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A combined experimental and quantum chemical analysis to explore the nonlinear optical activity of guanidinium L-monohydrogen tartrate

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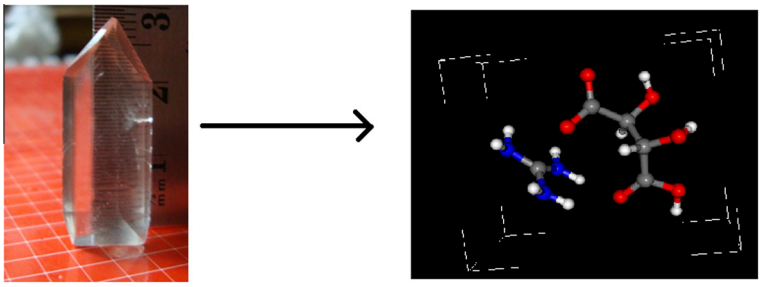
HIGHLIGHTS

- Optically transparent GuHT crystal was grown.
- Second harmonic generation nonlinearity was 0.5 times of KDP.
- NLO parameters have been calculated and compared.
- HOMO–LUMO analysis was performed.

GRAPHICAL ABSTRACT



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ABSTRACT

Single crystal of guanidinium L-monohydrogen tartrate (GuHT) was grown by slow evaporation technique and was characterized by single crystal X-ray diffraction to confirm its crystal structure. UV–vis spectral study reveal that the GuHT crystal is optically transparent and its band gap was estimated from the transmittance data. The laser induced surface damage threshold study was carried out for the grown crystal using Nd:YAG laser. The second harmonic generation (SHG) nonlinearity of the grown crystalline sample was measured by Kurtz and Perry powder technique. The optimized molecular geometry, first order hyperpolarizability, dipole moment and polarizability of GuHT were obtained by density functional theory (DFT) using B3LYP/6-31G (d,p) level of basis set. The thermodynamic functions of the title compound was computed. The HOMO–LUMO energy gap explains the charge transfer interactions that take place within the molecule.

Introduction

Organic nonlinear optical (NLO) crystals have been greatly investigated in recent years due to their rapid response in electro-optic effect compared to inorganic materials and high nonlinearities. The organic nonlinear optical crystals play a major role in electro-optic modulation, second harmonic generation, frequency mixing, optical parametric oscillation etc. [1,2]. Organic NLO materials offer the potential of relatively low-power laser-driven nonlinear optical system due to their optical properties, such as fast optical response time, non-resonant susceptibility and high second harmonic generation (SHG) nonlinearity compared to inorganic materials. Moreover the specific advantage of organic materials over inorganic materials is that the properties of organic compound can be easily tailored using molecular engineering and chemical synthesis [3]. Organic materials possess large second order molecular polarizabilities (β), more versatile for synthetic manipulations and are more amenable to structural variations. Many strategies for forming acentric structures showing SHG have been followed and hydrogen bonded networks appear to be the most exciting among all these approaches [4]. Thus the attention of researchers is focused especially on the group of hydrogen bonded solids that exhibits potential non-linear optical

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properties. Guanidine cation is a strong base which may be easily protonated by most organic and inorganic acids because of the presence of six potential donor sites for hydrogen bonding interactions. Thus, the guanidine compounds are potential materials for nonlinear optical applications. Some potential guanidinium based NLO materials synthesized with L-tartaric acid via strong hydrogen bond interactions are aminoguanidinium (1+) hydrogen L-tartrate monohydrate [5], guanidinium L-tartrate monohydrate [6]. These organic compounds show good nonlinear optical (NLO) efficiency due to the presence of π bonds, which help in the molecular engineering for the tailor made applications. Such materials of optical interest were reported previously from our laboratory namely guanidinium 4-nitrobenzoate [7], bis guanidinium hydrogen phosphate monohydrate [8] and guanidinium 3-nitrobenzoate [9]. In this present investigation, we report on the synthesis, structural, linear and nonlinear optical properties, laser damage threshold and quantum chemical analyses of guanidinium L-monohydrogen tartrate (GuHT) crystals.

Experimental procedure

Material synthesis

The analytical reagent (AR) grade guanidine carbonate (Himedia) and L-tartaric acid (Merck) were used for synthesizing the title salt. The title compound was synthesized in the stoichiometric 1:2 ratio by using the following reaction,

$$[C(NH_2)_3]_2 \cdot CO_3 + 2C_4H_6O_6 \rightarrow 2[C(NH_2)_3 \cdot C_4H_5O_6] + H_2O + CO_2 \uparrow$$

The calculated amount of L-tartaric acid was first dissolved in Millipore water of resistivity 18.2 MΩ/cm with continuous stirring using a magnetic stirrer. The calculated amount of guanidine carbonate was added to this solution until effervescence ceased. The resulting solution was stirred for 6 h in order to achieve homogeneity at room temperature. The purity of the synthesized salt was improved by successive recrystallization process. The recrystallized salt was dissolved in water at room temperature and optically transparent crystal of GuHT was grown by slow evaporation method. The grown GuHT crystal as harvested after 24 days is shown in Fig. 1.

Characterization

The single crystal X-ray diffraction (SXRD) analysis was carried out for GuHT crystal using ENRAF NONIUS – CAD 4 X-ray diffractometer to study its unit cell dimensions and morphology. The UV–vis transmittance spectrum for GuHT crystal was recorded in the wavelength range from 200–800 nm to determine its optical transmittance range using LabIndia Model UV 3092 Spectro-photometer. The laser induced surface damage threshold study was carried out for the grown crystal using Nd:YAG laser. The second harmonic generation nonlinearity of GuHT was measured using Kurtz and Perry technique.

Computational details

The DFT calculations were performed on a Pentium IV personal computer using the Gaussian-03W program package [10]. The molecular structure of GuHT was optimized using B3LYP, hybrid function consisting of Becke's three-parameter non-local exchange function with the correlation function of Lee et al. [11]. In order to obtain accurate geometry and to calculate nonlinear optical parameters like polarizability, dipole moment and first order hyperpolarizability, B3LYP/6-31G (d,p) basis set was employed.

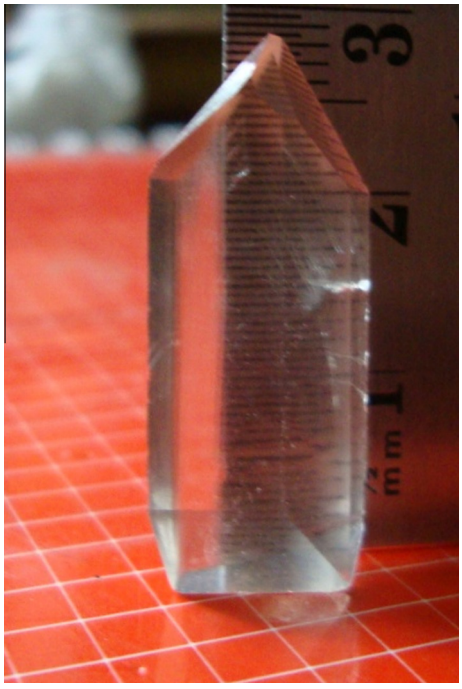

Fig. 1. Photograph of as grown GuHT single crystal.

Results and discussion

Single crystal X-ray diffraction analysis

The good quality single crystal of GuHT was subjected to single crystal X-ray diffraction analysis in order to reveal its unit cell parameters, space group and crystal system. It is observed that the GuHT crystal belongs to orthorhombic crystal system with non-centrosymmetric $P2_12_12_1$ space group. The unit cell parameters are, a = 11.346 (3) Å, b = 11.157 (3) Å, c = 6.669 (3) Å and was found to be in good agreement with the reported data [12].

Prediction of crystal morphology

The morphology of GuHT crystal exhibits seven well developed faces out of which (0 0 1) is more prominent plane and is shown in Fig. 2.

UV–vis – spectral analysis

The optical property of the GuHT crystal was studied by UV–vis spectral analysis. The UV–vis spectrum of the title compound was recorded in the range 200–800 nm using a cut and polished crystal sample of thickness 2 mm. The UV–vis transmission spectrum of the GuHT crystal is depicted in Fig. 3. It is to be noted, that the

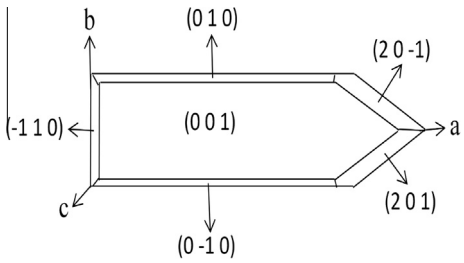

Fig. 2. Morphology of GuHT crystal.