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Synthesis and characterization of semi-organic nonlinear optical material: Sodium *para*-nitrophenolate *para*-nitrophenol dihydrate

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ABSTRACT

Single crystal of sodium *para*-nitrophenolate *para*-nitrophenol dihydrate (SPPD) was grown using slow evaporation solution growth technique with the crystal dimensions of 17 mm × 11 mm × 6 mm. The structure of the SPPD crystal was examined by X-ray diffraction analysis and the functional groups, hydrogen bonding interactions were identified using FT-IR and FT-Raman spectra. The UV–vis-NIR absorption spectrum revealed that the UV lower cut-off wavelength was 260 nm and the optical band gap of the crystal was 4.76 eV. The material was thermally stable up to 128 °C as determined by the TG-DTA curves. The mechanical behavior of the grown crystal was studied using Vickers microhardness. Dielectric constant and dielectric loss were also measured as a function of frequency between 5 Hz and 5 MHz and temperature between 40 and 100 °C, respectively. The second-harmonic generation efficiency was found to be five times greater than that of KDP. The third-order nonlinear parameters such as nonlinear refractive index (n_2), nonlinear absorption coefficient (β) and third-order susceptibility $|\chi^{(3)}|$ were calculated using Z-scan technique.

1. Introduction

Nonlinear optical (NLO) materials are plays a major role in the field of optoelectronics and photonics [1]. NLO crystals with high conversion efficiency for second-harmonic generation and transparent in the visible and ultraviolet regions are required for optical device applications [2,3]. Hence, new nonlinear optical materials with large second-order nonlinearities, large optical transmission window are needed for various applications. The organic NLO materials have large nonlinear optical co-efficient compared to the inorganic materials, but their use is impeded by their poor mechanical and thermal properties and low laser damage threshold [4–6]. The pure inorganic materials have tremendous mechanical and thermal properties but possess relatively modest optical nonlinearities due to the lack of π-electron delocalization [7,8]. In view of developing, new types of hybrid NLO materials have been explored from organic and inorganic complexes called semi-organic. In these materials, a high optical nonlinearity of pure organic compound is combined with the favorable mechanical and thermal properties of inorganic materials. In the case of metal-organic co-ordination complexes, the organic ligand is usually more dominant for NLO effect, since the metal compounds have high transparency in the visible region [9].

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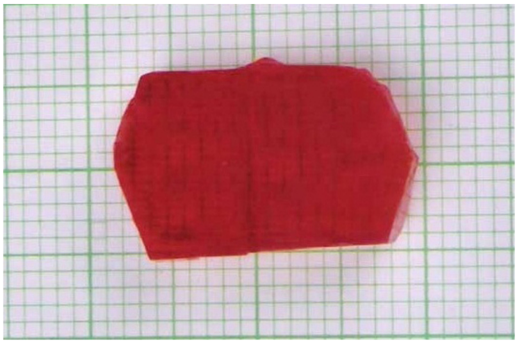

Fig. 1. The photograph of the as grown SPPD crystal.

The presence of hydroxyl, nitro and phenyl groups form a conjugated molecular configuration with remarkable electron transfer. This title compound has a metal complex of donor-acceptor substituted aromatic moieties. Moreover, it can form a three-dimensional network of bonding with inter- and intramolecular hydrogen bonds. Consequently, it is responsible for the charge transfer that takes place on SPPD. Similarly, the ionic bond along with extensive hydrogen bonding is responsible for the mechanical and thermal stability of target system [10]. In recent days, an extensive study has been carried out on NLO crystals which have conjugation along with electron donor and acceptor substitutions. Due to the presence of delocalized electrons, these materials generally have high second-harmonic generation (SHG) efficiency. *Para*-nitrophenol matches with this criterion for its electron donor substituent namely hydroxyl group and electron acceptor substituent such as nitro group. In the present work we report the synthesis, crystal growth and characterization studies of sodium *para*-nitrophenolate *para*-nitrophenol dihydrate. It is a kind of semi-organic material which has noteworthy NLO activity. The crystal structures, the unit cell parameters [11], the UV–vis-NIR spectral studies, thermal and mechanical properties of the SPPD crystal have already been reported [12]. To the best of our knowledge, powder X-ray diffraction, electronic absorption spectrum, FT-IR, FT-Raman spectral studies, dielectric and third-order nonlinear optical properties of the sodium *para*-nitrophenolate *para*-nitrophenol dihydrate crystal are reported at the first time.

2. Experimental

2.1. Synthesis

The SPPD crystals were grown by adopting two different solvents namely water and methanol. The performance of crystal growth on methanol solvent was found to be more effective in comparison with water, since the size and the quality of the grown crystal found to be more appreciative. The crystal growth procedure includes the following steps. The analytical grade *para*-nitrophenol and sodium hydroxide were taken in a stoichiometric ratio of 2:1 and dissolved in methanol solvent. The purity of the synthesized salt was further increased by successive recrystallization process. The resultant solution was completely stirred to obtain a homogenous solution after which it was filtered and kept inside a constant temperature bath with a controlled temperature accuracy of $\pm 0.01\,^{\circ}$C. A cooling rate of $0.1\,^{\circ}$C per day was employed and supersaturation was achieved gradually to initiate nucleation followed by growth. The crimson color single crystal of dimensions with $17 \times 11 \times 6\,mm^3$ was obtained after a period of 20 days and the photograph of the as grown crystal is shown in Fig. 1.

2.2. Characterization

To identify the reflection planes, powder X-ray diffraction pattern of the powdered sample were analyzed using Rigaku Ultima X-ray diffractometer with CuKα radiation ($\lambda = 1.5406$ Å). All the samples were scanned over the range of 10–70°. The optical absorption spectrum was recorded in the region 200–1100 nm using lambda–35, UV–vis-NIR spectrometer. The FT-IR spectrum of the crystal was recorded using Perkin-Elmer RXI spectrometer in the region 400–4000 cm^{-1}. FT-Raman measurement was performed at room temperature between from 50 to 4000 cm^{-1} using Bruker RFS-27 FT-Raman spectrometer. The thermal stability was studied by thermo gravimetric (TG) and differential thermal analysis (DTA) using a SDT Q V8.3 system in the temperature from $30\,^{\circ}$C to $1200\,^{\circ}$C at a heating rate of $20\,^{\circ}$C/min in nitrogen atmosphere. The hardness of the crystal was measured using Riechert Polyvar 2met fitted with a Vickers diamond pyramidal indenter attached with a photomicroscope. The dielectric study was carried out using the instrument of HIOKI 3532-50 LCR meter in the frequency range of 5Hz–5 MHz. The second harmonic generation (SHG) efficiency of SPPD was measured by Kurtz and Perry powder technique using a Q-switched Nd:YAG laser ($\lambda = 1064$ nm). The third-order NLO properties were examined by Z-scan technique using He-Ne laser of wavelength 632.8 nm.