP crystal has UV cut off below 410 nm, which is sufficient for SHG laser radiation of 1064nm or other application in the blue region. It further indicates that the crystal has wide transparency window between 300nm and 1100nm. The wide transparency in the entire visible region is one of the additional key requirements for having efficient NLO character [9].

The measured transmittance (T) was used to calculate the absorption coefficient (α) using the formula

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

where t is the thickness of the sample.

Optical band gap (E_g) was evaluated from the transmission spectra and optical absorption coefficient (α) near the absorption edge is given by [10]

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

where A is a constant, E_g the optical band gap, h the Planck constant and n the frequency of the incident photons. The band gap of DMAP crystal was estimated by plotting $(\alpha h\nu)^{1/2}$ versus $h\nu$ as shown in Fig. 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 2.60 eV.
Extinction coefficient (K) can be obtained from the following equation:

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

The transmittance (T) is given by [11]

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

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

Hence,

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

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

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

The refractive index (n) is 1.30 at λ =1100 nm.
From the optical constants, electric susceptibility (χ_c) can be calculated according to the following relation [12]

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \qquad (7)$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \qquad (8)$$

where ε_0 is the dielectric constant in the absence of any contribution from free carriers. The value of electric susceptibility χ_C is 0.0421 at λ =1100 nm. The real part dielectric constant ε_r and imaginary part dielectric constant ε_i can be calculated from the following relations [13]

$$\varepsilon_r = n^2 - k^2 \quad \& \quad \varepsilon_i = 2nk \qquad (9)$$

The value of real ε_r and ε_i imaginary dielectric constants at λ =1100 nm are 1.72 and 3.24 x 10^{-4}, respectively.

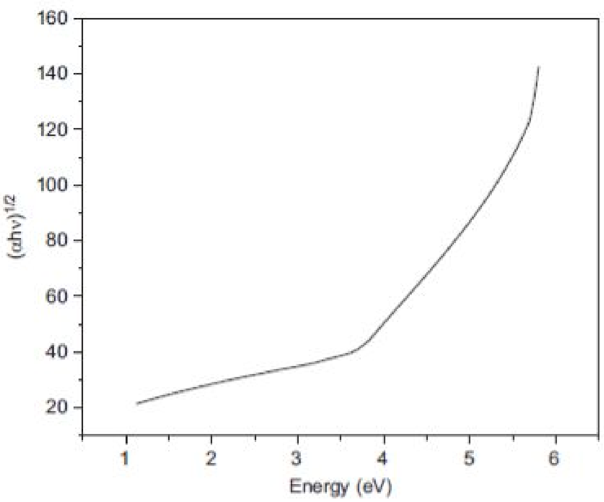

Fig. 3. Plot of $(\alpha h\nu)^{1/2}$ versus $h\nu$ for DMAP single crystal

3.4 Dielectric studies

The dielectric constant and the dielectric loss of the DMAP crystals were studied at different temperatures using a HIOKI 3532 LCR HITESTER in the frequency region from 50 Hz to 5 MHz. Fig. 4 shows the plot of dielectric constant versus log frequency. The high value of dielectric constant 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 [14]. From the plot, it is also observed that dielectric constant increases with an increase in temperature. The variation of dielectric loss with frequency is shown in Fig. 5. The characteristics of low dielectric loss with high frequency for the sample suggest that it possesses enhanced optical quality with lesser defects and this parameter is imperative for nonlinear optical applications [15].

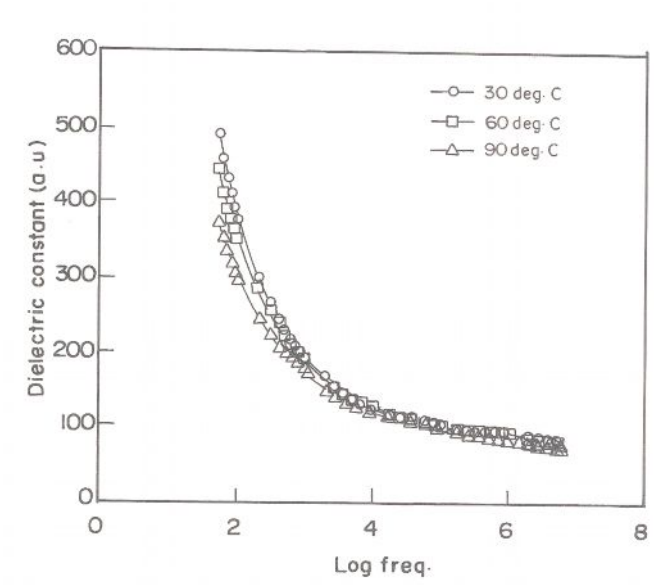

Fig. 4. Variation of dielectric constant with frequency

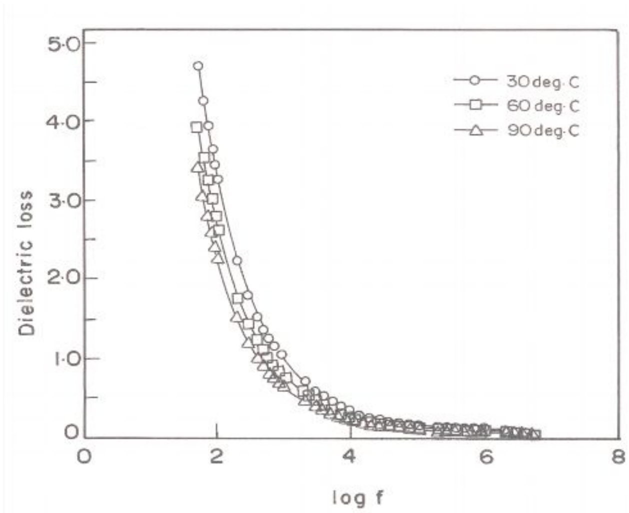

Fig. 5 Variation of dielectric loss with frequency

4. CONCLUSION

Good quality single crystals of DMAP were grown by slow evaporation technique. Optical band gap (E_g), absorption coefficient (α), extinction coefficient (K), refractive index (n), electric susceptibility χ_c and dielectric constants were calculated as a function of wavelength. The frequency dependence of dielectric constant decreases with increasing frequency at different temperatures.

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