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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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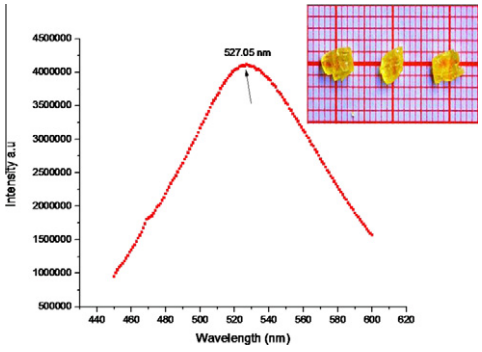
HIGHLIGHTS

- A novel organic nonlinear optical material FONS has been synthesized.
- 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.

GRAPHICAL ABSTRACT



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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 "$P2_1$". 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 ^{1}H 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 the 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).

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 diffractometer and BRUKER X-ray diffractometer with Cu Kα (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 $CDCl_3$ 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

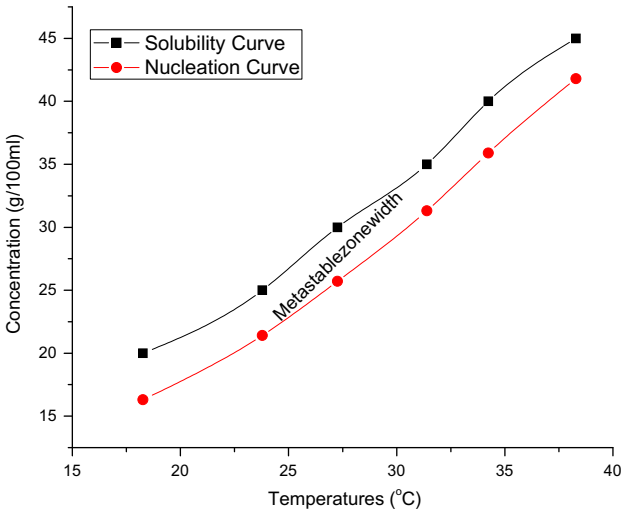


Fig. 1. Metastable zone width for FONS.

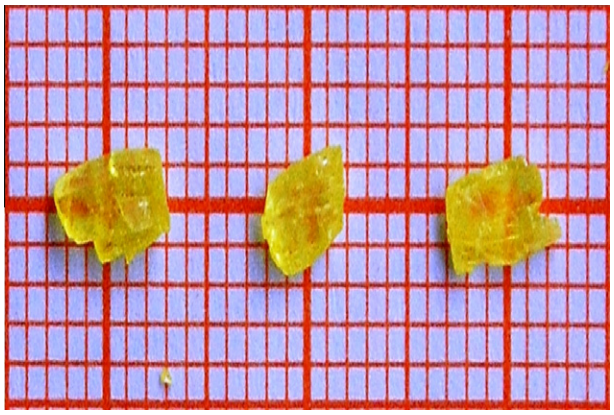
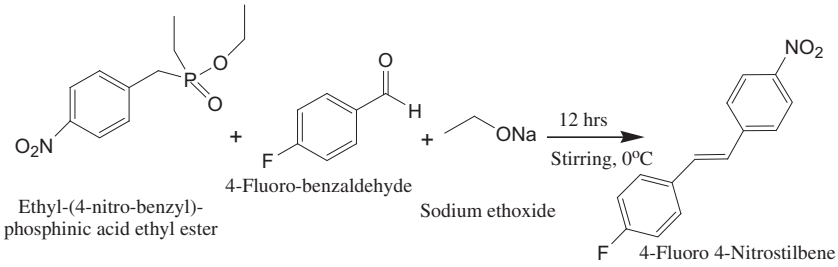


Fig. 2. Grown FONS crystals.



Scheme 1. Synthesis of FONS material.