Synthesis, Spectral analysis, Optical and Thermal properties of new organic NLO crystal: N,N'-Diphenylguanidinium Nitrate (DPGN)

G. Saravana Kumar, P. Murugakoothan

PII: S1386-1425(14)00632-5
DOI: http://dx.doi.org/10.1016/j.saa.2014.04.059
Reference: SAA 12023

To appear in: *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*

Received Date: 20 November 2013
Revised Date: 6 March 2014
Accepted Date: 7 April 2014

Please cite this article as: G. Saravana Kumar, P. Murugakoothan, Synthesis, Spectral analysis, Optical and Thermal properties of new organic NLO crystal: N,N'-Diphenylguanidinium Nitrate (DPGN), *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy* (2014), doi: http://dx.doi.org/10.1016/j.saa.2014.04.059

Synthesis, Spectral analysis, Optical and Thermal properties of new organic NLO crystal: N,N'-Diphenylguanidinium Nitrate (DPGN)

*Saravana Kumar.G, Murugakoothan. P**

MRDL, PG & Research Department of Physics, Pachaiyappa's College, Chennai – 600 030, India

Abstract

A new organic NLO material N,N'-Diphenylguanidinium Nitrate (DPGN) single crystal was grown by slow evaporation technique using methanol as solvent. Single crystal X-ray diffraction and powder X-ray diffraction experiments were carried out in order to confirm the structure and crystalline nature of DPGN crystal. Wide band gap of 3.9 eV with transmittance of 57% up to 800 nm is observed for the grown crystal using UV–vis spectral analysis. The chemical bonding and presence of various functional groups were confirmed by the FT-IR and FT-Raman spectral studies. The thermal behavior of DPGN crystal was analyzed by simultaneous TG-DTA studies. The second harmonic generation (SHG) nonlinearity of the grown crystal was measured by Kurtz and Perry powder technique and was found to be comparable with that of the standard reference material potassium dihydrogen phosphate (KDP) crystal.

Keywords: Powder X-Ray diffraction, Spectral analysis, nonlinear optical material.

*Corresponding author. Tel.: 91-944 444 7586.

E-mail address: murugakoothan03@yahoo.co.in (P.Murugakoothan).

1. Introduction

Nonlinear optical materials find a number of applications, like frequency conversion, light modulation, optical switching and optical memory storage. Recent researches reveal that the organic nonlinear optical materials are used for developing relatively low power laser-driven nonlinear optical system. They exhibit less optical response time but high second harmonic generation (SHG) efficiency compared to that of inorganic materials [1, 2]. The development of optical devices, such as photonic integrated circuitry, depends strongly on the design of highly efficient nonlinear optical (NLO) materials. Among the different types of NLO materials, organic materials are shown to be superior to their inorganic counter parts in terms of synthesis, crystal fabrication, potential to create large devices and much faster optical nonlinearities [3]. Guanidinium family complexes have been chosen for study as potential material for nonlinear optics. Guanidine is an important compound that has many biological, chemical and medical applications [4]. Guanidine as well biguanide, can be employed in material engineering of a promising class of NLO compounds based on salts combining a cation derived from a polarizable organic molecule with an anion capable of forming hydrogen bonded crystal structures [5]. Thus the attention of researchers is focused especially on the group of hydrogen bonded solids that exhibits potential non-linear optical properties. Some potential guandinium based NLO materials synthesized with L-tartaric acid via strong hydrogen bond interactions are aminoguanidinium (1+) hydrogen L-tartrate monohydrate [6], guanidinium L-tartrate hydrate [7]. Keeping this in mind we have focused on the substituted guanidine family, i.e., N,N'-Diphenylguanidine (DPG) which is also known as melaniline that have been widely used as a primary and secondary accelerator in the vulcanization of rubber. In this context, herein we report on the synthesis, spectral analysis, optical and thermal properties of new organic NLO crystal: N,N'-Diphenylguanidinium Nitrate (DPGN).

2. Experimental Procedure

2.1 Material synthesis

The title compound was synthesized by mixing equimolar portions of N,N'-Diphenylguanidine and nitric acid using methanol as solvent. At first the starting material, nitric acid was dissolved in methanol and then further N,N'-Diphenylguanidine was added to this solution, by continuous stirring, until complete neutralization occurred resulting in a pale brown colored solution. The solution was made to stir for 6 hours using a magnetic stirrer in order to achieve homogeneity at room temperature and the resulting solution was filtered in a 500 mL clean borosil beaker through Whatmann filter paper. The beaker was covered with aluminium foil in order to control the rate of evaporation. The purity of the synthesized salt was further improved by successive recrystallization. The reaction scheme is given in Fig.1. A well defined pale brown colored transparent single crystal of DPGN was harvested after a period of 46 days and the photograph of the as grown DPGN crystal is shown in Fig.2.

2.2 Characterization studies

The single crystal X-ray diffraction data of N,N'-Diphenylguanidinium Nitrate was obtained using ENRAF NONIUS CAD-4 single crystal X-ray diffractometer. X-ray powder diffraction analysis of DPGN crystal was carried out using Rich Seifert diffractometer with CuKα (λ = 1.5405 Å) radiation over the range of 10–70^{o} at a scanning rate of 1^{o}/min. The optical transmission spectrum was recorded in the wavelength region 200–800 nm using Varian Carry

SE model spectrometer. FT-IR and FT- Raman spectra were recorded to elucidate the chemical bonding and molecular structure of DPGN. The FT-IR spectrum was recorded in the range 400–4000 cm^{-1} by PERKIN-ELMER spectrometer using the KBr pellet technique. FT- Raman spectrum was recorded using FT-RAMAN spectrometer (Perkin-Elmer GX 2000) in the range 4000-400 cm^{-1}. Thermo gravimetric and differential thermal analysis was carried out using NETZSCH STA 409 thermal analyzer instrument in nitrogen atmosphere at a heating rate of 10^{o}C/min. in the temperature range of 30 – 500 ^{o}C. The second harmonic generation nonlinearity was measured using Kurtz and Perry technique.

3. Results and Discussions

3.1 X-ray diffraction analysis

The single crystal X-ray diffraction analysis of DPGN was carried out to evaluate the crystal system, space group and the cell parameters. It is observed that the DPGN belongs to orthorhombic crystal system with space group $Pna2_1$ and the measured cell parameters were a = 16.97 Å, b = 13.89 Å, c = 5.79 Å, V = 1364 $Å^3$and $\alpha = \beta = \gamma = 90^{o}$. The obtained cell parameters and cell volume are found to be in good agreement with the reported value [8]. X-ray powder diffraction pattern of DPGN is shown in Fig. 3. The presence of prominent Bragg peaks at specific 2θ angles in the powder X-ray diffraction confirms the perfect crystalline nature of DPGN crystal.

3.2 UV-vis-spectral analysis

UV-vis spectral study gives important structural information because absorption of UV and visible light involves promotion of the electrons in π and σ orbital from the ground state to higher energy states [9]. The UV-vis transmission spectrum of DPGN crystal sample was recorded in the range of 200 – 800 nm using a polished crystal sample of thickness 1.5 mm.

Title compound is found to be active in the UV region having a transmittance of about 57% with the lower cut-off wavelength of 310 nm. The recorded optical transmittance spectrum is shown in Fig.4. It is well known that the parameters, such as optical transmittance range and lower cutoff region are important to tailor the material for optical applications. The spectrum shows that there are no significant absorptions in the range of 310 – 800 nm. The transmission window in the visible region enables good optical transmission of the second harmonic frequencies of Nd:YAG laser.

The measured transmittance was used to calculate the absorption coefficient (α) using the relation:

$$\alpha = \frac{2.3026}{t}\log\left(1/T\right) \qquad (1)$$

where T is the transmittance and t is the thickness of the crystal sample.

In the high photon energy region, the energy dependence of absorption coefficient suggests the occurrence of direct band gap of the crystal obeying the following equation for high photon energies $(h\nu)$ [10]

$$(\alpha h\nu)^2 = A\left(E_g - h\nu\right) \qquad (2)$$

where α is the absorption coefficient, h is the Planck's constant, A is a constant, ν is the frequency of the incident photon and E_g is the optical band gap.

The Tauc's graph [11] plotted between $(\alpha h\nu)^2$ and the photon energy $(h\nu)$ is shown in Fig.5. The band gap of the crystal was evaluated by extrapolating the linear part of the graph to the energy axis and is found to be 3.9 eV. The wide band gap of DPGN crystals confirms the large transmittance in the visible region.

3.3 Spectral analysis

The chemical bonding of the grown compound were analyzed by recording FT-IR and FT-Raman spectra. The spectral analysis of DPGN was carried out on the characteristic group vibrations of guanidinium groups, nitrate ions and phenyl rings. The FT-IR and FT-Raman spectra of DPGN compound were presented in Fig.6 and Fig.7. The vibrational frequency of various functional groups of DPGN and the frequency assignments are presented in Table 1.

Hydrogen Bond

The very broad nature of the spectrum in the region above 3000 cm^{-1} in IR clearly shows the strong hydrogen bond interactions between the anions and cations. The hydrogen bond interaction paves way for the second harmonic generation.

Guanidinium vibrations

The high frequency absorption peak at 3352 cm^{-1} and 3223 cm^{-1} in IR are assigned to NH_2 asymmetric and symmetric stretching mode respectively. The characteristic band observed at 995 cm^{-1} in the Raman spectrum is assigned to the symmetric C-N stretching vibrations. The IR counterpart is observed as very weak intensity at 1002 cm^{-1}. The band observed in IR spectrum at 1645 cm^{-1} is assigned to the asymmetric C-N stretching mode. In Raman spectrum a weak band corresponding to this type of vibration is observed at 1662 cm^{-1}. The very strong band at 1582 cm^{-1} in the IR spectrum arises from the NH_2 bending vibrations. The Raman counter parts for these vibrations appear at 1547 cm^{-1}. The bands at 1092 cm^{-1} and 1087 cm^{-1} in the IR and Raman spectra corresponds to the NH_2 rocking in-plane vibrations.

Phenyl ring vibrations

The phenyl ring is a cyclic group of atoms with formula C_6H_5. Phenyl groups have six carbon atoms bonded together in a hexagonal planar ring, five of which are bonded to individual hydrogen atoms, with the remaining carbon bonded to a substituent. The phenyl group vibrations are assigned on the basis of C-C, C-H vibrations. Though the title compound has two mono substituted phenyl rings there are no separate vibrations for the both. The C-H stretching frequencies of the monosubstituted benzene are expected in the region 3010 – 3120 cm^{-1} [12]. The very strong band at 3070 cm^{-1} in the IR spectrum is attributed to the C-H stretching of the phenyl rings. The Raman counter part of this vibration occurs at 3071 cm^{-1}. The strong intensity band at 1158 cm^{-1} in IR spectrum is assigned to the in-plane C-H bending of monosubstituted benzene ring. The Raman counterpart is found to occur at 1159 $cm^{-1}$with strong intensity. The allowed vibrational frequencies arising from the C-H out of plane bending vibrations of the monosubstituted benzene ring are expected in the region 1000 – 650 cm^{-1} [12] . The medium band observed at 883 cm^{-1} in IR is assigned to the C-H out of plane bending vibrations. The Raman counterpart arising from this vibration is found to occur with a strong intensity at 884 cm^{-1}. The C-C stretching modes of vibrations are expected in the range 1300 cm^{-1} [12]. The strong intensity band at 1306 cm^{-1} in Raman is assigned to the C-C stretching mode of vibration. The IR counterpart for this mode is found to occur at 1307 cm^{-1} with very strong intensity.

Nitrate ions

The presence of nitrate anions in the title compound can be confirmed by the presence of characteristic vibrations arising due to N-O stretching and the in-plane and out of plane bending vibrations of nitrate ions. The N-O stretch of nitrate groups appears as an intense band in the region between 1400 and 1340 cm^{-1}. The in-plane and out of plane bending vibrations of the nitrate groups appear in the region around 720 cm^{-1} and 840 – 810 cm^{-1}[13]. The very strong intensity band at 1385 cm^{-1} in IR spectrum is assigned to the N-O stretching. The very strong IR intensity at 754 cm^{-1} and weak band at 754 cm^{-1} is assigned to the N-O in plane bending vibrations. The strong band occurring at 825 cm^{-1} is arising due to N-O out of plane bending vibrations. The IR and Raman spectrum of DPGN consists of the characteristic vibrations of both the cation and anion and thus it can be claimed that the title compound are not separate entities but it is N,N'-Diphenylguanidinium Nitrate.

3.4 Thermal Properties

The thermal stability of DPGN was studied by thermo gravimetric (TG) and Differential thermal analyses (DTA). The DPGN sample weighing 10.672 mg was analysed and the thermogram is depicted in Fig.8. The DTA curve indicates the same changes as shown in TG curve. From the TG curve, it is evident that the material is stable up to 196 °C and moisture free. The DTA curve shows an endothermic peak at 196 °C, no weight loss in TG, which can be attributed to the melting point of the sample. The compound starts to decompose around, 200 °C. The TG curve shows two stages weight loss pattern when the material was heated from 34 to 500 °C. The first major weight loss was occurred between the temperatures 200 and 258 °C with the elimination of 40.18 % of the material into gaseous products as seen in the low temperature region. The second stage weight loss noticed between the temperatures 268 and 498 °C experiences a weight loss of about 27.95%. The residue left out at the end is about 31.87% by weight at 498.1 °C. This may be due to the residual carbon mass at the end of the decomposition reactions as the theoretical elemental analysis shows that the percentage of carbon in the title compound is nearly 56.93%. From the above discussions it can be concluded that the DPGN crystals can be used for NLO applications till 196 °C.

3.5 Nonlinear optical study

The effectively valuable tool for screening materials for second harmonic generation is the Kurtz-Perry powder technique [14]. This technique enables to measure the second harmonic generation non-linearity of the materials with respect to standard reference material Potassium dihydrogen phosphate (KDP). A fundamental beam of wavelength 1064 nm with pulse duration of 10 ns and frequency repetition of 10 Hz from Q-switched Nd:YAG laser was used as the source and passed through the powder sample. The SHG behavior was confirmed from the output of the laser beam which had bright green emission ($\lambda = 532$ nm) from the powder sample. The SHG output was converted into electrical signal and was displayed on a digital storage oscilloscope. The optical signal incident on photomultiplier tube was converted into voltage output. The second harmonic signal of 14.2 mV was obtained for DPGN powder crystal sample 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 nonlinearity of DPGN is 0.92 times that of standard NLO material KDP.

4. Conclusions

A new organic nonlinear optical DPGN single crystal has been grown by slow evaporation technique at room temperature using methanol as solvent. The unit cell parameters have been evaluated by single crystal XRD technique. The good crystalline nature of DPGN powdered sample was confirmed by powder XRD analysis. The DPGN crystal exhibits good optical transparency in the entire visible region of UV–vis spectrum. The optical band gap of the grown crystal has been calculated as 3.9 eV. The chemical bonding and the presence of various functional groups was elucidated using FT-IR and FT-Raman spectral analyses. The thermal stability of DPGN has been analyzed by simultaneous TG-DTA studies and it reveals that the title compound can be used for NLO applications till 196°C. The powder SHG analysis reveals that the nonlinearity of this crystal is 0.92 times that of KDP. The promising crystal growth, characteristics and properties of DPGN crystal nominate it as a potential material for photonics, electro-optics and SHG devices applications.

Acknowledgements

The authors acknowledge Prof. P. K. Das, Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore for extending the laser facilities for the SHG measurement. Authors also acknowledge SAIF, IIT, Chennai for providing the analytical instrument facilities.

References

1. M. Kitazawa, R. Higuchi, M. Takahashi, Appl. Phys. Lett. 64 (1994) 2477-2479.
2. W.S. Wang, M.D. Aggarwal, J. Choi, T. Gebre, A.D. Shields, B.G. Penn, D.O. Frazier, J. Cryst.Growth 198 (1999) 578-582.
3. G. Jordon, T. Kobayashi, WJ. Blau, S. Pfeiffer, H.H. Horhold, Adv. Func. Mater. 13 (2003) 751–754.
4. T. Arumanayagam and P. Murugakoothan, Mater. Lett. 65 (2011) 2748-2750.
5. C.B. Aakeroy, P.B. Hitchcock, B.D. Moyle, and K.R. Seddon, J. Chem. Soc. Chem. Commun. 2 (1993) 152-156.
6. Z. Machova, I. Nemec, K. Teubner, P. Nemec, P. Vanek, Z. Micka, J. Mol. Struct. 832 (2007) 101– 107.

7. W. Krumbe, S. Haussühl, R. Fröhlich, Zeitschrift fur Kristallographie 187 (1989) 309–318.
8. J. A. Paixao, P. S. Pereira Silva, A. Matos Beja, M. Ramos Silva and L. Alte da Veiga, Acta Cryst. C54 (1998) 805-808.
9. S. Masilamani, A. Mohamed Musthafa, Microchemical Journal 110 (2013) 749–752.
10. A. Ashour, N. El-Kadry, S.A. Mahmoud, Thin Solid Films 269 (1995) 117–120.
11. J. Tauc, R. Grigorovici, A. Vancu, Phys. Status Solidi B 15 (1966) 627–637.
12. C. James, V.S. Jayakumar, I. Hubert Joe, J. Mol. Struct. 830 (2007) 156-166.
13. B.C. Smith, Infrared Spectral interpretations: A systematic Approach, CRC press, LLC, 1999.
14. S.K. Kurtz and T.T. Perry, J. Appl. Phys. 39 (1968) 3798–3813.

Figure captions

Fig.1. Chemical reaction scheme
Fig.2. Photograph of as grown DPGN single crystal
Fig.3. Powder X-ray diffraction pattern of DPGN
Fig.4. Optical transmittance spectrum of DPGN crystal
Fig.5. Plot of $(\alpha h\nu)^2$ vs. photon energy of DPGN crystal
Fig.6 FT-IR spectrum of DPGN
Fig.7. FT-Raman spectrum of DPGN
Fig.8. TG-DTA thermogram of DPGN

Table captions

Table.1. Vibrational band assignments of DPGN

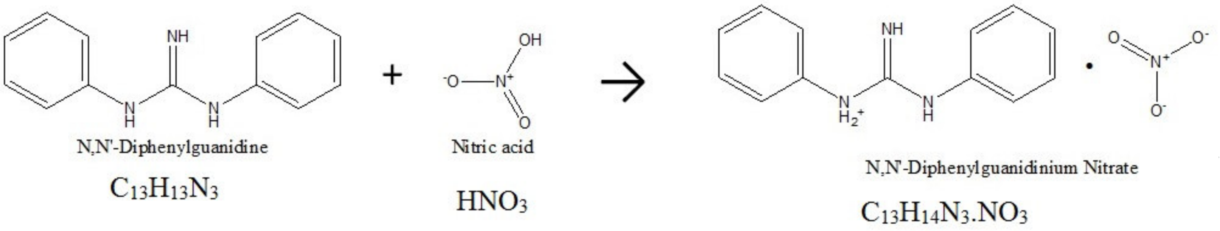


Fig.1. Chemical reaction scheme

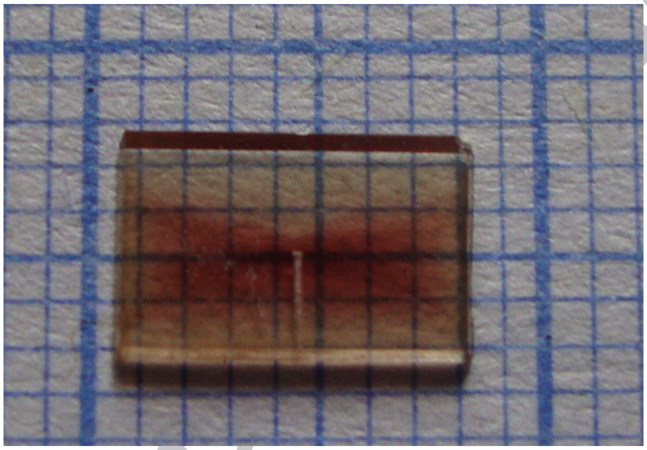


Fig.2. Photograph of as grown DPGN single crystal

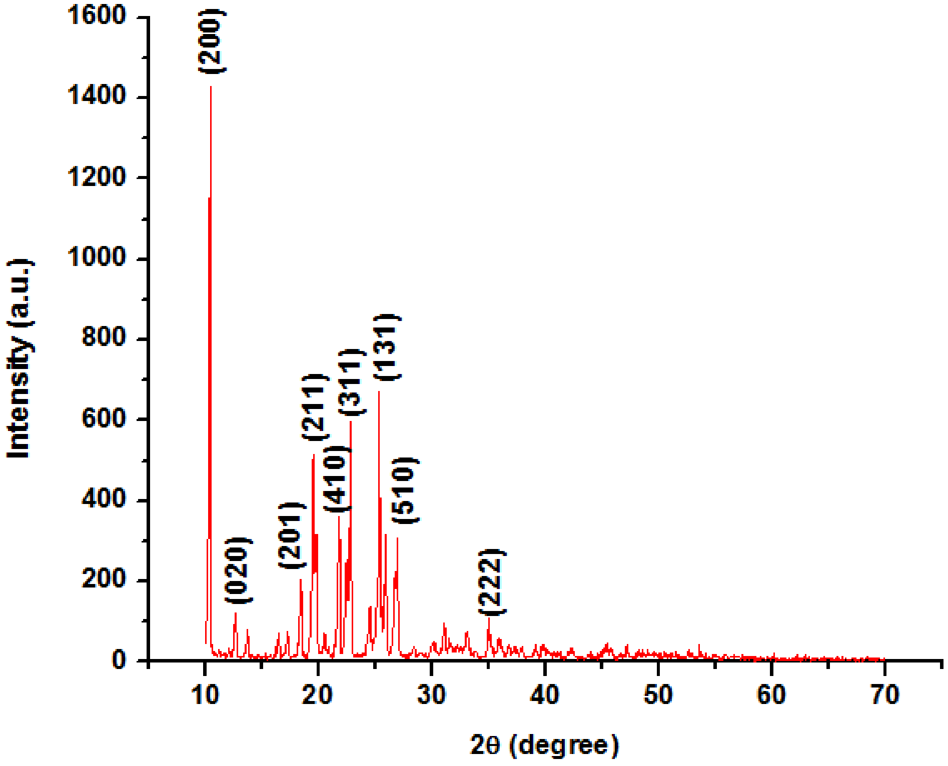


Fig.3. Powder X-ray diffraction pattern of DPGN

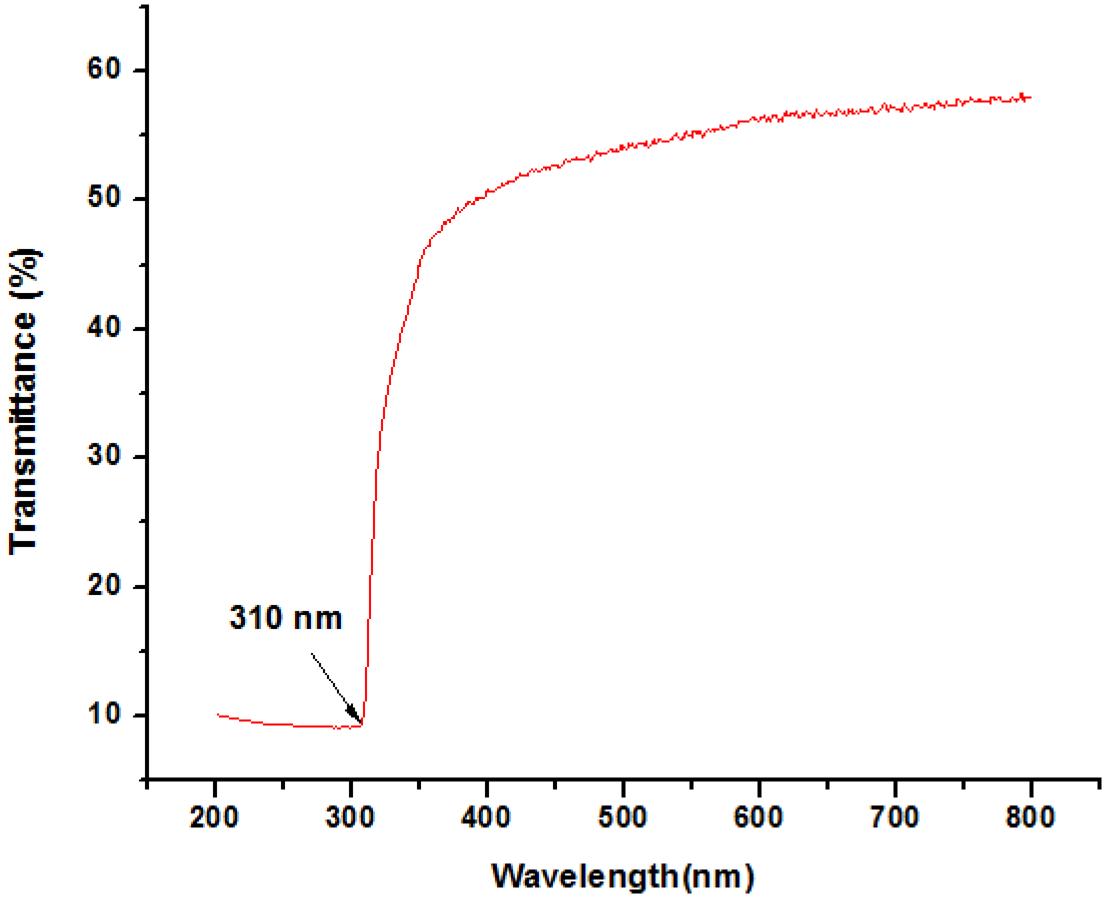


Fig.4. Optical transmittance spectrum of DPGN crystal

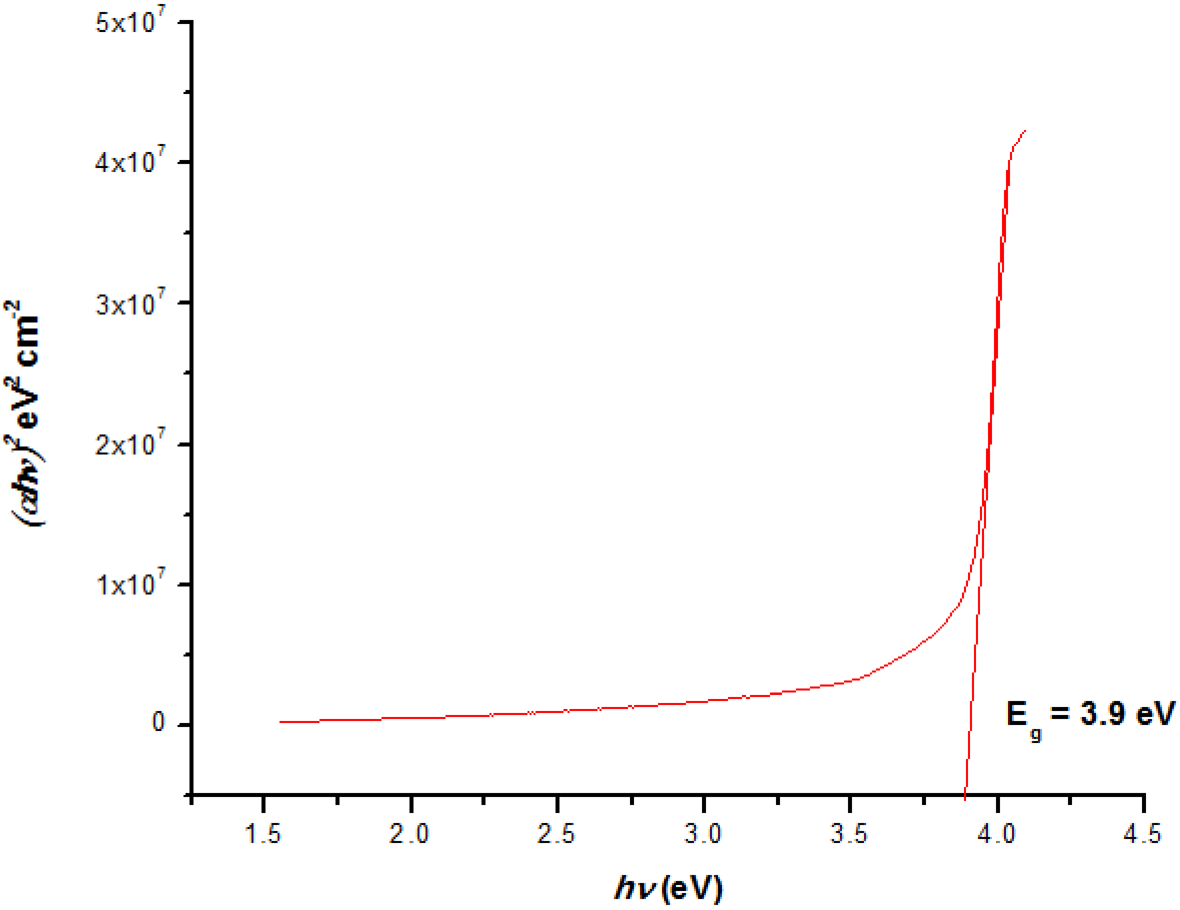


Fig.5. Plot of $(\alpha h\nu)^2$ vs. photon energy of DPGN crystal

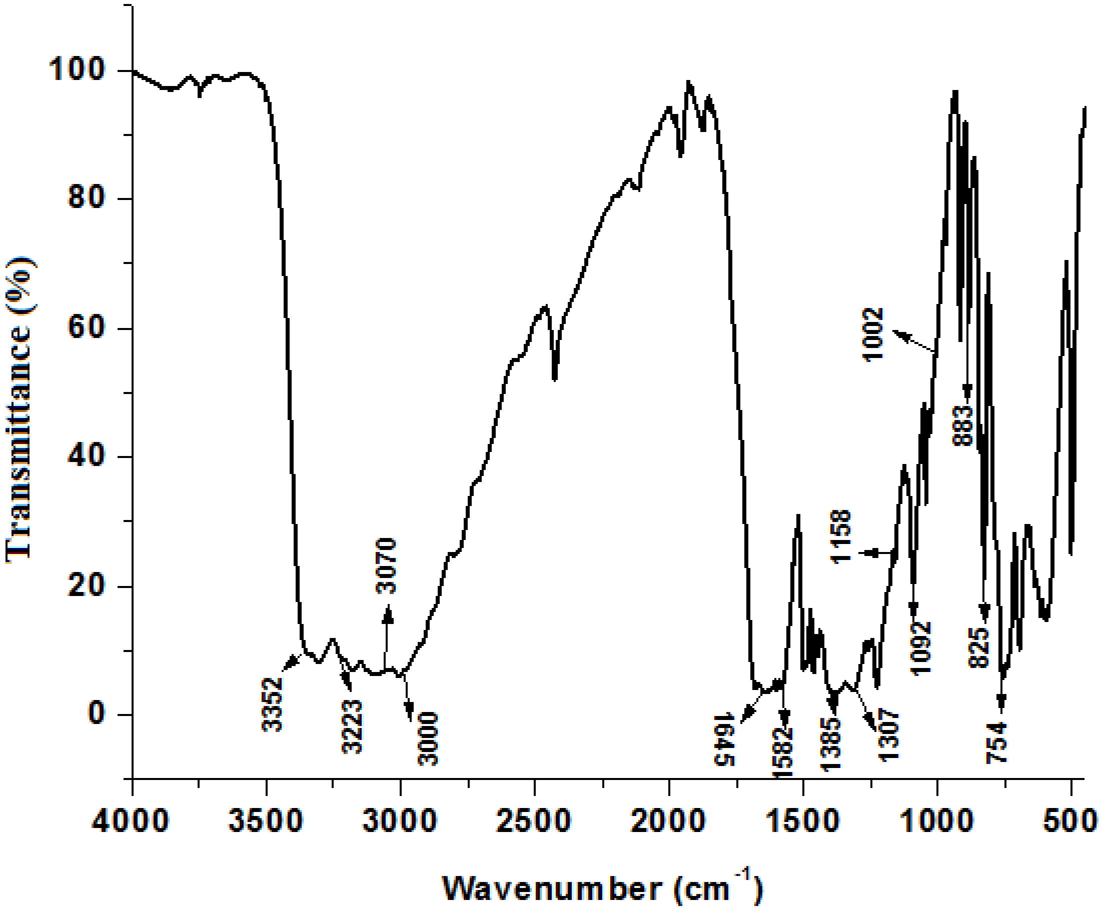


Fig.6. FT-IR spectrum of DPGN

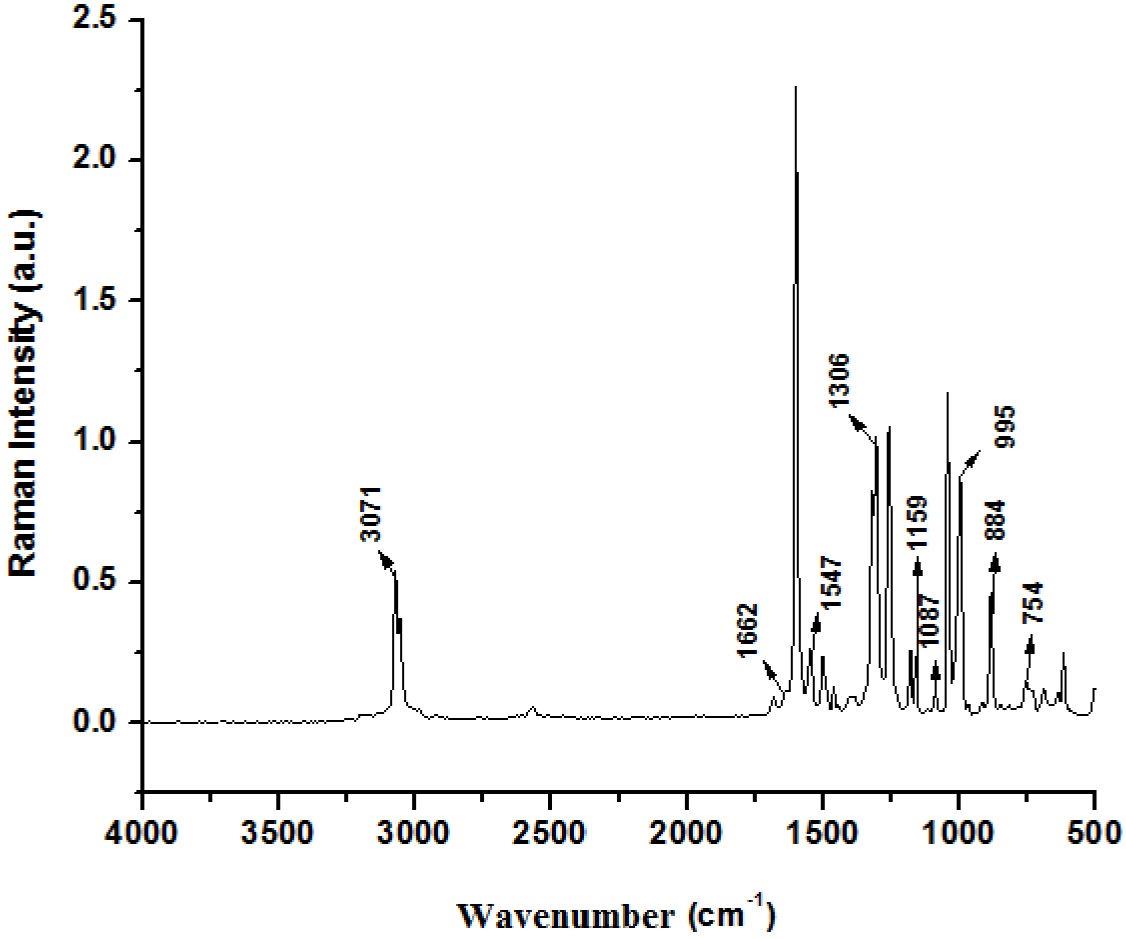


Fig.7. FT-Raman spectrum of DPGN

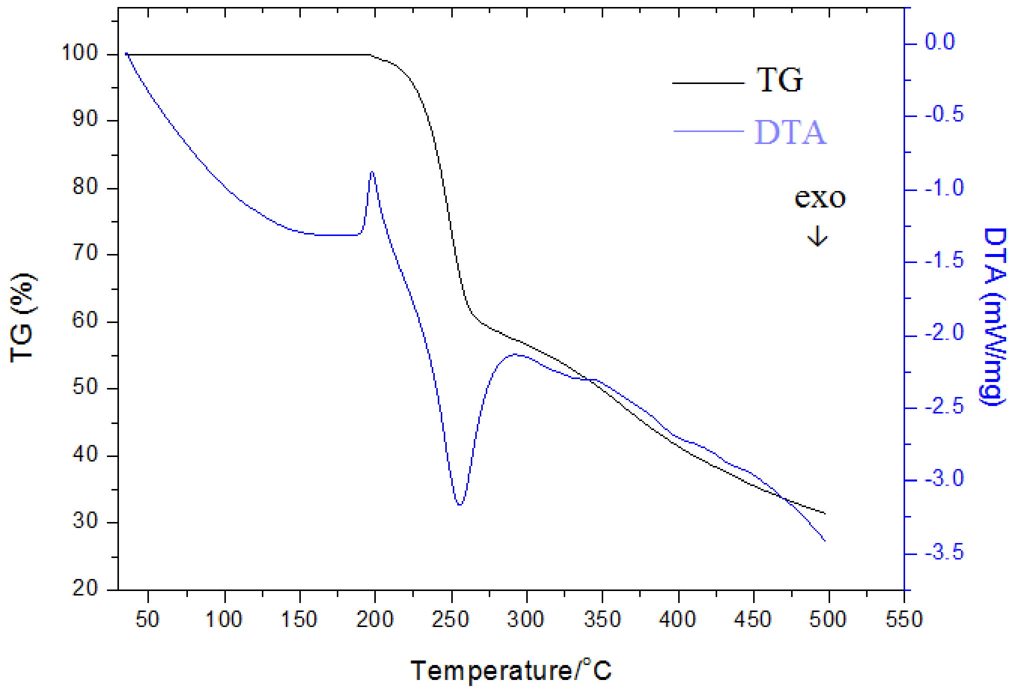
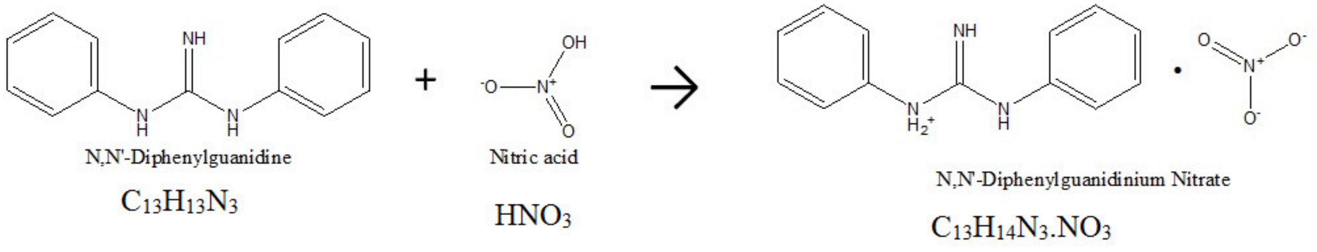


Fig.8. TG-DTA thermogram of DPGN

Table.1. Vibrational band assignments of DPGN

FT-IR	FT-Raman	Vibrational assignments
3352	-	NH_2 Asymmetric stretching
3223	-	NH_2 Symmetric stretching
3070	3071	C-H stretching of the phenyl rings
1645	1662	Asymmetric C-N stretching
1582	1547	NH_2 bending vibrations
1385	-	N-O stretching of Nitrate
1307	1306	C-C stretching of Phenyl rings
1158	1159	in-plane C-H bending of Phenyl ring
1092	1087	NH_2 rocking in-plane vibrations
1002	995	C-N symmetric stretching
883	884	out-of plane C-H bending of Phenyl ring
825	-	N-O out of plane bending of Nitrate
754	754	N-O in plane bending of Nitrate

Graphical abstract



Highlights

- High quality DPGN crystal was grown.
- DPGN crystal exhibit good thermal stability
- Nonlinear optical efficiency almost equivalent to KDP