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# Growth and physical characterization of organic nonlinear optical single crystal: N,N′-diphenylguanidinium formate

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ABSTRACT

A second-harmonic generation (SHG) crystal N,N′-diphenylguanidinium formate (DPGF) with good quality was successfully grown by the slow evaporation method. Single crystal X-ray diffraction study confirms that the DPGF crystallizes in orthorhombic crystal system with space group $P2_1cn$. The powder XRD pattern shows the various planes of DPGF crystal. The $^{1}H$ and $^{13}C$ NMR spectral studies further confirm the molecular structure of the grown crystal. The various functional groups present in the grown crystal have been identified by Fourier transform infrared spectroscopy. The UV–vis–NIR spectrum was recorded to find the optical transmittance window, lower cut off wavelength and band gap of the DPGF crystal. Photoluminescence spectrum shows broad emission peak observed at 367 nm. Thermal stability of the title crystal was evaluated by thermogravimetric (TG) and differential thermal analysis. Vicker's microhardness study was carried out to reveal the mechanical properties of the grown crystal. The second harmonic conversion efficiency of DPGF crystal was 1.8 times than that of KDP crystal. Gaussian 03 W program has been used to calculate the molecular orbital and first order hyperpolarizability of the molecule. The calculated first order hyperpolarizability value of DPGF is found to be 16 times greater than that of urea.

## 1. Introduction

The potential applications of organic non-linear optical material towards electro-optic modulation and frequency conversion field have received a great deal of interest in the recent decades [1,2]. The inestimable stretchability of organic molecules enables them to designing, tuning and acquiring novel nonlinear optical (NLO) materials [3]. The high electronic susceptibility and large response time make the organic nonlinear optical materials more effective than inorganic materials [4,5]. Large optical nonlinearity and low cut off wavelengths in UV region are some of the essential properties of organic crystals which are mandatory for nonlinear optical devices [6]. The formation of “push-pull” conjugated structure in organic molecules along with remarkable nonlinear optical activity is strongly expected, due to the presence of π-electron conjugated moiety substituted by electron acceptor group on one end of the conjugated structure and electron donor group on the another end. The ground state charge asymmetry of the molecule required for second-order nonlinearity and it is provided by the donor and acceptor groups [7,8]. These charge transfer interactions together with intermolecular hydrogen bonding increases the hyperpolarizability (β), and hence improves the second harmonic generation (SHG) property of the molecule [9,10].

Guanidine is a strong base material which has been widely used in many applications include materials science, biological and medicinal chemistry. Their derivatives are widely used as antibacterial in medicine and as vulcanization in rubber industry [11–13]. Further guanidine and its derivative crystal show very good nonlinear optical property [14]. N,N′-diphenylguanidine (DPG) is a family of guanidine crystals which exhibit better non-linear optical properties and commonly used as an accelerators for the vulcanization of rubber prepared for manufacture of tires, footwear etc. [15]. N,N′-diphenylguanidinium nitrate, N,N′-diphenylguanidinium dihydrogen phosphate and N,N′-diphenylguanidinium hydrogen(+)-L-tartrate are some of the diphenylguanidine based single crystals which are reported to be second harmonic generation (SHG) active [16–18].

Paixao et al., reported the crystal structure of N,N′-diphenylguanidinium formate (DPGF) in 1999 [19]. To the best of our knowledge, there was no further reports are available for this material. We have successfully grown N,N′-diphenylguanidinium formate single crystal and report their structural, optical, spectral, thermal and non-linear

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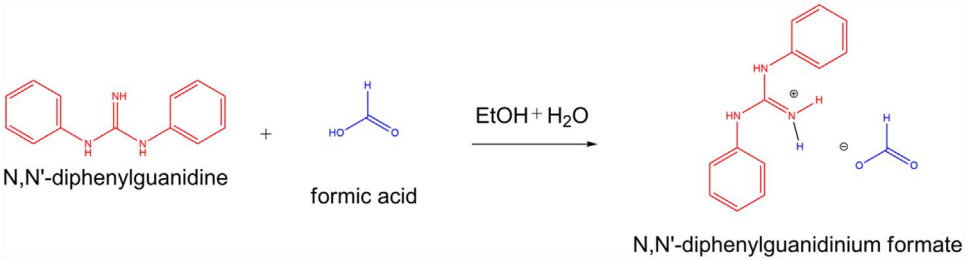


**Fig. 1.** Chemical reaction scheme of DPGF.

optical properties for the first time. In addition to these the molecular orbitals and first order hyperpolarizability calculations were performed using Gaussian 03 program to calculate its charge distribution and nonlinear activity.

## 2. Experimental procedure

### 2.1. Solubility and crystal growth

The DPGF compound was synthesized by taking equimolar ratio of N,N′-Diphenylguanidine and Formic acid dissolved in an ethanol-water solution, (because DPG shows less solubility in water) whose reaction scheme is shown in Fig. 1. The synthesized material was further purified by successive recrystallization process in an ethanol-water mixed solvent.

The solubility study of DPGF in ethanol-water mixed solvent was assessed as a function of temperature in the range between 30 and 45 °C. The experiment was performed in a constant temperature bath with a cryostat facility, where the solute concentration was analyzed gravimetrically. The DPGF exhibits a positive solubility temperature gradient and the solubility increases linearly with temperature shown in Fig. S1. To grow DPGF single crystals, slow evaporation solution growth technique was employed. Saturated solution of DPGF was prepared at room temperature and stirred for two hours to get a homogeneous mixture. The prepared solution will be filtered using Whatman filter paper and placed in a 100 ml beaker. The beaker was covered with an aluminium foil with a hole at the center to control the rate of evaporation. Fig. 2 shows the grown DPGF single crystal of dimensions 8×4×1 $mm^3$ harvested after the period of 45 days. The morphology of a grown crystal is shown in Fig. S2.

## 3. Results and discussion

### 3.1. Single crystal X-ray diffraction

The Unit cell parameters of the grown DPGF crystal were collected at room temperature using Enraf-Nonius CAD4 diffractometer with MoKα radiation. From the single crystal XRD analysis, it is confirmed that the grown crystal belongs to orthorhombic system with a space group $P2_1cn$ and its unit cell values are a=6.374(3) Å, b=12.532(3) Å, c=16.636(1) Å, α=β=γ=90°, V=1328.8(2) $Å^3$. These values are in good agreement with the reported value [19] shown in Table 1.

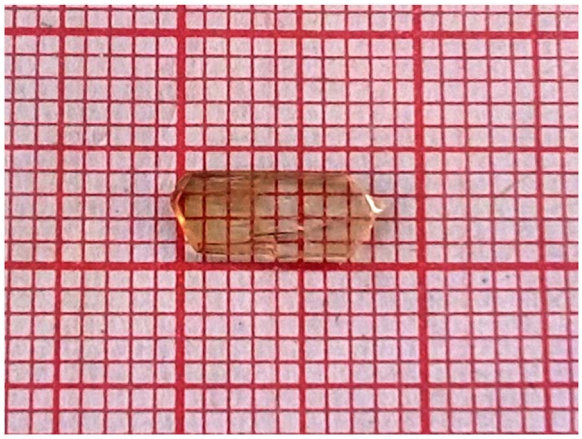

**Fig. 2.** Photograph of DPGF crystal.

**Table 1**
XRD result of reported and present study of DPGF crystal.

| Parameter | Reported result (17) | Present result |
|---|---|---|
| a (Å) | 6.363(4) | 6.374(3) |
| b (Å) | 12.535(4) | 12.532(3) |
| c (Å) | 16.641(3) | 16.636(1) |
| α | 90.00° | 90.00° |
| β | 90.00° | 90.00° |
| γ | 90.00° | 90.00° |
| Volume ($Å^3$) | 1327.3(3) | 1328.8(2) |
| System | Orthorhombic | Orthorhombic |
| Space group | $P2_1cn$ | $P2_1cn$ |

### 3.2. Powder X-ray diffraction

The grown DPGF single crystal was uniformly crushed into a powder form and then subjected to powder X-ray diffraction. PAN analytical X-pert pro diffractometer with $CuK_\alpha$ (λ=1.540 Å) radiation were used for obtaining XRD Pattern of the above mentioned sample. The obtained two-theta values for various planes of reflection were indexed using MERCURY software package [20]. The experimental and simulated powder X-ray diffraction pattern is shown in Fig. 3. In accordance with the chemical bonding theory of a crystal growth system [21], the sharp and well defined peaks signify the good crystalline nature of the compound.

### 3.3. $^1H$ and $^{13}C$ NMR spectral analysis

The crystallized compound was characterized by $^1H$ NMR and $^{13}C$ NMR spectroscopy using Bruker 300 MHz spectrometer in a deuterated DMSO solvent for the confirmation of molecular structure. The $^1H$ NMR and $^{13}C$ NMR spectra of the title compound are shown in Figs. 4 and 5 respectively. The sharp singlet at δ 8.36 ppm clearly indicates the presence of formate proton and also the compound does not have any aliphatic protons. The $^1H$ NMR spectrum shows that all peaks were present in the aromatic region. The set of protons around the region δ 7.1 ppm to δ 7.3 ppm indicating the presence of two phenyl rings and also one of the amine NH appeared in this region. Remaining amino protons are labile in nature (it may/may not appear in $^1H$ NMR). ($^1H$ NMR (300 MHz, DMSO) δ 8.36 (s, 1 H), 7.39 (s, 1 H), 7.35 (d, *J*=7.6 Hz, 4 H), 7.25 (d, *J*=7.6 Hz, 4 H), 7.14 (t, *J*=7.3 Hz, 2 H)).

Similarly, the $^{13}C$ NMR also confirms the compound contains only aromatic carbons. The peak appeared at δ 167.80 ppm indicates the presence of carboxylate carbon. The peak appeared at δ 153.16 ppm indicates the presence of guanidine carbon. The total number of carbon signals is 6. This is exactly matching with carbon count of crystallized compound. The structure of the crystallized compound is confirmed