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Third order optical studies on Sankaranarayanan–Ramasamy method grown Imidazole–Imidazolium Picrate monohydrate (IIP) organic crystals for Nonlinear optical applications

P.Vivek, P. Murugakoothan*

MRDL, PG and Research Department of Physics, Pachaiyappa's College, Chennai- 600 030, India.

***Corres.author: murugakoothan03@yahoo.co.in**

Abstract: Nonlinear optical bulk single crystal of Imidazole–imidazolium picrate monohydrate (IIP) has been grown by Sankaranarayanan–Ramasamy (SR) method. The single crystal X-ray diffraction study reveals orthorhombic crystal system. The third order nonlinear refractive index and nonlinear absorption coefficient were measured by Z-scan technique. The birefringence behaviour and second harmonic generation efficiency of grown crystal was measured.
Keywords: Third order optical studies, Sankaranarayanan–Ramasamy method, Imidazole–Imidazolium Picrate monohydrate (IIP), organic crystals, Nonlinear optical applications.

1. Introduction and Experimental Procedure

Organic nonlinear optical crystals play an important role in second-harmonic generation (SHG), frequency mixing, electro optic modulation, optical parametric oscillation etc [1]. IIP is one of the organic materials with a good nonlinear optical efficiency. The imidazole, an aromatic heterocyclic alkaloid is present in commercial pharmaceutical products as an antifungal agent. The asymmetric unit of IIP contains two imidazole molecules as cationic unit, one picrate ion and one molecule of water. The growth of good quality and large size NLO crystals with orientation control is needed for application. Hence, the IIP crystal was grown by SR method.

1.1 Unidirectional growth of IIP

The higher growth rate of (1 1 0) plane [2] was encouraged to grow a bulk size crystal using SR method. The supersaturated solution was prepared using acetonitrile solvent and slowly decanted into the ampoule without disturbing the seed crystal. The top of ring heater was controlled at 35 °C to increase the evaporation rate and the temperature around the growth region was controlled at 32 °C with ± 0.01 °C accuracy. The bulk crystal was grown with 46 mm length and 21 mm diameter after 32 days. The SR method grown IIP crystal is shown in figure 1.

Fig. 1 As grown IIP crystal

2. Results and Discussions

2.1 Single Crystal X- ray Diffraction

The single crystal XRD study reveals the title material belongs to orthorhombic crystal system with space group $P2_12_12_1$ and the unit cell parameters are, a = 3.818 Å , b = 20.816 Å , c = 21.442 Å and V = 1704.11 Å^3. This is found to be in good agreement with the reported value [2].

2.2 Z - Scan measurements

The Z-scan is a standard technique for accurate measurement of intensity dependent nonlinear susceptibilities, nonlinear refractive index (NLR), n_2 and nonlinear absorption coefficient (NLA), β. Figure 2 (a) illustrates the Z-scan data for closed aperture set up of IIP crystal. The peak followed by a valley transmittance is the signature for negative nonlinearity [3] and is known as the self- defocussing effect. This is due to the local variation of refractive index with temperature. Figure 2(b) depicts the open aperture curve of IIP single crystal. A typical Z-scan data with open aperture is insensitive to nonlinear refraction. Therefore, the data are expected to be symmetric with respect to focus. For materials with multi-photon absorption, there is a minimum transmittance in focus (valley) and for saturable absorber sample, there is a maximum transmittance in the focus (peak). Multi-photon absorption suppresses the peak and enhances the valley, while saturation produces the opposite effect [4]. The experimental observation shows a valley in the open aperture data which confirms the occurrence of multiphoton absorption in SR grown IIP single crystal.

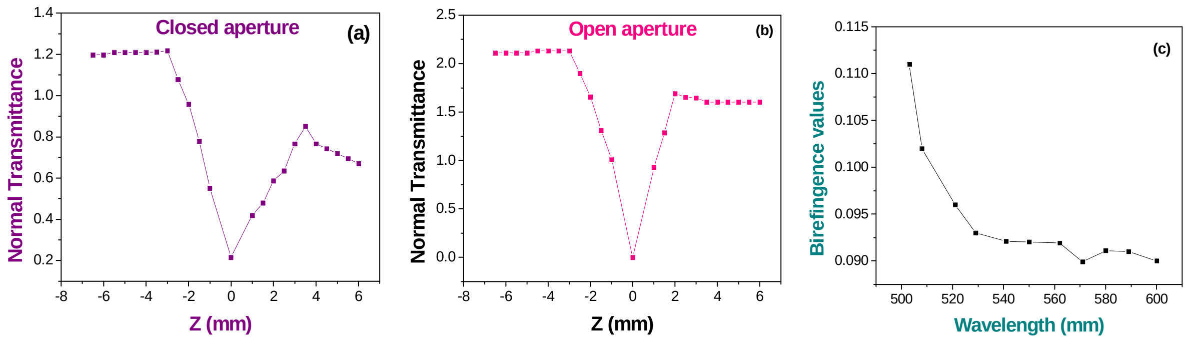

Fig. 2 Plot of (a) normal transmittance with closed aperture as a function of Z position,
(b) normal transmittance with open aperture as a function of Z position and
(c) dispersion of birefringence with wavelength of IIP crystal.

The measurable quantity ΔT_{p-v}, the difference between the peak and valley transmittances, T_p-T_v as a function of $|\Delta\varphi_0|$ is given by-

$$|\Delta\varphi_0| = \frac{\Delta T_{p-v}}{0.406(1-S)^{0.25}} \quad (1)$$

where, S is the aperture linear transmittance and $|\Delta\varphi_0|$ is the on axis phase shift.

$$S = 1 - \exp\left(\frac{-2{r_0}^2}{{\omega_0}^2}\right) \quad (2)$$

where, r_o is the aperture radius and ω_0 is the beam radius.

The on-axis phase shift is related to the third order nonlinear refractive index:

$$n_2 = \frac{\Delta\varphi_0\lambda}{2\pi I_0 L_{eff}} \quad (3)$$

$$L_{eff} = \left[\frac{(1 - \exp(-\alpha L))}{\alpha}\right] \quad (4)$$

where, L_{eff} is the effective thickness of the sample, α is the linear absorption coefficient, L is the thickness of the sample, I_0 is the on-axis irradiance at focus and n_2 is the nonlinear refractive index. From open aperture Z-scan data, the nonlinear absorption coefficient β was estimated.

$$\beta = \frac{2\sqrt{2}\Delta T}{I_0 L_{eff}} \quad (5)$$

The real and imaginary parts of the third order nonlinear optical susceptibility $\chi^{(3)}$ were determined from experimental determination of n_2 and β according to the following relations:

$$\mathrm{Re}\,\chi^{(3)} = 10^{-4}\,\frac{\varepsilon_0 C^2 {n_0}^2 n_2}{\pi} \quad (6)$$

$$\mathrm{Im}\,\chi^{(3)} = 10^{-2}\,\frac{\varepsilon_0 C^2 {n_0}^2 n_2 \lambda\beta}{4\pi^2} \quad (7)$$

The absolute value of $\chi^{(3)}$ was calculated from the following relation,

$$|\chi^{(3)}| = [(\mathrm{Re}(\chi^{(3)})^2 + (\mathrm{Im}(\chi^{(3)})^2]^2 \quad (8)$$

The estimated nonlinear refractive index (n_2), change in refractive index (Δn), absorption coefficient (β) and third order susceptibility ($\chi^{(3)}$) values of IIP crystal are *-3.906 X 10^{-6} cm^2/W, -1.34 X 10^{-3}, 0.0492 cm/W and 2.362 X 10^{-4} esu* respectively. The non-linear absorption is attributed to a multi-photon absorption process and the nonlinear refraction leads to the self-defocusing nature of the crystal.

2.3 Birefringence

Birefringence study was carried out on the SR grown IIP crystal with 0.2 mm thickness. The birefringence was calculated using the formula Δn = kλ/t, where 'λ' is the wavelength of the source used,'t' is the thickness of the specimen and 'k' is the fringe order. The recorded spectrum of birefringence vs. wavelength is shown in figure 2(c). From this measurement, the IIP possesses good birefringence values in visible wavelength region between *0.111 and 0.091*.

2.4 Nonlinear optical study

The second harmonic signal of 39 mV was obtained for IIP crystal, while the standard potassium dihydrogen phosphate (KDP) crystal gives a SHG signal of 11 mV for the same input energy. It shows that the SHG effective nonlinearity of IIP is 3.6 times that of standard NLO material KDP.

2.5 Conclusions

Unidirectional bulk single crystal of IIP was grown by SR method. Third order nonlinear optical studies showed that the IIP crystal has defocusing nature with nonlinear refractive index and nonlinear absorption coefficient. The birefringence value of IIP single crystal indicates good optical homogeneity. The powder SHG effective nonlinearity of this material is 3.6 times that of KDP. The promising crystal growth and characteristics of IIP crystal nominates it as a potential material for photonics, electro-optic and SHG device applications.

3. References

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