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Structural, optical and electrical characteristics of a new NLO crystal

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ABSTRACT

A new nonlinear optical (NLO) organic crystal 1-[4-({(*E*)-[4-(methylsulfanyl)phenyl]methylidene}amino)phenyl]ethanone (MMP) has been grown by slow evaporation technique at ambient temperature. The crystal structure of MMP was determined by single crystal X-ray diffraction. MMP crystallizes in non-centrosymmetric monoclinic system with space group $P2_1$. The FT-IR spectrum recorded for new crystal confirmed the presence of various functional groups in the material. MMP was found to be thermally stable up to 300 °C. The grown crystal was optically transparent in the wavelength range of 400–1100 nm. The second harmonic generation (SHG) efficiency of the crystal was measured by the classical powder technique using Nd:YAG laser and was found to be 4.13 times more efficient than reference material, urea. Third order nonlinear parameters were measured by employing the Z-scan technique. The laser damage threshold for MMP crystal was determined to be 4.26 GW/cm^2. The Brewster angle technique was employed to measure the refractive index of the crystal and the values for green and red wavelengths were found to be 1.35 and 1.33, respectively. The dielectric and electrical measurements were carried out to study the different polarization mechanisms and conductivity of the crystal.

1. Introduction

The development of optical devices, such as photonic integrated circuitry, depends strongly on the design of highly efficient nonlinear optical (NLO) materials. Among such NLO materials, organic materials are shown to be superior to their inorganic counterparts in terms of synthesis, crystal fabrication, potential to create large devices and much faster optical nonlinearities [1,2]. Various organic single crystals like stilbazolium crystals [2], OH1 [3] and crystals of other charge transfer complexes [4], such as chalcones [5], have been attractive for frequency conversion, integrated circuitry and terahertz (THz) applications [6]. Organic derivatives having polarizable electrons (e.g., π-electrons) spread over a large distance with various combinations of terminal electron donor and/or acceptor groups have been the objective of recent research, particularly in view of their large molecular hyperpolarizabilities and good crystallizability [7–11], which may lead to a wide range of applications in integrated optics (second harmonic generation (SHG), frequency mixing, electro-optic modulation, parametric effects, etc.) [12,13]. The design and synthesis of organic molecules exhibiting second-order nonlinear optical (NLO) properties has also been motivated by their tremendous potential for application in optical communications, optical computing, data storage, dynamic holography, harmonic generators, frequency mixing and optical switching [10,14]. In this perspective the synthesis, growth and various characterization studies of crystal (MMP), possessing π-conjugated donor–π–acceptor system is imperative to explore its possible applications in nonlinear optics. The nonlinearity in the organic materials originates from a strong delocalization of 'π' electrons along the length of molecules [15]. It is, therefore, possible to tune or tailor the molecular structure to enhance the nonlinear optical properties. Most of the optical device applications also require a thorough understanding of its third order nonlinear optical properties, which is an important part of this investigation. Second harmonic generation (SHG) efficiency of crystalline materials depends both on the magnitude of molecular hyperpolarizability (β) and on the orientation of the molecules in the crystal lattice [16]. Organic molecules, in general, are potentially more attractive and versatile than inorganic compounds because of their large β-values, fast response time, high resistance to optical damage and almost unlimited possibilities of designing molecules suitable for SHG [17,18]. But practical applications are limited due to poor chemical stability, absorption of visible light due to conjugation, poor phase matching properties and inability to grow bulk crystals. This paper deals with the details of synthesis, growth, structure and characterization of a new organic material MMP.

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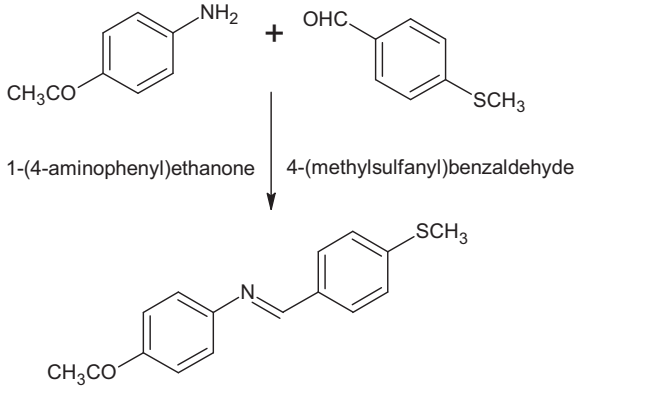
The molecular structure of present crystal consists of *N*-[(*E*)-phenylmethylidene]aniline unit, attached with two groups $COCH_3$ (electron acceptor) and SCH_3 (electron donor) to form 1-[4-({(*E*)-[4-(methylsulfanyl)phenyl]methylidene}amino)phenyl]ethanone (MMP). The methylidene backbone is an asymmetric transmitter and increases molecular nonlinearity for electron donating and withdrawing group substitutions.

2. Experimental procedure

Commercially available 4-aminoacetophenone and 4-methylthiobenzaldehyde were used without further purification. A mixture of equimolar quantities (0.01 M each) of 4-aminoacetophenone (Sigma-Aldrich 99% pure) and 4-methylthiobenzaldehyde (Sigma-Aldrich 95% pure) in ethanol (60 ml) were stirred for 2 h. Then the contents of flask were poured into ice cold water (250 ml) and left for 12 h. The resulting crude solid was collected by filtration, dried and purified by repeated crystallization from acetone. The schematic representation of the reaction is given in Scheme 1. The solubility of the compound was determined by adding solvent to a known amount of compound till it was completely dissolved. It was found that compound was insoluble in water, soluble in acetone, methanol and N, N-dimethyl formamide (DMF). Methanol was found to be the best solvent for MMP crystal. Single crystals of MMP were grown in methanol solution using the slow evaporation technique at ambient temperature. Crystals grown in solvent acetone were not transparent, due to high rate of evaporation.

The single crystal X-ray diffraction data was collected on Bruker Kappa Apex using Apex2 software package. The radiation used was graphite monochromatic MoK_α radiation. All the data were corrected for Lorentz factor and empirical absorption. The structure was solved by direct method and all the non-hydrogen atoms and hydrogen atoms were found in difference electron density maps. The atomic coordinates and anisotropic temperature factors for non-hydrogen atoms were refined by the full-matrix least square method using SHELXTL program package [19]. The FT-IR analysis of MMP was carried out to investigate the presence of functional groups and their vibrational modes [20]. The sample was prepared by mixing MMP with KBr pellet. The spectrum was recorded between 400 and 4000 cm^{-1} using a Thermo Nicolet Avatar, 370 FT-IR spectrometer. To investigate the thermal stability [21] of MMP, thermogravimetric analysis was carried out. Powdered sample of the crystal was selected for this purpose and the analysis was carried out under the nitrogen atmosphere at a heating rate of 10 °C/min using Perkin-Elemer simultaneous TGA/DTA analyzer. The UV–VIS–NIR absorption spectrum of the crystals was recorded using a Cary 5E high resolution spectrophotometer, in the wavelength range of 350–1100 nm. Crystals with parallel surfaces and thickness of ~1 mm were used for this purpose.



1-[4-({(*E*)-[4-(methylsulfanyl)phenyl]methylidene}amino)phenyl]ethanone

Scheme 1. Synthesis of MMP.

In order to determine SHG efficiency, the crystal was ground into uniform powder and then packed in a micro-capillary of uniform bore and exposed to a Q-switched Nd:YAG laser of wavelength 1064 nm. The laser was incident normally on the sample capillary tube and output from the sample was passed through Monochromater to collect the intensity of 532 nm component. The Z-scan experiment was performed with a picosecond (ps) amplifier (seed pulse was from Micra laser oscillator (COHERENT)) generating ~2 ps pulses at a repetition of 1 kHz. The experiment was done at a wavelength of 800 nm. The average and peak powers were ~2 W, ~1 GW, respectively. The diameter of the beam from the amplifier was ~4 mm. Using ND filters the input energy/power was controlled. The laser damage threshold (LDT) studies were carried out on solution grown MMP single crystals using a Q-switched Nd:YAG laser source of pulse width 6 ns at a wavelength of 1064 nm and a 10 Hz repetition rate, operating in TEM_{00} mode. The refractive index value of the MMP crystal understudy was determined by employing the Brewster angle method. The linearly polarized light from the laser source operating in TEM_{00} mode was incident on plane surface of the crystal. He–Ne lasers of wavelength 543.5 (green) and 632.8 (red) are used as laser sources for the experiment. The dielectric properties were measured on the pellet samples using a Agilant 4263B LCZ metre for frequencies 100 HZ, 1k Hz, 10k Hz, 100k Hz with a applied voltage of 1 Vpp and over a temperature range of 30–110 °C. The sample was silver electrode by applying a thin layer of silver paint on both faces of the pellet. Then it was placed in a dry atmosphere for 24 h to ensure the maximum conductivity and adhesion of the silver paste. The pellet sample was mounted between two stainless steel electrodes being held by spring loaded contacts to form a cell consisting of parallel plate capacitor. For studying the effect of temperature on dielectric constant, the sample was enclosed in a resistance heated furnace and the temperature was monitored using a chromel–alumel thermocouple. The temperature of the sample was increased by regulating the input power. At each temperature the sample was kept for 15 min to ensure thermal equilibrium. The *I–V* dependence of the grown crystals were conducted using Kiethley 2361-V programmable source measured unit with METRICES-ICS software, by two probe method at room temperature. Crystal's pellets were pasted with good quality silver paint on both sides to ensure the good electrical contact. The measurements have been carried out in resistance mode by applying voltage in the range of 0–100 V, in steps of 2 V and current is measured.

3. Results and discussion

3.1. Crystal growth

Transparent plate like crystals appeared in the growth vessels within 2 weeks of solution evaporation. However bulk crystal with definite morphology of MMP did not grow, even after repeating the growth experiment several times. Only by continuous and repeated re-crystallization process it was possible to obtain good quality crystals. The crystals reached a maximum size of $4 \times 4 \times 2$ mm^3 over a time period of one month. Crystals obtained were non-hygroscopic and stable at room temperature. These crystals were white-reddish in color and grown in the form of plates (Fig. 1)