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Growth and characterization of benzaldehyde 4-nitro phenyl hydrazone (BPH) single crystal: A proficient second order nonlinear optical material

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ABSTRACT

The crystals (benzaldehyde 4-nitro phenyl hydrazone (BPH)) appropriate for NLO appliance were grown by the slow cooling method. The solubility and metastable zone width measurement of BPH specimen was studied. The material crystallizes in the monoclinic crystal system with noncentrosymmetric space group of *Cc*. The optical precision in the whole visible region was found to be excellent for non-linear optical claim. Excellence of the grown crystal is ascertained by the HRXRD and etching studies. Laser Damage Threshold and Photoluminescence studies designate that the grown crystal contains less imperfection. The mechanical behaviour of BPH sample at different temperatures was investigated to determine the hardness stability of the grown specimen. The piezoelectric temperament and the relative Second Harmonic Generation (for diverse particle sizes) of the material were also studied. The dielectric studies were executed at varied temperatures and frequencies to investigate the electrical properties. Photoconductivity measurement enumerates consummate of inducing dipoles due to strong incident radiation and also divulge the nonlinear behaviour of the material. The third order nonlinear optical properties of BPH crystals were deliberate by Z-scan method.

1. Introduction

The irresistible achievement of molecular engineering reveals to control nonlinear optical (NLO) properties which has encouraged the growth and characterization of assortment of innovative sort of NLO materials [1]. The nonlinear figure of merit and by the evenly pertinent optical excellence and sturdiness of the materials in the direction of diverse purposes primarily administrate desires of the nonlinear optical materials engineering. Engineering equipments with optimized second order nonlinear susceptibility always require the structural suppleness which is a positive feature of organic amalgam [2]. Generally, second-order nonlinear optical (NLO) chattels are merely discernible in non-centrosymmetric materials [3–6]. The augment of the optical response in organic compound is owing not merely to lofty level of the π-conjugated charge transfer but also to the milieu of the system conjugated and ionic appearance of structure, which acts, a determination function in the delocalization of π-electrons [7]. Numerous optical and electronic devices like optical disk data storage, optical information processing, optical memories, color displays, optical communication, optical computing, laser fusion reactions, laser remote sensing necessitate immensity in size, mechanically hard, chemically stable and transparent in intact visible region organic crystals [8–11]. In view of the above prerequisite, it is obligatory to explore a potential organic NLO crystal which acquires good optical quality, adequately greater nonlinear coefficient, precision in UV region and high damage threshold. In continuance of our exertion on high competent second order organic nonlinear optical materials [12], we report growth and anisotropic studies of the title amalgam (BPH) in the present investigation. Benzaldehyde 4-nitro phenyl hydrazone is a proficient second order organic nonlinear optical material which encloses a p-NO_2 group for probable intermolecular interaction with the NH group. These structures will also corroborate the meticulous structural type (E *vs* Z) espoused in benzaldehyde derivatives [13].

2. Experimental

2.1. Synthesis of BPH

The title compound apposite for anisotropic studies was synthesized by concoction of 0.5 g of p-nitrophenylhydrazine, 0.5 g

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of the aldehyde, ethanol (10–15 ml) and 2 plummets of frosty acetic acid was refluxed for 15 min. The apparent solution was cooled then p-nitrophenylhydrazone was sifted off. The scheme of reaction is shown in Fig. 1.

2.2. Growth of BPH seed by SEST method

The solution of recrystallized BPH was systematized using acetone as the solvent. The equipped solution was allowed to arid at room temperature. The yellow shade orange hue materials were obtained by slow evaporation solution growth technique at 32 °C using a constant temperature bath having a manage accurateness of ±0.01 °C. The transparency of the amalgamated material was further improved by successive recrystallization process.

2.3. Solubility and metastable stable zone width measurements

Metastable zone width is a vital parameter for the augmentation of bulk size crystals from solution since it is the direct gauge of the stability of the solution in its supersaturated region. The solubility of BPH in acetone was measured as a function of temperature in the range 30–55 °C. The solubility was ascertained by dissolving the three epoch's recrystallized solute in acetone in an airtight container maintained at a constant temperature with continuous stirring. The solution was continually stirred for 4 h using a magnetic stirrer for homogenization. The symmetry concentration of the solute was analysed gravimetrically after attaining the saturation. The solubility curve was thus obtained. Drenched solution of BPH has been prepared in harmony with the currently ascertained solubility curve for the nucleation experiments. The studies were performed in a constant temperature bath controlled to an exactness of ±0.01 °C, endow with a cryostat for cooling beneath room temperature. Metastable zone width of BPH was deliberate using the polythermal method [14]. The acquired solubility and nucleation curve for BPH is shown in Fig. 2. It is seen from the figure that the BPH has a constructive gradient of solubility. It also shows that title compound has good solubility in the solvent of acetone and the solubility augments almost linearly with temperature. The metastable zone width decreases with increasing temperature.

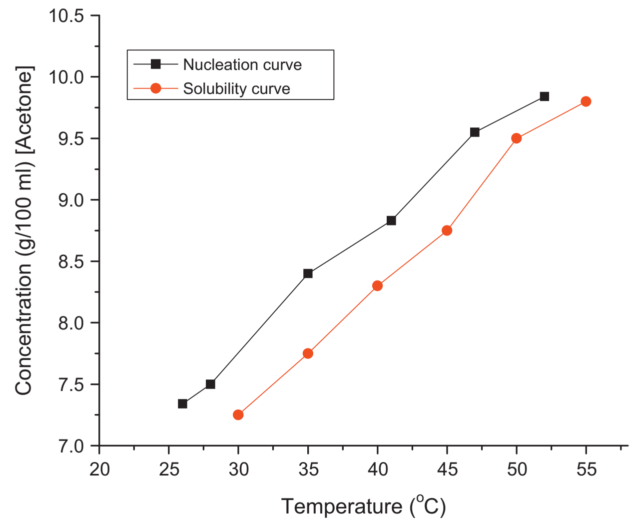


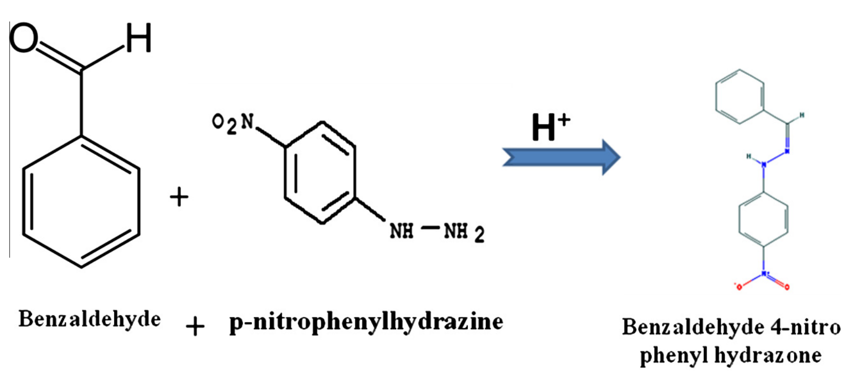
Fig. 2. Metastable zone width of BPH in acetone.

2.4. Growth of BPH seed by slow cooling method

The decontaminated seed crystals (gratis from macro defects) obtained by SEST method was used for bulk growth. The bulk growth of BPH single crystals were carried out by low temperature solution growth technique by slow cooling method. According to the solubility data of BPH in acetone, the saturated solution of BPH at 35 °C was prepared from recrystallized material. The solution was sifted to eradicate any other insoluble impurities. We carefully ensured that the prepared solution was glowing within the metastable zone width region. A constant temperature bath controlled at an accuracy of ±0.01 °C was used for the low temperature solution growth technique by slow cooling. Transparent and good quality seed crystals obtained from slow evaporation technique were selected for the growth of bulk BPH single crystals by slow cooling method. The solution was maintained at 35 °C in constant temperature bath for 2 days before seeding. The cooling rate of 0.4 °C/day was employed initially to attain 32 °C to instigate nucleation and the temperature has been subsequently abridged at a rate of 0.14 °C/day till 25 °C was reached. After the completion of the growth run, optically transparent crystal of size $20 \times 8 \times 18$ mm^3 was harvested in a period of 50 days (Fig. 3).

2.5. Material characterization techniques

Single crystal XRD studies of the grown crystals were carried out using Bruker kappa APEXII single crystal X-ray diffractometer.



$$C_7H_6O + C_6H_7N_3O_2 \xrightarrow{H^+} C_{13}H_{11}N_3O_2$$

Fig. 1. Reaction system of BPH.