Optics and Laser Technology 109 (2019) 496–503

Contents lists available at ScienceDirect

Optics and Laser Technology

journal homepage: www.elsevier.com/locate/optlastec

Full length article

Structural, spectral, thermal, and optical studies of stilbazolium derivative crystal: (E)-4-(3-hydroxy-4-methoxystyryl)-1-methyl pyridinium iodide monohydrate

K. Nivetha, W. Madhuri*

Centre for Crystal Growth, Vellore Institute of Technology, Vellore 632014, Tamil Nadu, India

HIGHLIGHTS

- Stilbazolium derivative crystal HMSI was synthesized by Knoevenagel condensation.
- It is transparent in the entire visible region with a lower cutoff of 450 nm.
- The HMSI crystal exhibits strong RSA and self-focusing effect.
- Third-order nonlinear optical susceptibility was found to be 9.89 × 10^{-6} esu.

ARTICLE INFO

Keywords:
Slow evaporation
Optical material
Stilbazolium derivative
Z-scan

ABSTRACT

In the current research, (E)-4-(3-hydroxy-4-methoxystyryl)-1-methyl pyridinium iodide monohydrate (HMSI) has been prepared through Knoevenagel condensation and crystallized by slow evaporation technique. Crystallographic analysis has been carried out to study the crystal structure and unit cell parameters. The fundamental vibration frequencies of specific chemical functional groups were detected by infrared absorption spectrum. Further the molecular structure of the grown crystal was confirmed by nuclear magnetic resonance spectroscopic analysis. Thermal stability (145 °C) and meting point (248 °C) of the HMSI material have been elaborated by means of thermogravimetric and differential scanning calorimetric (TG/DSC) analysis. The crystal was found to be transparent above 460 nm with the band gap of 2.63 eV obtained from transmission spectral analysis. The growth features of HMSI crystal were examined to check for the defects using an optical microscope. Crystal surface damage by Nd: YAG laser at 1.064 μm radiation was measured to be 1.98 GW/cm^2. Further, the nonlinear response of HMSI has been studied using Z-scan technique and it was found that the title crystal is capable of exhibiting self-focusing nature with reverse saturable absorption. The evaluated nonlinear susceptibility is in the order of 10^{-6} esu which is slightly higher compared to other third-order stilbazolium derivative crystals.

1. Introduction

The scientific and technological development has led to many significant functions for humanity, in which electronic, magnetic and optical ones are the essential requirements of our everyday lives. The intense research on crystal growth in organic crystals is of great importance for its use in electro-optical and nonlinear optical (NLO) devices [1]. Therefore, most of the research has been concentrated on finding crystalline organic materials consisting of molecules of stable chromophores with optimized orientation for large macroscopic NLO effects. Compared to inorganic materials, organic materials exhibit superior second and third order NLO properties, fast optical response, large nonlinear susceptibility, high chromophore density and ease of processability [2–5]. Generally, organic molecules have a donor-π-acceptor (D-π-A) architecture that exhibits a high degree of electron delocalization and substantial intramolecular charge transfer (ICT) [6]. This makes organic materials extremely attractive for various applications such as optical signal processing, optical switching, color displays, organic super conductors, etc. [7,8]. Materials that exhibit fast third-order NLO responses are of current interest, because they can be used to construct holographic memory devices, optical switching and limiting of laser pulses in the latest optical technology [9]. Since these processes

* Corresponding author.
E-mail address: madhuriw12@gmail.com (W. Madhuri).

https://doi.org/10.1016/j.optlastec.2018.08.035
Received 3 April 2018; Received in revised form 23 July 2018; Accepted 14 August 2018

can be promoted by the nonlinearity of the refractive index or by a change of absorption coefficient which is related to the real and imaginary parts of the third-order NLO susceptibility [10].

Stilbazolium derivatives are considered as promising materials for NLO, since they have a conjugated D-π-A structure, which generates a strong delocalization of electronic charge with the existence of hydrogen bonds. One of the main features of stilbazolium derivatives is the strong ICT transition that makes it a competitive candidate of organic NLO materials and provides high optical nonlinearities. Because of these significant properties, stilbazolium derivatives find many applications in various fields such as frequency conversion, electro-optic modulation, Terahertz (THz) detection and generation and photonics new technologies [11–14]. The main source of nonlinear is the stilbazolium cation, which is the most attractive chromophore; and by changing the substituents on the counter anion the nonlinear optical susceptibility and crystal structure of stilbazolium salts can be altered [15,16]. By this approach, many stilbazolium derivatives have been extensively studied on the basis of strong Coulombic interaction for its second order nonlinearity such as 4-N,N-dimethylamino-4′-N′-methyl-stilbazolium tosylate (DAST) [17], 4-N,N-dimethylamino-4′-N′-methyl-stilbazolium 2-naphthalenesulfonate (DSNS) [18], 4-N,N-dimethylamino- 4′-N′-methyl-stilbazolium 2,4,6-trimethyl benzenesulfonate (DSTMS) [15] and so on. However the strong Coulombic interaction in organic molecules can override the dipole-dipole interactions that favor centrosymmetric molecular packing. Recent researches have shown that stilbazolium derivatives with π-conjugate system exhibit third-order nonlinearity due to intramolecular charge-transfer (ICT) transition [19–23].

Considering the NLO properties of stilbazolium derivatives, a successful attempt has been made to grow stilbazolium derivative single crystal, (E)-4-(3-hydroxy-4-methoxystyryl)-1-methyl pyridinium iodide monohydrate (HMSI) by slow evaporation technique. Though the crystal structure of HMSI has been reported by Suchada Chantrapromma et al. [24], there is no report on the growth of this material for vital technological applications. In continuation with that, we present our results on growth, spectral, thermal, optical, etching and laser damage threshold studies of HMSI crystal. Since the crystal structure of HMSI has been identified as a $P2_1/c$ centrosymmetric space group [24], we have aimed to study the third-order NLO properties of the grown crystal. As far as we know, the studies mentioned here have been reported for the first time.

2. Experimental

2.1. Material synthesis

All reagents and solvents were commercially obtained and used as received. HMSI was synthesized by reacting equimolar amounts of 1,4-dimethyl pyridinium iodide (4.7 g, 20 mmol) and 3-hydroxy 4-methoxy benzaldehyde (3.0 g, 20 mmol) with piperidine catalyst in methanol solvent (15 mL) under reflux for 3 h (Knoevenagel condensation). The reaction scheme for HMSI is shown in Fig. 1. The mixture was cooled to room temperature and filtered for removal of a fine red solid, treated with a small amount of diethyl ether to wash out the unreacted impurities and dried. Then, the HMSI growth material of high purity was obtained by successive recrystallization from methanol to give the product in 79% yield.

2.2. Solubility, crystal growth and morphology

For device applications, a crystal of good quality and reasonable size is required. Single crystals of good quality can be grown by optimizing the conditions of growth using an appropriate solvent. Measurement of solubility provides information on the nucleation and the availability of solute material for the growth process. The solubility of HMSI material in single solvents such as ethanol, methanol, acetone and solvent mixtures such as methanol: acetone, methanol: chloroform, acetonitrile: ethanol and methanol: acetonitrile have been studied. Interestingly, the HMSI material exhibits an enhanced solubility in the mixed solvent of methanol: acetonitrile in a ratio of 1:1 compared to both single solvents and other solvent mixtures. The solubility study of HMSI was carried out in the temperature range between 30 and 45 °C in steps of 5 °C using a constant temperature bath with a control accuracy of ± 0.01 °C. The saturated solution was prepared by dissolving an appropriate amount of the purified salt in a mixture of methanol and acetonitrile with effective stirring in an airtight container at 30 °C. When saturation is reached, the concentration of the solute has been analyzed gravimetrically. The same procedure was adopted to determine the concentration of the solute for other temperatures of 35, 40 and 45 °C. The solubility increases almost linearly as the temperature increases and this indicates that the material has positive solubility gradient shown in Fig. 2.

The saturated solution was prepared at 35 °C according to the determined solubility data and stirred well for about 3 h to obtain a homogeneous mixture. It was then filtered, covered with an aluminum foil and perforations made uniformly to facilitate slow evaporation. The solution of HMSI was then housed in a dust-free ambience in constant temperature bath (accuracy ± 0.01 °C) at 35 °C and allowed it to crystallize. The grown HMSI crystal of dimension up to $9 \times 7 \times 2\,mm^3$ was obtained over a growth period of 30 days shown in Fig. 3a.

The morphology of a crystal depends on its chemical composition, structure and conditions of growth. The morphology of HMSI crystal was generated from Crystallographic Information File (CIF) as an input by WinXMorph software [25]. HMSI possesses nine well-developed faces (Fig. 3b) (1 0 −1), (1 0 0), (1 1 0), (0 −1 0), (0 0 1), (0 0 −1), (0 1 0), (−1 0 0) and (−1 0 1), of which faces of (0 1 0) and (0 −1 0) are more prominent. The major growth rate is identified along the '*a*' axis, which is the largest size, the shortest growth dimension is along the '*b*' axis, which is the largest unit cell axis. All characterizations were performed on (0 1 0) plane.

2.3. Characterization details

Structural examination of HMSI were performed employing a Bruker Kappa APEXII diffractometer equipped with Mo Kα radiation (λ = 0.71073 Å) at 293 K. The FTIR spectrum of HMSI was obtained from KBr pellet method in the vibrational absorption region of 4000–400 cm^{-1} on a Shimadzu IRAffinity spectrometer. The 400 MHz ^1H NMR spectrum was obtained using BRUKER FT-NMR spectrometer by dissolving the finely crushed HMSI crystal in DMSO-d_6 solvent. The powder sample of HMSI was scanned to record the thermogravimetric and differential scanning calorimetric analysis (TG/DSC) in nitrogen atmosphere with the temperature programmed from 35 to 700 °C using SDT Q600 thermal analyzer, regulated at a scanning rate of 20 °C/min. ELICO SL 218 double beam UV–Vis-NIR spectrometer was employed to record the optical transmittance spectrum of HMSI crystal with a thickness of about 1.2 mm in the spectral range of 200–800 nm. LDT measurements were carried out for HMSI crystal adopting Nd: YAG laser system (wavelength 1.064 μm, pulse width 10 ns, repetition rate 10 Hz). The third order nonlinearity of HMSI crystal was analysed by the Z-scan technique adopting 6328 Å continuous wave (CW) He-Ne laser. Etching study was performed on a crack free surface of HMSI crystak and their microstructures were analysed using a Carl Zeiss Optical Microscope with a 50X magnification.

3. Results and discussion

3.1. Crystal structure analysis

The analysis inferred that HMSI crystallizes in the monoclinic structure belonging to the space group $P2_1/c$ with corresponding cell parameters a = 8.1776 (1) Å, b = 17.9498 (2) Å, c = 10.3973 (1) Å,