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Synthesis, growth and characterization of a new nonlinear optical crystal: Glycinium hydrogen squarate (GHS)

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ABSTRACT

Single crystals of glycinium hydrogen squarate (GHS) have been successfully synthesized and purity of the material has been increased by repeated recrystallization process. Single crystals were grown by slow evaporation solution growth technique using water and ethanol as solvents at room temperature. Then the grown crystal was characterized by different techniques for finding its suitability for device fabrications. The grown crystal was characterized by single crystal XRD, powder XRD, FT-IR, UV–Vis–NIR, ^{1}H NMR, ^{13}C NMR, SHG and DTA/TGA analyses respectively. From the single crystal XRD diffraction, the crystal system was identified as monoclinic. The presence of functional groups were identified by FT-IR analysis. The UV transparency cut-off wavelength of the grown crystal occurs at 342 nm. ^{1}H NMR and ^{13}C NMR spectroscopic studies were employed to elucidate the structure of the grown crystal. The second harmonic generation efficiency test by Kurtz–Perry technique showed positive result. The decomposition temperature of the grown crystal was studied by DTA/TGA analysis. The results observed from the characterization analyses show its suitability for NLO applications.

1. Introduction

Nonlinear optical (NLO) materials are used in electro-optic switching elements for telecommunication, optical information processing, optical parametric oscillator, degenerate four wave mixing, optical disk data storage, laser remote sensing, laser driven fusion, colour display and medical diagnostic, etc. [1]. The NLO process requires materials that manipulate the amplitude, phase, polarization and frequency of optical beams. At present, the aim is to develop materials satisfying all the technological requirements such as wide transparency range, fast response, and high damage threshold [2]. It is well known that certain classes of organic compounds show very high NLO and electro-optical effects. The linearity is based on molecular units, containing donor and acceptor groups at the opposite ends of the molecule which produces dipolar structure [3]. It has been long recognized that the electronic structure and the strength of donor and acceptor groups are responsible for achieving large molecular hyperpolarizabilities. Optimization of polarizability on molecular level is directed towards the synthesis of chromophores exhibiting intense low-lying absorption maxima with high dipoles of the charge transfer transition and large difference between ground and excited state dipole moments. These molecular parameters could be used as characteristics for their NLO potential [4].

The interest towards squaric acid derivatives is dictated both by the numerous potential fields of applications and by the simplicity of their pattern for theoretical investigations. Squaric acid (3,4-dihydroxy-3-cyclobutene 1,2-dione) is a typical two dimensional hydrogen bonded system with large isotope effect [5]. The transfer of hydrogen atom from its equilibrium position is responsible for second harmonic generation (SHG) in squaric acid. The SHG intensity is relatively strong and seems to increase linearly at temperature below about 340 K [6]. A new nonlinear optical material known as glycinium hydrogen squarate (GHS) has been synthesized and the characteristics of the grown crystals have been studied by different instrumentation methods.

2. Experimental details

Glycine and squaric acid (AR grade) were used as starting materials for growing GHS single crystals. Glycine and squaric acid were dissolved separately in deionized water and ethanol in the ratio 1:1 and were mixed together to prepare a supersaturated solution. This solution is filtered twice to ascertain the growth of pure crystals. Crystal growth process was carried out in an aqueous medium. The

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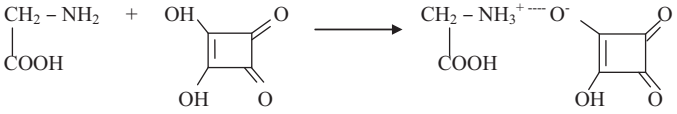
Fig. 1. Photograph of GHS crystal.

scheme of the reaction involved is depicted below:



The saturated solution was maintained in an undisturbed condition and the beaker was covered with a polythene paper. A few holes were made on the polythene cover to facilitate slow evaporation. By adopting the solution growth method, single crystals of glycinium hydrogen squarate (GHS) were grown from the supersaturated solution at room temperature. Glycine interacts with squaric acid through a single N—H—O hydrogen bond. The solution was periodically inspected and on the 25th day, the crystal started growing. Further, the crystal was permitted to grow for another 20 days in order to obtain a nominal size suitable for characterization. The single crystals of dimension upto 10 mm × 3 mm × 2 mm were harvested and the photograph of GHS crystal is shown in Fig. 1.

3. Characterization

The lattice parameters and the crystal systems have been determined using single crystal X-ray diffraction analysis (Model: Bruker AXS Kappa APEX II single crystal CCD diffractometer) and the result is compared with powder X-ray diffraction analysis (Rich Seifert diffractometer). The functional groups presented in the title compound have been identified from the FTIR analysis using KBr pellet technique in the region from 400 cm^{-1} to 4000 cm^{-1} (Bruker IFS 66V model FTIR spectrometer). Optical behaviour of GHS was measured by Perkin Elmer Lambda 35 UV-VIS-NIR Spectrophotometer in the wavelength range of 190–1100 nm. The ^{1}H NMR and ^{13}C NMR of the grown sample have been taken using Bruker 300 MHz ultrashield NMR spectrometer. The SHG test was carried out using Kurtz–Perry technique. The thermal stability of GHS was studied by thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) by using SDT Q600 V8.3 Build 101 thermal analyzer instrument ranging from room temperature to 1100 °C at a heating rate of 20 °C per minute under nitrogen atmosphere.

4. Results and discussion

4.1. Single crystal XRD

Precise single crystal X-ray diffraction data for the GHS crystal was collected using X-ray diffractometer equipped with graphite monochromated Mo(Kα) (λ = 0.7107 Å) radiation. The observed results indicate that the crystal belongs to monoclinic crystal system and the determined unit cell parameters are given below in a comparative statement:

Comparative statement for lattice parameters of glycine, squaric acid and GHS crystals.

Crystal	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Crystal system
Glycine	6.996	6.996	5.471	90	90	120	Hexagonal
Squaric acid	6.13	5.27	6.14	90	90	90	Tetragonal
GHS	16.78	8.27	15.73	90	100	90	Monoclinic

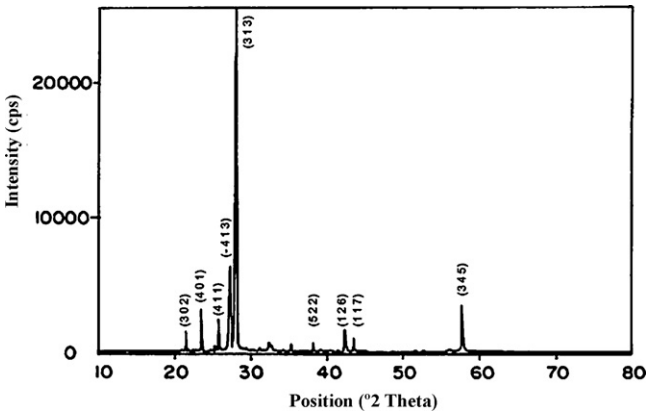


Fig. 2. Powder XRD of GHS crystal.

Table 1
The cell parameters of GHS crystal.

XRD	a (Å)	b (Å)	c (Å)	α (°)	β (°)	γ (°)	Volume (Å³)
Single crystal	16.78	8.27	15.73	90	100.39	90	2147
Powder	16.81	8.27	15.75	90	100.22	90	2155

4.2. Powder XRD analysis

Powder X-ray diffraction analysis of grown GHS crystals have been carried out using Rich Seifert diffractometer with Cu Kα (λ = 1.54060 Å) radiation on crushed powder of GHS crystals. The recorded powder X-ray pattern is shown in Fig. 2. The differences in amplitude of the peak can be attributed to the difference in grain size and orientation of the powdered grains of GHS crystal. The observed diffraction pattern is indexed by Reitveld index software package. These lattice parameters calculated by Reitveld unitcell software package are compared with cell parameters observed from single crystal X-ray diffraction method and tabulated in Table 1. The data obtained by powder XRD analysis are in accordance with the single crystal XRD data. The values of *h*, *k*, *l* and 2*θ* values are stacked in Table 2.

Table 2
Powder XRD data of GHS crystal.

Position 2θ	d-spacing (Å)	(h k l)
21.3592	4.1601	(3 0 2)
23.3386	3.8115	(4 0 1)
25.6290	3.4759	(4 1 1)
27.2138	3.2769	(−4 1 3)
27.8582	3.1999	(3 1 3)
32.4115	2.7626	(−3 1 5)
35.2786	2.5441	(1 3 2)
38.1194	2.3608	(5 2 2)
42.3941	2.1321	(1 2 6)
43.5519	2.0781	(1 1 7)
55.7455	1.6490	(4 0 8)
57.6359	1.5980	(3 4 5)