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G Saravana Kumar, R Roop Kumar, P Murugakoothan. A Combined Experimental and Theoretical Investigations on N, N'- Diphenylguanidine Based Single Crystals For Nonlinear Optical Applications . Mechanics, Materials Science & Engineering MMSE Journal. Open Access, 2017, 9, 10.2412/mmse.96.99.996 . hal-01504668

HAL Id: hal-01504668

<https://hal.science/hal-01504668>

Submitted on 10 Apr 2017

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A Combined Experimental and Theoretical Investigations on N, N'-Diphenylguanidine Based Single Crystals For Nonlinear Optical Applications

G. Saravana Kumar¹, R. Roop Kumar², P. Murugakoothan^{1, a}

1 – MRDL, PG and Research Department of Physics, Pachaiyappa's College, Chennai-600030, India

2 – Birla Institute of Technology and Science, Pilani, Dubai Campus, Dubai, United Arab Emirates

a – murugakoothan03@yahoo.co.in



DOI 10.2412/mmse.96.99.996 provided by Seo4U.link

Keywords: crystal growth, single crystal XRD, density functional theory (DFT), nonlinear optical materials (NLO).

ABSTRACT. Good quality N,N'-Diphenylguanidine based nonlinear optical single crystals were grown by slow evaporation technique. The cell parameters and space group were confirmed by single crystal X-ray diffraction analysis. The UV-vis study was carried out to assess the transmittance of the title crystals. The optical band gap was determined from the UV-vis analysis. The HOMO-LUMO analysis was carried out using DFT calculations. The presence of second harmonic generation (SHG) was confirmed by Kurtz-Perry powder technique. The existence of microscopic nonlinear optical property was investigated using DFT analysis. The laser and mechanical stability was studied by laser damage threshold (LDT) and Vicker's microhardness analysis.

Introduction. Nonlinear optical (NLO) materials have attracted and are gaining enormous demand due to their wide applications in the recent technologies, like optoelectronics, lasers, data storage systems and optical communications. In addition to their large NLO response, the advantage of organic materials is that they offer high degree of synthetic flexibility to tailor their optical properties through structural modification [1]. Guanidinium derivatives are of great biological importance due to its presence as the functional group of amino acid arginine, the muscular energy-intermediate creatine, the pyrimidine bases of DNA, and a number of other biologically active molecules [2]. Guanidine and its derivatives are now gaining importance in the field of nonlinear optics [3]. Computational methods are important tools to provide prior information on the structure dependent nonlinear optical response of the molecules and several properties of interest. In this present investigation, we are reporting the crystal growth, structural analysis, linear and nonlinear optical properties, laser damage threshold (LDT) and mechanical properties of N,N'-Diphenylguanidine based series of crystals namely N,N'-diphenylguanidinium nitrate (DPGN), N,N'-diphenylguanidinium hydrogen(+)-L-tartrate monohydrate (DPGTM) and N,N'-diphenylguanidinium dihydrogen phosphite (DPGP) along with the Density Functional Theory (DFT) analysis for linear and nonlinear optical properties.

Experimental Procedure. The single crystals of DPGN, DPGTM and DPGP were synthesized using analytical grade N,N'- diphenylguanidine and the corresponding acids namely, nitric acid, L-tartaric acid and phosphorus acid in stoichiometric ratio (1:1) by slow evaporation technique. The synthesized salt was purified by successive recrystallization. For the synthesis and growth of DPGN single crystal, the calculated amount of N,N'- diphenylguanidine and nitric acid were dissolved using methanol. However for the case of DPGTM and DPGP a mixed solvent of ethanol+water in an equimolar ratio of 1:1 was used. The respective solutions were allowed to stir well in order to obtain homogeneity. The solutions were filtered, transferred to a beaker and was covered with aluminium foil and kept

undisturbed. Good quality single crystals of DPGN, DPGTM and DPGP were harvested after a period of 40, 96 and 36 days respectively and the photographs are shown in Fig. 1.

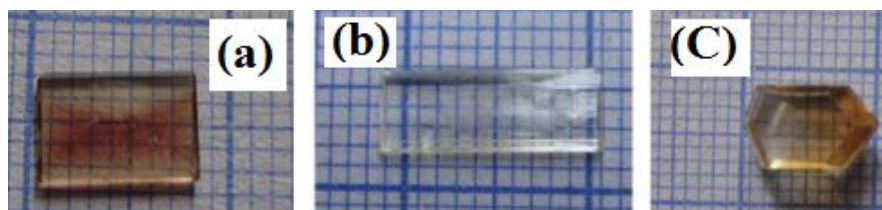


Fig. 1. As grown single crystal of (a) DPGN, (b) DPGTM and (c) DPGP.

Characterization technique. The single crystal X-ray diffraction analysis of the grown N,N'-Diphenylguanidine series of crystals was carried out using ENRAF NONIUS CAD4 automatic X-ray diffractometer with $\text{MoK}\alpha(\lambda = 0.7170 \text{ \AA})$ radiation. UV-vis transmission spectrum was recorded using VARIAN CARY 5E UV-vis spectrophotometer. The second harmonic generation nonlinearity of N,N'-diphenylguanidine based crystals in the present work was studied by Kurtz-Perry powder test. An actively Q-switched Nd:YAG laser in TEM_{00} mode with pulse width 10 ns and repetition rate 10 Hz was used for the laser induced damage threshold study. Selected smooth and flat surface of the grown crystals was subjected to micro hardness study at room temperature using Vicker's hardness tester (LEITZ WETZLER). The theoretical calculations for microscopic linear and nonlinear optical properties were carried out using DFT by employing GAUSSIAN 03 W computational software.

Results and discussion.

Structural analysis. The single crystal X-ray diffraction study reveals that the DPGN and DPGTM crystals belong to orthorhombic crystal system with $Pna2_1$ and $P2_12_12_1$ as space group, and the DPGP crystal belongs to tetragonal crystal system with $P4_3$ as space group. The unit cell parameters and space group of DPGN, DPGTM and DPGP agrees well with the reported data [4, 5, 6]. Geometry optimization of DPGN, DPGTM and DPGP was carried out from the X-ray experimental atomic position Crystallographic Information File (CIF) of the corresponding structure and then all other calculations engaging density functional theory (DFT) were performed by the resultant optimized structural parameters. The optimized structures of DPGN, DPGTM and DPGP are shown in Fig. 2.

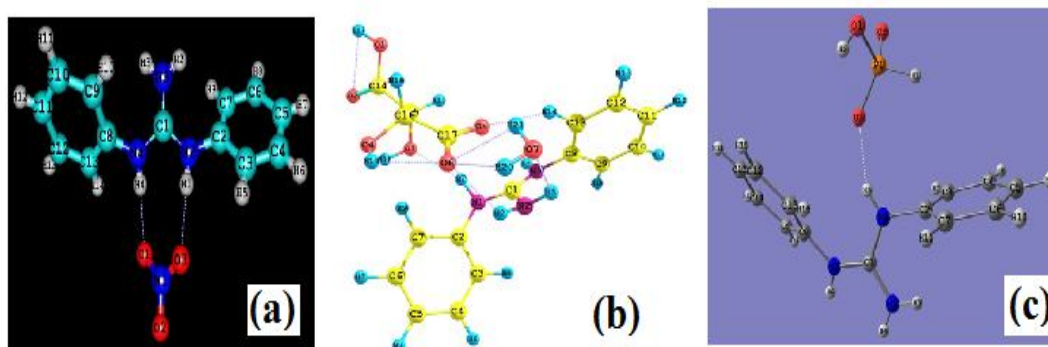


Fig. 2. Optimized geometrical structure of (a) DPGN, (b) DPGTM and (c) DPGP.

Linear optical properties. The transmission range of the as grown N,N'-diphenylguanidine crystals, was determined by recording the optical transmission spectrum in the wavelength range 200 - 800 nm. The polished crystals of thickness 2 mm were used for this measurement. The transmittance

spectra of DPGN, DPGTM and DPGP are shown in Fig.3. The cut-off wavelengths of DPGN, DPGTM and DPGP were found to be 310 nm, 298 nm and 294 nm respectively. The percentage of transmission of about 56%, 76% and 70% for DPGN, DPGTM and DPGP is attributed to better quality of the grown crystals. The Tauc's graph plotted between the square of the product of absorption coefficient and the incident photon energy $(\alpha h\nu)^2$ with the photon energy $(h\nu)$ at room temperature shows a linear behavior and was used to determine optical band gap value for the title crystals by extrapolation of the linear portion near the onset of absorption edge to the energy axis and are shown in Fig. 4.

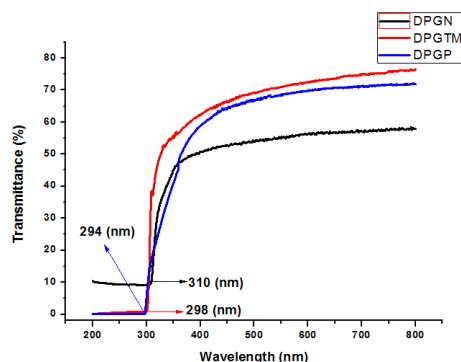


Fig. 3. UV-vis transmission spectra.

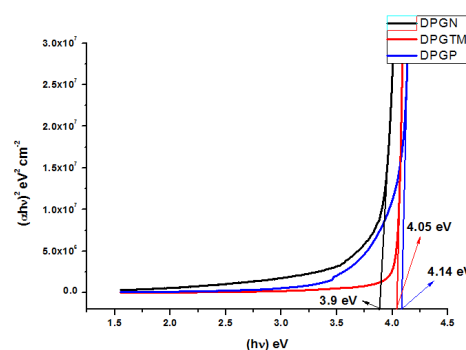


Fig. 4. Tauc's plot between $(\alpha h\nu)^2$ and $(h\nu)$.

HOMO – LUMO analysis. The molecular structure of DPGN and DPGP was optimized using B3LYP, hybrid function consisting of Becke's three-parameter non-local exchange function with the correlation function of Lee, Yang and Parr employing B3LYP/6-31G (d, p) basis set. However for DPGTM the same level of theory was employed with B3LYP/6-31G (d) as basis set. The HOMO – LUMO analysis was carried out for DPGN, DPGTM and DPGP from their corresponding optimized molecular structure. The HOMO–LUMO energy gaps are 4.87 eV, 5.04 eV and 5.34 eV for DPGN, DPGTM and DPGP respectively. The HOMO – LUMO plots of DPGN, DPGTM and DPGP are shown in Fig. 5. (a), (b) and (c) respectively.

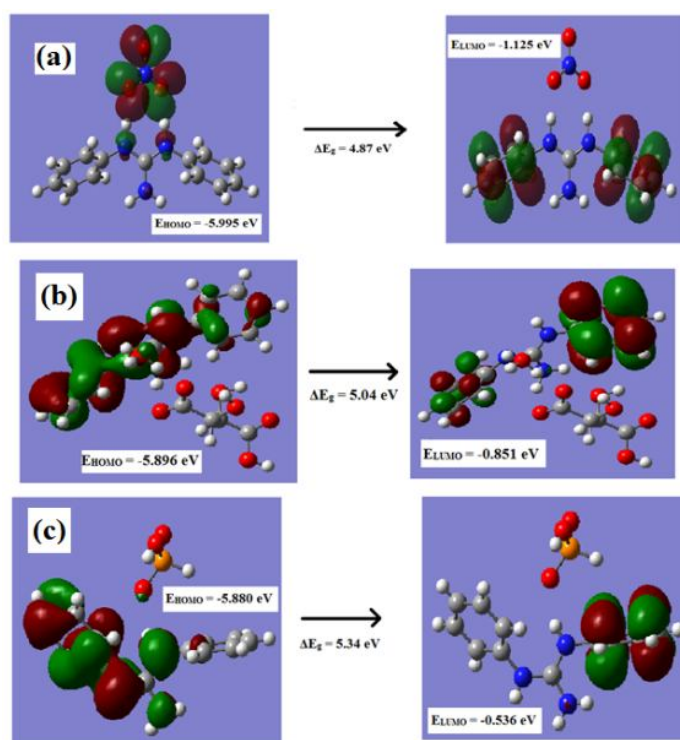


Fig. 5. HOMO – LUMO plots of (a) DPGN, (b) DPGTM and (c) DPGP.

Nonlinear optical study

The second harmonic generation nonlinearity of the as-grown N,N'-diphenylguanidine based crystals in the present work was studied by Kurtz – Perry powder test [7]. A fundamental beam from Q-switched Nd: YAG laser ($\lambda = 1064$ nm) was passed through the powder sample of grown crystals. The SHG behavior is confirmed from the output of the laser beam which had bright green emission ($\lambda = 532$ nm) from the powder sample. The second harmonic signals of 14.2 mV, 14 mV and 15.2 mV were obtained for DPGN, DPGTM and DPGP powder crystalline samples respectively, for an input energy of 5 mJ/pulse, while the standard potassium dihydrogen phosphate (KDP) powder crystal sample gave a SHG signal of 15.4 mV for the same input energy. It shows that the SHG effective nonlinearities of DPGN, DPGTM and DPGP are 0.92, 0.90 and 0.98 times respectively that of standard NLO material KDP.

Nonlinear optical calculations

In a medium, the nonlinear optical effects arise when the medium interact with the electromagnetic field of intense laser beam. Since the Gaussian 03 output values of the polarizability and the hyperpolarizability tensors components are reported in atomic units (a.u.), the calculated values have been converted into electrostatic units (esu) [$\alpha : 1$ a.u. = 0.1482×10^{-24} esu ; $\beta : 1$ a.u. = 8.3693×10^{-33} esu]. The computed values of dipole moment (μ_i), polarizability (α), first order hyperpolarizability (β_{tot}) of DPGN, DPGTM and DPGP compounds with B3LYP/6-31 G (d,p), B3LYP/6-31 G (d), B3LYP/6-31 G (d,p) basis set are presented in Table. 1.

Table 1. Computed Nonlinear optical parameters.

Parameters	DPGN	DPGTM	DPGP
Dipole moment ($\mu_{i (tot)}$)	10.421 D	4.3552 D	9.9678 D
Polarizability (α_{tot})	21.95×10^{-24} esu	26.17×10^{-24} esu	21.01×10^{-24} esu
First order hyperpolarizability, (β_{tot})	84.052×10^{-31} esu	30.2353×10^{-31} esu	27.057×10^{-31} esu

This high value of (β) and the non-zero value of (μ_i) are responsible for the enhancement of second harmonic generation properties of the title compounds at molecular level.

Laser induced damage threshold study. The laser parameters, such as energy, wavelength, pulse duration, longitudinal and traverse mode structure, beam size and location of beam are the factors on which the laser damage threshold depends upon [8]. A well-polished sample of the grown crystals with clean surface and prominent face was subjected to the multiple shot (10 shots per second) LDT study. Energy density or energy fluence is a measure used to describe the energy delivered per unit area. The energy density of the input laser beam for which the crystal gets damaged was recorded using a power meter. The radius of laser beam was 1 mm. The energy density was calculated using the formula, Energy density = E / A , where, E the input energy (mJ) and A the area of the circular spot (mm) expressed in J/cm². The energy fluence of DPGN, DPGTM and DPGP were found to be 20.7, 13.1 and 6 J/cm² respectively.

Microhardness analysis. The hardness measurement for DPGN, DPGTM and DPGP crystals was carried out on their prominent planes respectively. The micro hardness value was calculated using the relation, $H_v = 1.8544 (P/d^2)$ kg/mm². The micro hardness measurements were made for the applied loads varying from 5 to 35 g by keeping the constant dwell time of 3 s for all cases. A plot between the hardness number and load for the grown crystals are shown in Fig. 6.

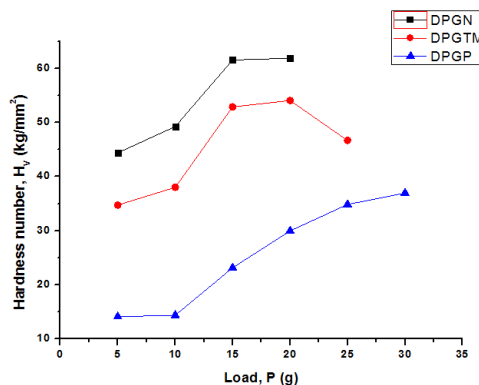


Fig. 6. Plot of hardness number vs. load.

We clearly infer from the Fig.6., that the micro hardness number increases with increasing the load. This trend is in agreement with the reverse indentation size effect (RISE). The load above these values develops multiple cracks on the crystal surface due to the release of internal stresses generated locally by indentation.

Summary. Optically good quality single crystals of DPGN, DPGTM and DPGP were grown by slow evaporation technique. The single X-ray diffraction (SXRD) study confirms that the title crystals are crystallized in non-centrosymmetric space group. The DFT was employed to optimize the structural geometry of the title compounds and was found to be true without any negative frequencies. The percentage of transmission, the transparency range and the band gap energy of the grown crystals were determined from UV-vis transmittance analysis. The title crystals are high band gap energy compounds with good transmission in the entire visible region. The HOMO – LUMO band gap were computed. All the grown crystals are found to be NLO active and SHG nonlinearity is almost equivalent to that of KDP. The nonlinear optical parameters, such as dipole moment, polarizability and first order hyperpolarizability were computed in order to understand NLO behaviour at molecular level. The laser damage threshold and Vicker's micro hardness study confirm that the grown crystals exhibit higher stability to laser and mechanically stress.

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Cite the paper

G. Saravana Kumar, R. Roop Kumar, P. Murugakoothan, (2017). [A Combined Experimental and Theoretical Investigations on N,N'-Diphenylguanidine Based Single Crystals For Nonlinear Optical Applications](#). *Mechanics, Materials Science & Engineering*, Vol 9. [10.2412/mmse.96.99.996](#)