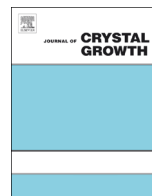




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Synthesis, growth, structural, optical, thermal, dielectric and mechanical studies of an organic guanidinium p-nitrophenolate crystal

M. Dhavamurthy^a, G. Peramaiyan^b, R. Mohan^{a,*}^a Department of Physics, Presidency College, Chennai 600005, India^b Department of Physics, Vel Tech Dr. RR & Dr. SR Technical University, Avadi, Chennai 600062, India

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ABSTRACT

Guanidinium p-nitrophenolate (GUNP), a novel organic compound, was synthesized and crystals were grown from methanol solution by a slow evaporation solution growth technique. A single crystal X-ray diffraction study elucidated the crystal structure of GUNP belonging to the orthorhombic crystal system with space group Pnma. Thermal studies revealed that the GUNP crystal is thermally stable up to 192 °C. The lower cut-off wavelength of GUNP was found to be 505 nm by UV–vis–NIR spectral studies. The luminescence properties of the GUNP crystal were investigated. The three independent tensor coefficients ϵ_{11} , ϵ_{22} and ϵ_{33} of the dielectric permittivity were calculated. The mechanical properties of the grown crystal were studied by Vickers' microhardness hardness technique.

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1. Introduction

In recent years, organic compounds with large π -electron delocalization have attracted interest from materials scientists because of their large optical nonlinearity and potential applications in optical signal processing, optical communication, photorefractivity and they often possess interesting ferroelectric, ferromagnetic, superconducting properties, etc. [1]. For intelligent crystal engineering, rational control over the molecular self-assembly processes is critical and unpredictable. Crystal engineering is a bottom-up construction of functional materials from molecular building blocks. These building blocks are influenced by relatively strong interactions that often display considerable consistency and are known as supramolecular synthons. In a supramolecular structure, the control of molecular orientation is tedious and is recognized as a major obstacle in materials design. In this view, many attempts to control the structure of solids have focused on crystal engineering through charge transfer, electrostatic, hydrogen bond and π - π interactions. Recent research has revealed that many attempts have been made in forming acentric crystal structures by hydrogen bonding interactions for second generation nonlinear optical applications. However, centrosymmetric crystal structures are preferred because of

more favorable intermolecular dipole–dipole interactions with close packing and are generally preferred for third order nonlinear optical, optical limiting and three dimensional fluorescence microscopy applications. Due to the strong base character of guanidine, it can be considered as a super-base that readily undergoes protonation to generate a resonance-stabilized guanidinium cation. Guanidine is used in various supramolecular recognition processes across the spectrum of organic, biological and medicinal chemistry with special interest motivated by their potential applications in nonlinear optics [2–7]. Therefore, research is actively progressing in the field of the nonlinear optical mechanism; new organic materials such as guanidinium 4-aminobenzoate, guanidium perchlorate, guanidinium sulfonates, etc., have been reported [8–11]. Although some guanidine and p-nitrophenol complexes have centric and acentric supramolecular architectures, the growth of these crystals has been limited due their poor solubility. As the poor solubility restricts the size and optical transparency of guanidinium crystals, both guanidine and p-nitrophenol based crystals with high nonlinearity have not been used for nonlinear optical device applications. In addition to the growth and optical transparency, NLO and luminescent crystals should possess enough tolerance to withstand a high power laser and have a high degree of luminescence. In this case, the knowledge of the laser damage threshold and photoluminescence studies on optical crystals are extremely important during their practical applications. In the present investigation, the synthesis, crystal growth, optical, thermal, dielectric and mechanical properties of guanidium 4-nitrophenolate have been reported.

* Corresponding author. Tel.: +91 9444455983; fax: +91 44 2235 2870.
 E-mail address: professormohan@yahoo.co.in (R. Mohan).

2. Experimental

2.1. Material synthesis and crystal growth

Equimolar quantities of the parent compounds guanidine carbonate (Merck, 99%) and p-nitrophenol (Merck, 99%) were dissolved in methanol. It is a proton transfer reaction where a proton is transferred from the electron donor group of p-nitrophenol to the electron acceptor group of guanidine. The synthesized salt was further purified by recrystallization. The reaction scheme of the title compound is shown in Fig. 1. The solubility of guanidinium p-nitrophenolate in methanol was assessed as a function of temperature in the range 35–50 °C. The concentration of the solute at specific temperature was determined by a gravimetric method. The GUNP compound exhibits a positive solubility gradient with moderate solubility as shown in Fig. 2. A saturated growth solution of GUNP in methanol was prepared at room temperature and was filtered. The pH value of the working solution was measured to be 4. The growth solution was kept in constant temperate water bath at the preparative temperature and was then allowed to evaporate slowly. The growth rate was observed to be 0.3 mm/day. A yellow colored single crystal of size $14 \times 11 \times 7$ mm³ was harvested from the mother solution after a growth period of 35 days. The as-grown single crystal of GUNP is shown in Fig. 3.

3. Characterization

3.1. Single crystal X-ray diffraction and morphological studies

A Bruker kappa APEXII single crystal X-ray Diffractometer with MoK α ($\lambda=0.71073$ Å) radiation was used for X-ray diffraction studies. The structure was solved by direct methods using the program SHELXS-97 and refined by a full-matrix least-squares method using SHELXL-97 [12]. The *R*-value of the full-matrix least-squares refinement is given in Table 1. The GUNP crystal belongs to the orthorhombic crystal system with space group Pnma. The cell parameters are $a=6.8261(3)$ Å, $b=21.9513(8)$ Å, $c=12.0454(6)$ Å and volume $V=1804.90(14)$ Å³. The asymmetric unit of the title compound is comprised of a guanidinium cation and a p-nitrophenolate anion (Fig. 4). Both the cation and the anion lie on a crystallographic mirror plane and contain two half-molecules of cation. The compound is formed by three O atoms of anion and four N atoms of cation as indicated by the intermolecular interactions N(6)–H(6A)...O(6), N(3)–H(3A)...O(5), N(4)–H(4B)...O(4) and N(5)–H(5A)...O(6) angles of 160.2°, 169.2°, 147.3° and 152.4°, respectively. The intermolecular interactions N(6)–H(6A)...O(6) (Table 2) form bifurcated acceptor hydrogen bonds that generate R₂¹(6) ring motifs. The C14–N6 and C14–N5 bond lengths in the propeller-shaped guanidinium cation are almost equal [1.308(2) and 1.315(3) Å respectively], indicating that the usual model of electron delocalization is observed in this moiety. In the crystal packing structure (Fig. 5), all guanidinium hydrogen atoms participate

in intermolecular hydrogen bonds. The morphology of the GUNP crystal showed that it has a polyhedral shape with 16 symmetrical facets as shown in Fig. 6. The crystallographic planes (001), (00–1), (010), (0–10), (0–11), (011), (0–1–1), (01–1), (111), (1–11), (11–1), (1–1–1), (–1–1–1), (–11–1), (–111) and (–1–11) are clearly identified. It is observed that the growth rate of the GUNP crystal along the 'b'-axis is higher than those of the 'a' and 'c'-axes.

3.2. UV–vis–NIR spectral study

A UV–vis transmission spectrum of a GUNP crystal was recorded in the range 190–900 nm using a T90+ PG instrument spectrophotometer. The crystal has a sufficient transmission in the visible and NIR regions (Fig. 7). The lower cut-off wavelength of GUNP was found to be 505 nm and the absorption was due to the promotion of an electron from a 'non-bonding' (lone-pair) *n* orbital to an 'anti-bonding' π orbital designated as π^* ($n \rightarrow \pi^*$). No characteristic absorption was observed in the visible region. From the fundamental absorption at 505 nm, the band gap energy of the material is calculated from the standard formula [13] and is found to be 2.42 eV (Fig. 8).

3.3. Photoluminescence study

Fluorescence may be expected generally in molecules that are aromatic or contain multiple conjugated double bonds with a high degree of resonance stability. The emission spectra of GUNP were recorded using a FP-6500 spectrofluorometer. The recorded

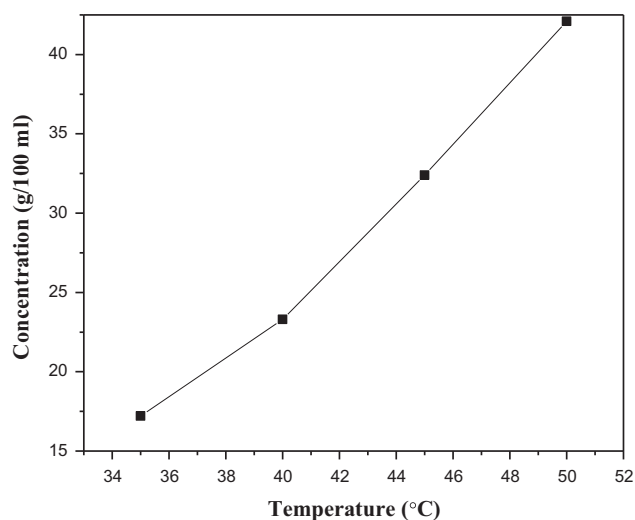


Fig. 2. Solubility curve of GUNP in methanol.

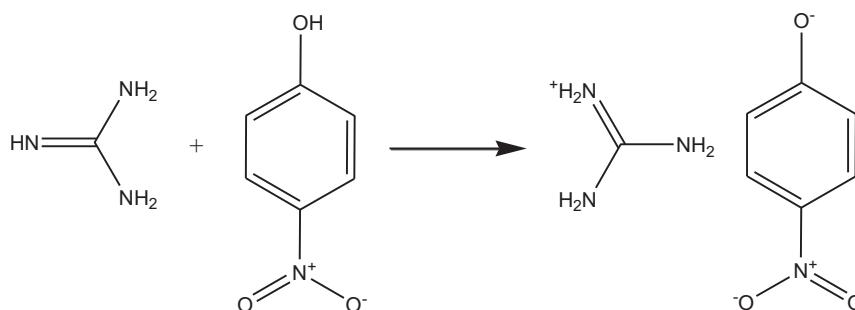


Fig. 1. Reaction scheme of GUNP.

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