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INVESTIGATION –GROWTH-CHARACTERIZATION OF IMIDAZOLE-IMIDAZOLIUM PICRATE MONOHYDRATE

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Abstract *An organic nonlinear optical material Imidazole–imidazolium picrate monohydrate (IIP) was grown by the slow evaporation technique using water as a solvent. The structural, thermal, optical properties were studied for the grown crystal. Crystal parameters were determined using ENRAF NONIUS CAD 4 diffractometer. The FT-IR spectra was recorded on BRUKER IFS 66V FT-IR SPECTROMETER using KBr pellet in the range 4000 cm^{-1} to 500 cm^{-1} . The electronic band gap energy for the crystal was calculated to be 3.86 eV. The SHG efficiency of IIP is nearly 2.3 times more than that of KDP. The thermal stability of the crystal has been determined using TG/DTA studies.*

Key Words: IIP, FT-IR, SHG, UV, TG-DTA, KDP.

1. INTRODUCTION

Nonlinear optical (NLO) materials have attracted and are gaining enormous demand due to their wide applications in the recent technologies, like optoelectronics, lasers, data storage systems and optical communications. In addition to their large NLO response, the advantage of organic materials is that they offer high degree of synthetic flexibility to tailor their optical properties through structural modification and exhibit very high laser damage threshold [1, 2]. Organic nonlinear optical (NLO) materials formed from amino acids have potential applications in second harmonic generation (SHG), optical storage, optical communications, photonics, electro-optic modulation, etc.[3–5]. The applications of imidazole in medicinal chemistry or chemistry of natural products/alkaloids or of 1, 3-disubstituted imidazole salts as ionic liquids [6–8] are also well known. The imidazole, an aromatic heterocyclic alkaloids present in commercial pharmaceutical products as an anti-fungal agent. The asymmetric unit contains two imidazole molecules as cationic unit, one picrate ion and one molecule of water.

EXPERIMENTAL PROCEDURE

1.1 Synthesis and solubility

The starting material was synthesized from the AR Grade Imidazole and picric acid in the molar ratio 2:1 using water as the solvent. The solution is allowed to stir for 24 hours and the obtained solution is filtered and kept undisturbed in the room temperature. The solvents are allowed to evaporate into the atmosphere. The solubility data was determined by dissolving the synthesized salt of Imidazolium-Imidazole picrate monohydrate (IIP) in 100 ml of mixed solvent of distilled water and acetone at a constant temperature. The solubility of IIP increases with the temperature and thus exhibit positive solubility coefficient. Transparent tiny single crystals were obtained from the recrystallization salt in a time of about 50 days with the dimensions of about 8 x 4 x 7 mm^3 . The solubility curve is shown in figure 1. The as grown crystal photograph is shown in figure 2 . The crystal parameter is given in table 1.

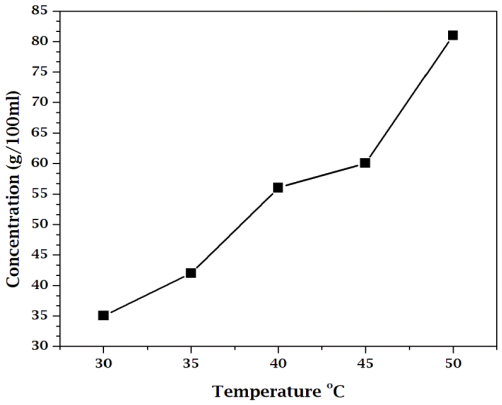

Figure 1: Solubility curve of IIP crystal

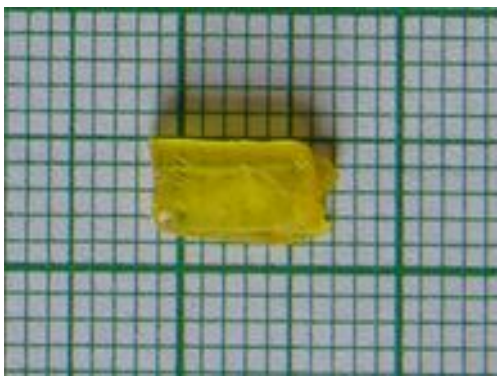

Figure 2: Photograph of as grown IIP single crystal

Table 1: crystal parameter of IIP single crystal

Empirical Formula	$C_{12}H_{13}N_7O_8$	
Formula weight	383.29	
Crystal system, Space group	orthorhombic, $P2_12_12_1$	
Unit cell dimensions	a =3.813Å b=20.807Å c=21.444Å	β=α=**γ** =90°
Cell volume	1701.304 Å^3	

2 .RESULTS AND DISCUSSION

2.1 Powder X-ray diffraction analysis

In the X-ray powder diffraction (PXRD) spectrum of the crystals, Rich Seifert and Co diffractometer with CuKα radiation is used to identify the structure of the title compound. From the results obtained it is found that IIP belongs to the orthorhombic system and the space group being $P2_12_12_1$. The recorded powder XRD pattern is given in Figure 3.

2.2 Vibrational analysis

BRUKER IFS 66V FT-IR SPECTROMETER using KBr pellet was recorded in the FT-IR spectra of IIP in the range 4000 cm^{-1} to 500 cm^{-1}

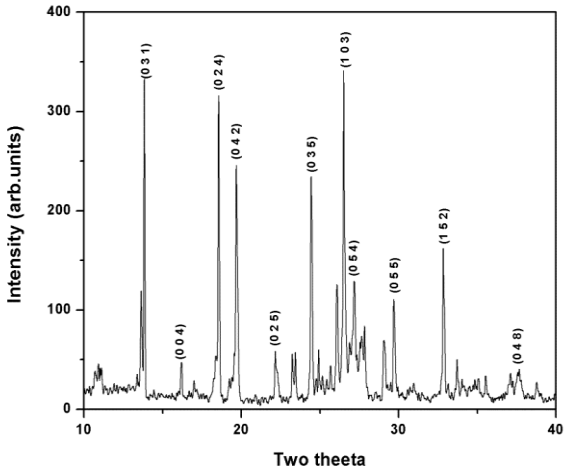

Figure 3: Powder XRD pattern of IIP single crystal

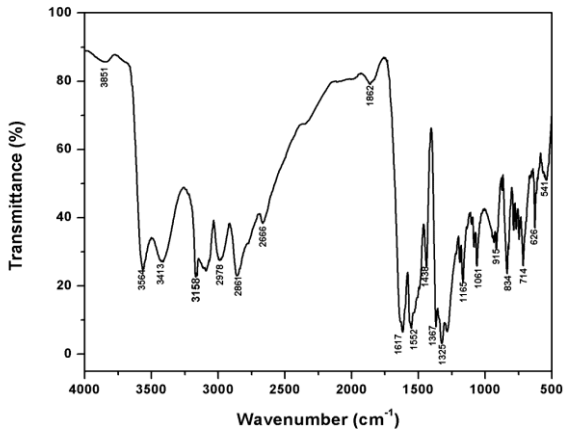

Figure 4: FT-IR spectrum of IIP

The observed FT-IR is shown in Figure 4. FT-IR experimental frequencies, reduced mass and force constant of IIP are shown in Table 2. The title molecule has 40 atoms. It has 114 normal vibrational modes. 77 of these modes are in-plane symmetric (A′) and 37 out-of-plane symmetric (A″) with respect to the reflection on the symmetry plane.

$$\Gamma_{N\text{-}6} = 77\ A' \text{ (in-plane)} + 37A'' \text{(out-of-plane)}$$

respectively

2.3 UV-Vis studies

Optical absorption spectrum of the title crystal was recorded using a UV–vis Spectrometer within visible range and the UV cut-off wavelength of IIP is found to be 231 nm The energy of the photon (hν) has been calculated for a range of wavelengths from 200 to 1100 nm. A graph was plotted between $(\alpha h\nu)^2$ and hν (Fig 6). The electronic band gap energy for the crystal was calculated to be 3.86 eV.

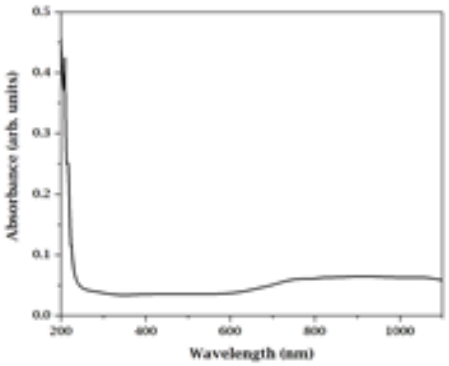

Figure 5: Optical Absorption spectrum of IIP

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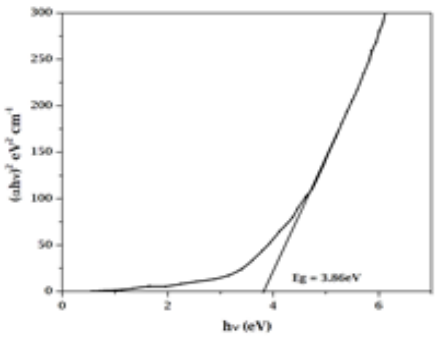

Figure 6: Energy band gap of IIP

2.4 SHG Studies

The SHG effective nonlinearity of IIP powder was determined using Kurtz and Perry powder technique. It enables to measure the SHG effective nonlinearity of new materials relative to standard potassium dihydrogen phosphate (KDP). A Q-switched Nd:YAG laser operating at 1064 nm and 8 ns pulse. For a laser input pulse of 5.6 mJ/pulse, SHG signals of 90 mV and 210 mV were obtained for KDP and IIP samples respectively. Hence, it is observed that the SHG efficiency of IIP is nearly 2.3 times more than that of KDP.

2.5 Thermal analysis

The thermal behavior of IIP was studied by Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) with the material mass of 22.26mg. The TGA and DTA of IIP were carried out using the instrument NETZSCH STA 409C from 100-900 °C in nitrogen atmosphere at the heating rate of of10 k/min. The TGA and DTA curves were recorded in the temperature range of 100–900°C. The crystal shows three stages of weight loss, the initial weight loss of 4.123% is attributed to adsorbed water. The first stage from 180°C to 320°C confirms the presence of lattice water molecules, the second and third stage attribute to 74.905%. A residue of 7.882% remains after 900°C.

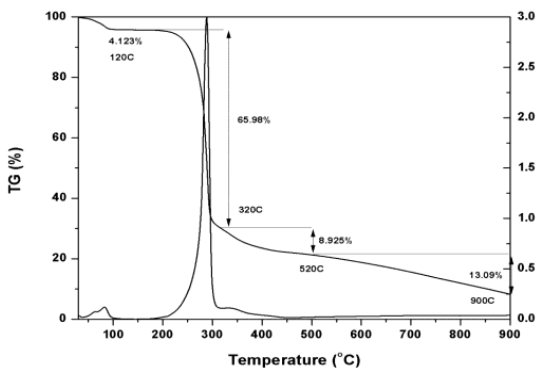

Figure 7: TG-DTA curves of IIP single crystal

3. Conclusion

Organic IIP single crystal of good quality was grown by slow evaporation technique. Powder XRD studies show that IIP crystals the grown crystal belongs to orthorhombic crystal system having non-Centro symmetry with $P2_12_12_1$ space group. DFT calculations give the minimum energy state for the IIP molecule. The presence of functional groups in the title compound was analyzed by FT-IR studies. First order hyperpolarizability of IIP is calculated as 4.4254 x 10^{-30}esu. The optical band gap of the material is found as 3.86 eV. Low dielectric constant and dielectric loss of IIP confirms the polarizing ability and hence NLO nature. From Thermal analysis it is found that the candidate material exhibits three stages of weight loss. Mechanical strength and SHG studies were carried out and the efficiency of the IIP crystal is found to be 2.3 times that of KDP crystal.

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