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Studies on the structure, growth and characterization of morpholinium perchlorate single crystals

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ABSTRACT

Morpholinium perchlorate, an organic nonlinear optical material was synthesized and the crystals were grown by the slow evaporation solution growth technique. Single crystal X-ray diffraction study revealed that the grown crystal belongs to orthorhombic system with space group of $P2_12_12_1$. The structure of the compound was also confirmed by ^{1}H NMR studies. The Fourier transform infrared analysis was used to identify the various functional groups present in the title compound. The UV–visible absorption spectrum was recorded to study the optical transmittance in the range from 200 to 1100 nm. The optical band gap, reflectance, refractive index (n), extinction coefficient and electric susceptibility were calculated using transmittance data. The mechanical stability of the grown crystal was studied by Vickers's micro hardness test. The PL spectrum of the title compound shows red emission at 648 nm.

1. Introduction

The technological society of optoelectronics and photonics has created more attention on organic optical materials. Nowadays organic and semiorganic NLO materials are emerging as an alternative to inorganic materials because of their efficient molecular nonlinearity over a broad frequency range, low cost, low refractive index, low dielectric constant, inherent synthetic flexibility, moderate optical damage density, fast response with the better process ability and ease of fabrication into devices. The organic nonlinear optical materials generally have the larger second order nonlinear optical coefficient and hence they are being used in many applications such as second harmonic generation, sum frequency generation, THz wave generation, optical parametric oscillators, etc., [1–5]. Researches to explore the third order nonlinear optical phenomena in organic and inorganic single crystals have received limited attention compared to second order nonlinear optical materials. For the past ten years, the third order nonlinear optical materials from the organometallic, organic, inorganic and semi organic single crystalline compounds have received great deal of attention due to their potential applications in all optical switching, optical limiters, optical information storage, all optical logic gates, laser radiation protection etc., [6,7]. Crystals of organic salts are often colorless, transparent, inexpensive to produce and easy to grow [8]. Morpholine is colorless, oily and volatile in nature having great importance in industrial purposes [9]. Molecular ionic simple complex crystals like perchlorate with Morpholine (of ratio 1:1), shows nonlinear optical physical properties unique to the crystal structure. The distinct features of molecular ionic crystal give empathizing correlation between the crystal packing and physical properties. This initiated many researchers to synthesize and to grow the newly designed molecular ionic crystals. In this paper we present the structure of morpholinium perchlorate (MP) at room temperature, crystal growth and its characterization.

2. Experiment

The title material MP was synthesized by the chemical reaction of commercially available Morpholine (Merck) with Perchloric acid (SRL), taken in the stoichiometric ratio 1:1 by dissolving in the mixture of (1:1) ethanol and deionized water. The chemical reaction is shown in Fig. 1. Stoichiometrically calculated amounts of the materials were transferred into a beaker and dissolved in ethanol and deionized water which is stirred well with the help of a magnetic stirrer to make a homogeneous solution of the material at a temperature of 50 °C for a proper chemical reaction. The white precipitate was obtained after two hours. The precipitate is allowed to dry. The dried salt was collected and used for the further growth of MP. The synthesized material was purified by the repeated recrystallization process. The dried precipitate was dissolved using the same solvent. But the crystallization did not occur in this solution as it has high viscosity and low pH value. The selection of solvent is

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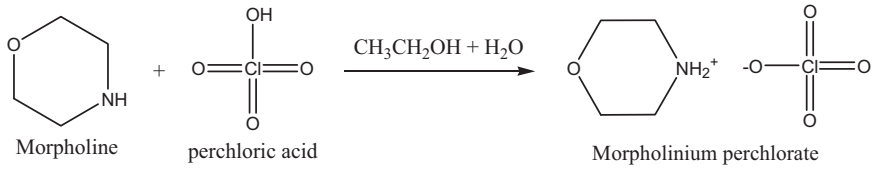

Fig. 1. Reaction scheme of MP.

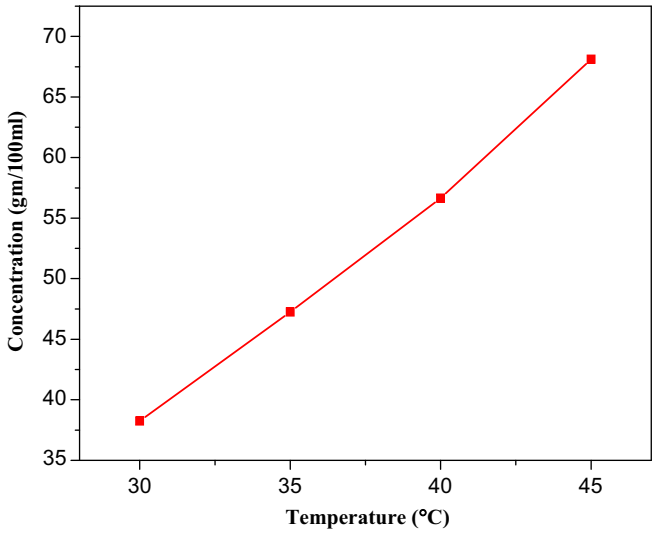

Fig. 2. Solubility diagram of MP.

Fig. 3. As grown single crystals of morpholinium perchlorate (MP).

important to grow good quality single crystals of considerable size. The solubility test can be performed to choose the solvent for crystal growth. The solubility was measured by taking excess amount of MP in the solvent and it is continuously stirred to achieve uniform concentration over the entire volume of the solution. Solubility curve for MP was determined by using acetone as a solvent in the temperature range from 30 to 45 °C with the interval of 5 °C. The studies were carried out in a constant-temperature water bath with a cryostat facility with an accuracy of ±0.01 K. MP exhibits a positive solubility – temperature gradient in acetone solution. The solubility almost increases linearly with the increase of temperature. Fig. 2 depicts the solubility curve of MP. The obtained dried precipitate was dissolved using acetone and then allowed to evaporate at room temperature to yield the crystalline powder salt of MP. The well-defined single crystals of MP were harvested from mother solution after a growth period of 45 days. The grown single crystals of MP are shown in Fig. 3

3. Characterization

As grown MP crystals have been subjected to various characterization studies to analyze the structural, thermal, optical and mechanical properties The single crystal X-ray diffraction measurements were done using a Bruker AXS Kappa APEX II single crystal CCD diffractometer equipped with graphite-monochromated MoKα radiation (λ=0.71,073 Å) at room temperature with a crystal of dimension $0.35\times0.25\times0.2$ mm^3. Accurate unit cell parameters were determined from the reflections of 36 frames measured in three different crystallographic zones. The data collection, data reduction and absorption correction were performed by APEX2, SAINT-plus and SADABS program using SHELXL-97 [10]. The structure was solved by direct methods procedure and the non-hydrogen atoms were subjected to anisotropic refinement by full-matrix least squares on F^2 using SHELXL-97 program [11]. The positions of all the hydrogen atoms were identified from difference electron density map, and they were constrained to ride on the corresponding non-hydrogen atoms. The hydrogen atom bound to carbon atoms were constrained to a distance of C–H=0.97 Å and U_{iso} (H)= 1.2 U_{eq} (C). The final refinement converges to an *R*-values of R_1=0.0485 and WR_2=0.1330. The ORTEP drawing was performed with the ORTEP3 program [12]. The crystallographic refinement parameters are listed in Table 1. The possible hydrogen bonds observed in the structure are listed in Table 2. The crystalline perfection of the grown single crystals was characterized by HRXRD by employing a multicrystal X-ray diffractometer developed at NPL [13]. The well-collimated and monochromated MoKα_1 beam obtained from the three monochromator Si crystals set in dispersive (+,−,−) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+,−,−,+) configuration. Due to dispersive configuration, though the lattice constant of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve (DC) of the specimen crystal is insignificant. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4″. The rocking or diffraction curves were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θ_B (taken as zero for the sake of convenience) starting from a suitable arbitrary glancing angle and ending at a glancing angle after the peak so that all the meaningful scattered intensities on both sides of the peak are included in the diffraction curve. The DC was recorded by the so-called ω scan wherein the detector was kept at the same angular position $2\theta_B$ with wide opening for its slit. This arrangement is very appropriate to record the short range order scattering caused by the defects or by the scattering from local Bragg diffractions from agglomerated point defects or due to low angle and very low angle structural grain boundaries [14]. Before recording the diffraction curve to remove the non-crystallized solute atoms which remained on the surface of the crystal and the possible layers which may sometimes form on the surfaces on crystals grown by solution methods [15] and also to ensure the surface planarity, the specimen was first lapped and chemically etched in a non-preferential etchant of water and acetone mixture in 1:2 volume ratio. The FTIR spectrum of MP crystals was recorded in the range 4000–400 cm^{-1}