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Growth, optical, thermal and laser damage threshold studies of 4-aminopyridinium 4-nitrophenolate 4-nitrophenol crystal

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ABSTRACT

Organic nonlinear optical (NLO) single crystals of 4-aminopyridinium 4-nitrophenolate 4-nitrophenol (4AP4NP) were grown by the slow evaporation solution growth technique. The unit cell parameters and space group of 4AP4NP crystal were found out by single crystal X-ray diffraction analysis. From the UV–vis–NIR spectral studies, the lower cut-off wavelength of the grown crystal was found to be 474 nm. The laser damage threshold study shows that 4AP4NP crystal withstands the laser radiation up to 3.67 GW cm^{-2}. Thermogravimetric and differential thermal analyses revealed that 4AP4ANP is thermally stable up to 175 °C. The specific heat capacity of 4AP4NP was measured to be 3.9135 J g^{-1} K^{-1} at 33 °C. Kurtz and Perry powder study reveals that 4AP4NP is a phase-matchable NLO material. The four independent tensor coefficients of dielectric permittivity were found to be $\varepsilon_{11}=25.09$, $\varepsilon_{22}=25.84$, $\varepsilon_{33}=26.69$ and $\varepsilon_{13}=0.8$ from the dielectric measurement.

1. Introduction

Organic nonlinear optical (NLO) crystals play an important role in electro-optic modulation, frequency mixing, second harmonic generation and optical parametric oscillation, etc [1,2]. Organic molecules consist of polar and chiral types with π-electron conjugated moiety substituted by an electron donor group on one end of the conjugated structure and an electron acceptor group on the other end, forming a conjugated structure. The conjugated π-electron moiety paves a pathway for the redistribution of electronic charge across the entire length of conjugation under the perturbation of external electric field. The donor and acceptor groups provide the ground-state charge asymmetry of the molecule, which is required for second order nonlinearity. An essential criterion for second order nonlinearity is noncentrosymmetric structure [3,4]. The use of p-nitrophenol for the production of crystalline salts with aromatic base suitable for the single crystal characterization has been employed extensively. Such salts, particularly the 1:2 p-nitrophenolate, have been employed as polar materials suitable for nonlinear optical applications [5–7]. Recently, the crystal structure of 4-aminopyridinium 4-nitrophenolate 4-nitrophenol with noncentrosymmetric crystal structure has been reported [8]. Though some p-nitrophenoate crystals have a noncentrosymmetric system, the growth of these crystals has been limited due to their poor solubility. As the poor solubility restricts the size, some class of these crystals has been used rarely for second harmonic generation (SHG) applications. In addition to the growth, nonlinear optical crystals should be optically transparent in the particular wavelength region of interest, phase-matchable and also possess enough laser damage threshold. The knowledge of laser damage threshold, specific heat capacity and nonlinear optical studies are extremely important for their device applications. In the present investigation, the optical transparency, thermal stability, second harmonic generation efficiency, laser damage threshold have been studied systematically on 4-aminopyridinium 4-nitrophenolate 4-nitrophenol (4AP4NP) crystals.

2. Experimental

2.1. Synthesis, solubility and growth

Commercially available high pure raw materials, 4-aminopyridine (Merck 99.9%) and 4-nitrophenol (Merck 99.5%) were weighed stoichiometrically and dissolved in toluene for the synthesis of 4AP4NP based on the following reaction as shown in Fig. 1. Then, the clear solution was heated up to 45 °C and maintained at the same temperature. The yellow precipitate after an hour confirmed the formation of 4AP4NP compound. The obtained precipitate was washed with toluene solvent for five times and dried using a hot air oven.

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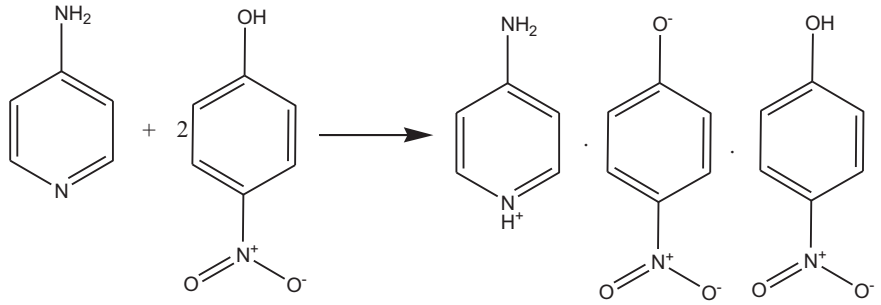

Fig. 1. Reaction scheme for 4AP4NP compound.

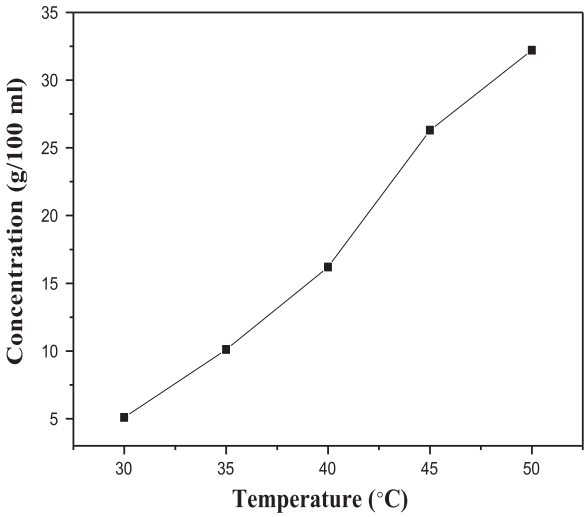

Fig. 2. Solubility of curve of 4AN4NP in ethanol solvent.

The solubility of 4AP4NP in ethanol was estimated as a function of temperature ranging from 30 to 50 °C. The solubility of 4AP4NP in ethanol was found to have positive solubility gradient (Fig. 2). In accordance with the solubility data, the growth solution was prepared at 35 °C. Then, the prepared solution was filtered and covered tightly using a polythene sheet. In order to control the evaporation, a small hole was made on the sheet and left it in a constant temperature water bath for slow evaporation. The optical quality and well shaped speck were seen by spontaneous nucleation within 9 days. After a period of 21 days, single crystal of 4AP4NP with dimension of $15 \times 8 \times 5\ mm^3$ was harvested. The photograph of as-grown and cut and polished is shown in Fig. 3 (a) and (b).

3. Characterization

3.1. Single crystal X-ray diffraction studies

The unit cell parameters of 4AP4NP single crystal were estimated using a Bruker Kappa APEXII single crystal X-ray diffractometer with MoKα ($\lambda = 0.71073$ Å) radiation. The calculated cell parameters are $a = 5.603$ (Å), $b = 15.30$ (Å), $c = 10.779$ (Å), $\beta = 102.71°$ and $V = 901$ Å^3. 4AP4NP crystal belongs to a noncentrosymmetric system with space group $P2_1$. In the asymmetric unit of 4AP4NP salt, there are 4-aminopyridinium cation, 4-nitrophenolate anion and a neutral 4-nitrophenol. There is a proton transfer to the nitrogen atom of 4-aminopyridine from one of the 4-nitrophenol dimers. The 4-nitrophenol-4-nitrophenolate anionic dimers are held together by short intermolecular OH(4-nitrophenol)…O(4-nitrophenolate) hydrogen bond. The title compound is stabilized by N–H…O and O–H...O hydrogen bonds. The calculated cell parameter values of 4AP4NP are in good agreement with the reported values [8]. The morphology of 4AP4NP is shown in Fig. 4. The crystallographic planes (031), (001), (120), (111), (1−11), (120), (−211), (1−1−1) and (−1−21) were clearly identified. It is observed that the fastest growing face is 'a'. So the faces 'b' and 'c' become more prominent one and the other faces grow themselves out of existence. Thus the 4AP4NP crystal adopts a rectangular shape with its longest dimension oriented vertically.

3.2. Thermal studies

The thermal properties of 4AP4NP compound were analyzed by thermogravimetric and differential thermal (TGA/DTA) analyses using a SDT-Q600 TA thermal analyzer in the temperature range 26–1000 °C with a heating rate of 10 °C per minute in a nitrogen atmosphere. The sample weighing 2.16 mg was analyzed and the TG/DTA curves are depicted in Fig. 5. The DTA curve indicates the same changes as shown in TG curve. From the TG curve, it is evident that the material is stable up to 175 °C and moisture free. TG curve showed two stage mass loss pattern, when the material was heated from 26 to 1000 °C. The first mass loss occurred between the temperatures 176 °C and 200 °C with elimination of 2.13% of the material into gaseous products as seen in the low temperature region. The second stage mass loss noticed between 205 and 275.9 °C experiences a mass loss about 98.20%. The decomposition process was carried up to 1000 °C with the removal of the material into gaseous products (mixture of CO, CO_2, NO and hydrocarbon gases).

Thermogravimetric and differential scanning calorimetry (TG–DSC) studies were carried out to measure the specific heat capacity of 4AP4NP using a NETZSCH STA 449F3 thermal analyzer. Specific heat capacity (C_p) defines the damage threshold of laser crystals. A material with a higher specific heat capacity will generally show more resistance to laser damage. It was observed that the specific heat capacity of 4AP4NP is linear with temperature as shown in Fig. 6. The specific heat capacity increases from 3.91352 to 6.89558 J g^{-1} K^{-1} in the measured temperature range 33–140 °C. The specific heat capacity of 4AP4NP crystal is comparatively higher than that of DAPNP (1.279 J g^{-1} K^{-1}), KDP (0.853 J g^{-1} K^{-1}) and BBO (0.490 J g^{-1} K^{-1}) crystals [6,9,10].

3.3. UV–vis–NIR spectral studies

UV–vis–NIR transmission spectrum of 4AP4NP crystal was recorded in the range of 190–900 nm using 1.7 mm thickness crystal. UV–vis–NIR spectrum of the grown 4AP4NP crystal is shown in Fig. 7. 4AP4NP crystal has sufficient transmittance in the visible and near infrared regions and good transparency about 55% with a lower cut-off wavelength 474 nm. The absence of absorption in the region between 490 and 900 nm showed that 4AP4NP crystal could be exploited for nonlinear optical applications. It is noticed from the transmission spectrum that 4AP4NP crystal absorbs UV radiation and hence it can be used as an effective UV shelter.