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Synthesis, nucleation, growth, structural, spectral, thermal, linear and nonlinear optical studies of novel organic NLO crystal: 4-fluoro 4-nitrostilbene (FONS)

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HIGHLIGHTS

G R A P H I C A L A B S T R A C T

- A novel organic nonlinear optical material FONS has been synthesized.
 The good optical quality single
- ► The good optical quality single crystals were grown by slow evaporation method.
- The FONS crystal has a wide transparency in the range of 408– 1100 nm.
- ► Optical band gap (*E_g*) of the grown crystal is 3.27 eV.
- The PL measurements show that the material is suitable for green light emission.

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ABSTRACT

A novel organic nonlinear optical material 4-fluoro 4-nitrostilbene (FONS), with molecular formula $(C_{14}H_{10}FNO_2)$ has been synthesized. Using ethyl methyl ketone as solvent, the synthesized material has been repeatedly recrystallized to minimize the impurities and good optical quality single crystals were harvested by slow evaporation method. Single crystal X-ray diffraction analysis reveals that the grown FONS crystal belongs to monoclinic system with noncentrosymmetric space group "P2₁". The powder X-ray diffraction pattern of FONS has been recorded. Functional groups of the title compound were confirmed by FTIR and the molecular structure was confirmed by ¹H NMR. The UV-vis–NIR absorption study reveals no absorption in the visible region and the cut-off wavelength was found to be at 408 nm. Optical band gap (E_g) of the grown crystal was found to be 3.27 eV and also the optical constants were determined. Thermal behaviour of FONS has been studied by TGA/DTA analyses. From the mass spectrum, the ratio of compound formation of FONS was analyzed. The NLO property has been confirmed by Kurtz and Perry powder SHG technique and the SHG efficiency of FONS (262 mV) crystal was found to be 12 times greater than that of KDP (21.7 mV).

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Introduction

Recently significant research interest has been devoted on nonlinear optical (NLO) materials due to their remarkable contribution in the field of photonics and optoelectronics [1]. Among various NLO materials, organic materials have much more attention for their large electro optic coefficient and higher second order hyperpolarizabilities $\chi^{(2)}$. In this view, many researchers have spent their greater effort to develop the higher order nonlinear organic materials, leading to the discovery of DAST, DSNS and MMONS [2–4]. Among these materials, 3-methyl 4-methoxy 4-nitrostilbene (MMONS) crystal has large electro optic coefficients with r_{33} = 39.9 pm/V (0.6328 µm) and large nonlinear optical coefficients with d_{33} = 184 pm/V and d_{24} = 71 pm/V (1.064 µm) [5]. Optimizing the MMONS crystal is a good attempt to discover new derivative organic nonlinear optical crystals with high NLO efficiency. We have extended our optimization in

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synthesizing 4-fluoro 4-nitrostilbene (FONS) which is a new derivative of Stilbene family with good NLO efficiency. In FONS molecule a strong electron donor (fluoro group) was present on one end and an acceptor (nitro group) on the other end of the π conjugated structure which enhance the optical nonlinearity of the crystal. To our best knowledge, no work has been reported on FONS crystal in the literature till date. In this present communication, we report a novel organic nonlinear optical single crystal of FONS for the first time. The grown crystals were subjected to various characterization studies and the results are discussed in detail in the following sections.

Experimental

Material synthesis

The FONS ($C_{14}H_{10}FNO_2$) material was prepared by the addition of high purity diethyl p-nitrobenzyl phosphonate ($C_{11}H_{16}NO_4P$), 4-fluoro benzaldehyde (C_7H_5FO) and sodium ethoxide (C_2H_5ONa) in equimolar ratio. The mixture was dissolved in 35 ml of ethanol and kept inside the ultra cryostat water bath and stirred for 12 h at 0 °C [6]. The ethanol was removed by filtration and the resulting green coloured FONS were dried and the powdered material was collected after one day. The FONS material was 10 times recrystallized for purification. The reaction mechanism is as follows (Scheme 1).

Solubility and metastable zone width measurements

The solubility and metastable zone width studies were carried out using a constant temperature water bath of cryostat facility with accuracy ±0.01 °C. The solubility of FONS was determined in EMK at six different temperatures, i.e., 20 °C, 25 °C, 30 °C, 35 °C, 40 °C and 45 °C. The solubility was measured by adding the excess amount of solute in EMK at constant temperature with continuous stirring to attain homogeneous concentration. The saturated solution was analyzed gravimetrically. Using conventional polythermal method, the metastable zone width was determined by preparing the saturated solution according to the solubility data for the same temperature. The metastable zone width was determined for different temperatures (20-45 °C) with interval of 5 °C. The solubility and metastable zone width are shown in Fig. 1. The saturated solution (50 ml) of recrystallized material of FONS was prepared at 25 °C and taken in a completely closed beaker in order to control the solvent evaporation rate and kept for crystallization. After 5 days good optical quality crystals have been harvested and shown in Fig. 2.

Instruments for characterization

The grown FONS crystal was subjected to single crystal XRD and powder X-ray diffraction analyses using a NONIUS CAD4/MACH3



Fig. 1. Metastable zone width for FONS.



Fig. 2. Grown FONS crystals.

diffractometer and BRUKER X-ray diffractometer with Cu K α (λ = 1.5406 Å) respectively. The FTIR spectrum of FONS sample was recorded in the KBr pellet phase using SHIMADZU IRAFFINITY spectrometer in the region of 4000–400 cm⁻¹. Proton NMR spectrum was recorded using a BRUKER Spect instrument operating at 400 MHz with CDCl₃ as solvent to confirm the molecular structure of the grown FONS crystal. Optical behaviour of FONS was measured by ELICO SL 218 double beam spectrophotometer in the range of 190–1100 nm. Thermal behaviour of FONS was observed by TG–DTA curve using thermally analyzed TA Instruments SBT Q600 apparatus in a nitrogen atmosphere. Mass spectral analysis was carried out using JEOL GCMATE II GC–MS high resolution



Scheme 1. Synthesis of FONS material.



Fig. 3. Powder X-ray diffraction pattern of FONS.

double focusing instrument. The photoluminescence spectrum of FONS crystal was recorded using a Jobin Yvon-Spex spectrofluorometer and 450 W high pressure xenon lamps was used as an excitation source. The NLO property of the grown crystal was confirmed by Kurtz-Perry powder technique. The green light (532 nm) emission was collected by a photomultiplier tube (PMT Philips Photonics) after being monochromated (Coherent Molectron, USA 2000). The cathode ray oscilloscope (CRO) converts the incident optical signal to output voltage. The input laser energy of 2.4 mJ/ pulse was incident on the powdered sample. SEM and EDAX analyses were carried out using Quanta 200 FEG scanning electron microscope.

Results and discussion

Single crystal X-ray diffraction

The single crystal X-ray diffraction reveals that the crystal belongs to monoclinic crystal system with noncentrosymmetric space group *P*2₁, the unit cell parameters are a = 9.494(4) Å, b = 9.864(2) Å, c = 19.501(7) Å, $\alpha = \gamma = 90.00(0)^{\circ}$, $\beta = 100.96(2)^{\circ}$,

volume = 1793(1)Å³. The FONS crystal system satisfies one of the very essential and basic requirements for the SHG activity.

Powder X-ray diffraction analysis

Finely powdered sample of FONS was subjected to powder Xray diffraction analysis. The powder XRD spectrum was recorded at room temperature in step size 0.02° for the angular range 10- 35° of 2θ using Cu K α radiation (1.5406 Å). The reflections reveal the good crystallinity of the grown FONS crystal. Using TEROR program the lattice parameters were calculated and show good agreement with single crystal XRD results. The prominent peaks were indexed by using APPLEMAN program. The indexed powder XRD pattern is shown in Fig. 3.

Fourier transform infrared spectroscopy (FTIR) analysis

The Fourier transform infrared (FTIR) spectrum of the synthesized FONS material was recorded at room temperature in the range of 4000–400 cm⁻¹ and it is shown in Fig. 4. The peak observed at 1631.78 cm⁻¹ is due to the C=C stretching vibrations in the aromatic ring. A nitro symmetric stretching vibration (C–NO₂) can be attributed to the peak at 1502.55 cm⁻¹. The peak at 748.38 cm⁻¹ is assigned for C–F stretching vibrations. The aromatic C–H stretching vibration is confirmed by the presence of peaks at 3076.49 and 3107.32 cm⁻¹ [7].

SEM and EDAX analyses

The grown FONS crystal was subjected to scanning electron microscope and energy dispersive X-ray analyses to determine the surface morphology and elemental composition of the sample respectively. From the SEM analysis, it is observed that the microcrystals appeared on the grown surface and it is shown in Fig 5a. EDAX study confirms the elemental compounds of FONS such as carbon, oxygen, nitrogen and fluorine and it is shown in Fig. 5b.

Proton NMR analysis

Proton NMR spectrum was recorded for the FONS sample by dissolving it in CDCl₃. The signals at 8.230 ppm and 8.224 ppm (2H, doublet) are due to the vinylic protons in the structure. The aromatic protons produce signals around 7.058–7.656 ppm (8H,



Fig. 4. FTIR spectrum of FONS.



Fig. 5. (a) Scanning electron microscope (SEM) image (b) EDAX analysis.



Fig. 6. H¹NMR spectrum of FONS.

doublet). Thus the structure of the title compound was confirmed by the proton NMR spectral analysis. The 1 H NMR spectrum of FONS is shown in Fig. 6.

and the UV cut off wavelength was found to be at 408 nm [8]. The grown crystals band gap and large transmittance in the visible and NIR regions are shown in Fig. 7a. Thus it was confirmed that the material is good NLO candidate for optoelectronic applications.

UV-vis NIR absorbance spectral analysis

The optical behaviour of FONS crystal (1.5 mm thickness) was estimated by recording the UV-vis absorption spectrum (Fig. 7)

Determination of optical constants

From the optical transmittance (Fig. 7b) of grown FONS crystal it is very clear that the grown crystal has higher transparency



Fig. 7. (a) Absorption spectrum. (b) Transmittance spectrum.



Fig. 8. Plot of band gap $(\alpha hv)^2$ vs hv (eV).

(about 95%) in the entire visible region. The absorption coefficient (α) was calculated from the transmittance data (*T*) using the relation.

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

where *T* is the transmittance and *t* is the thickness of the sample. The optical band gap of FONS crystal was evaluated from the transmittance data (*T*) and absorption coefficient (α) near the absorption edge is given by [9]:

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

where *A* is a constant, *h* is Planck's constant, E_g is the optical band gap and *v* the frequency of the incident photons. The band gap of FONS crystal was estimated by plotting $(\alpha hv)^2$ vs *hv* and extrapolating the linear portion of $(\alpha hv)^2$ near onset of the absorption edge to the photon energy axis. Fig. 8. From the plot, it is found that the energy band gap of the grown FONS crystal is 3.27 eV. Extinction coefficient (*K*) of the FONS was calculated using the formula [10].

$$K = \frac{\lambda \alpha}{4\pi} \tag{3}$$











Fig. 11. Thermal analysis of FONS.





Fig. 13. Emission spectrum of FONS.

The spectrum of extinction coefficient as function of wavelength is shown in Fig. 9.

The K value is strongly dependent on the wavelength in the visible region. The extinction coefficient gives the fraction of the light lost due to the scattering and absorption per unit thickness in a sample medium. The variation K with wavelength values due to the interaction occurred between incident light and electrons. From the spectrum it is evident that the there is no loss near the wavelength of 430 nm. The transmittance (T) is given by:

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

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

Hence.

$$R = \frac{1 \pm \sqrt{(1 - \exp(-\alpha t) + \exp(\alpha t))}}{1 + \exp(-\alpha t)}$$
(5)

The wavelength dependent reflectance of FONS is shown in Fig. 10 in the range of 380–1100 nm. The reflectance of FONS decreases with increase of wavelength then becomes constant. The low reflectance shows the higher transmittance of the grown FONS crystal.

Thermal analysis

Thermal behaviour of the grown FONS crystal was obtained from the Thermograviometric (TG) and differential thermal (DTA) analyses and the resultant spectrum is shown in Fig. 11. From DTA curve, the first sharp endothermic peak at 140.33 °C indicates the melting point of the grown FONS crystal. The broad second peak at 334.47 °C was observed due to decomposition of the material. No exothermic and endothermic peaks were observed before the melting point, which shows that there is no decomposition and phase transition occurred up to the melting point [11]. Sharpness of the endothermic peaks indicates the good crystalline nature of the sample. The two exothermic peaks were observed at 367.81 °C and 510.46 °C. From TA curve, the fluorine atom eliminates at 220 °C and small weight loss (6.7%) occurred. From the analysis, it is clear that the material is stable up to 239.73 °C, after which major weight loss occurred and remained as a residue at 360.64 °C.

Mass spectral analysis

Mass spectroscopy analysis was carried out for FONS crystal to confirm the exact molecular mass. The peak at 243.0696 (m/z) indicates the presence of the 4-fluoro 4-nitrostilbene. The peak at 94.9584 (m/z) is due to the fragmentation of NO₂ group with aromatic ring. The loss of fluorine ion from the aromatic ring in the parent compound is assigned at 123.9439 (m/z) [12]. The recorded spectrum is shown in Fig. 12.

Photoluminescence studies

The photoluminescence emission spectrum was acquired at room temperature for the excitation wavelength of 350 nm in solid phase and a spectral resolution of 0.2 nm. The recorded emission spectrum is shown in Fig. 13. The high luminescence intensity (4113326.05 a.u) peak is observed at 527.05 nm. Using the conversion, wavelength to energy relation $E_g = (1.24/\lambda)$ eV, the band gap energy was calculated, where λ is the wavelength of fluorescence. The energy band gap of the FONS was calculated to be 2.354 eV. From the wavelength (527.05 nm) it is concluded that the FONS emits green fluorescence [13], which suggest that it is an excellent candidate for nonlinear optical applications and also it can be used as a good scintillator.

Second harmonic generation (SHG) efficiency measurement

The SHG efficiency of the grown FONS crystal was confirmed by Kurtz-Perry powder technique. The grown crystal was finely powdered and filled in the capillary tube which is illuminated by Qswitched Nd:YAG laser emitting a fundamental wavelength (1064 nm) [14]. The powdered sample of standard KDP was taken as a reference material. The output of FONS is 262 mV for the input energy 2.4 mJ/pulse while KDP gives 21.7 mV for the same input energy and hence the measured SHG efficiency of FONS crystal is ~12 times greater than that of KDP.

Conclusion

An organic nonlinear optical material FONS was synthesized and good optical quality single crystals were grown from EMK by slow evaporation method. The crystalline nature and structure was confirmed by X-ray diffraction analysis. Functional groups and molecular structure of the FONS crystal have been confirmed by FTIR and ¹H NMR spectral analyses respectively. The FONS crystal is highly transparent in the visible and IR regions with low cut off wavelength at 408 nm. The optical constants of the FONS crystals were determined. From the thermal analysis it was found that the material is stable up to 239.73 °C and the melting point is 140.33 °C. The obtained photoluminescence spectrum indicates that the material has green light emission at 527 nm. The SHG efficiency of FONS is 12 times greater than that of KDP and it shows that the crystal is very promising NLO material for frequency doubling and other optoelectronic applications.

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