

# Band gap Engineering and scaling of laser induced surface damage threshold properties of N,N'-Diphenylguanidinium based single crystals by organic and inorganic acids for nonlinear optic applications

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Crystals with high optical band gap and laser damage threshold have attracted much interest in the field of nonlinear optical applications. New and efficient organic nonlinear optical crystals of N,N'-Diphenylguanidinium compounds were synthesized and grown by solvent evaporation technique. The grown crystals were subjected to X-ray diffraction study for structural confirmation. The UV-vis-NIR transmittance spectra were recorded, and from these transmittance data the optical band gap and optical conductivity were calculated. 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. The laser induced surface damage threshold study for the grown crystals was carried out using Nd:YAG laser. It is well observed from these optical and laser induced surface damage threshold studies that the band gap and damage threshold properties can be tuned by the replacement of the functional group in the compounds.

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## 1. Introduction

The development of optical devices, such as photonic integrated circuitry, depends strongly on the design of highly efficient nonlinear optical (NLO) materials. Among such NLO materials, organic materials are shown to be superior to their inorganic counterparts in terms of synthesis, crystal fabrication, potential to create large devices and much faster optical nonlinearities [1]. Organic materials possess large second order molecular polarizabilities ( $\beta$ ), higher resistance to optical damage and more versatile for synthetic manipulations. They 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 [2]. Thus the attention of researchers is focused especially on the group of hydrogen bonded solids that exhibits potential nonlinear optical properties. Some potential guanidinium based NLO materials synthesized with L-tartaric acid via strong hydrogen bond interactions are aminoguanidinium (1+) hydrogen L-tartrate monohydrate [3], guanidinium L-tartrate hydrate [4]. We synthesized a series of compounds of guanidinium in our laboratory, zinc guanidinium sulfate [5] and Guanidinium 4-aminobenzoate [6] crystal. On continuing the search for potential NLO materials in guanidine family, we focused on N,N'-Diphenylguanidine (DPG), a substituted

guanidine family member. DPG which is also known as melaniline and have been widely used as a primary and secondary accelerator in the vulcanization of rubber. In the present study, we have analyzed the behavior of N,N'-Diphenylguanidinium cation with L-Tartaric acid and phosphorous acid to tailor the optical band gap and laser damage threshold for nonlinear application devices.

## 2. Experimental

Chemical reaction method is used for the synthesis of N,N'-Diphenylguanidinium Hydrogen (+)-L- Tartrate monohydrate (DPGTM) and N,N'- Diphenyl guanidinium dihydrogen phosphite (DPGP) crystals. High purity N,N'-Diphenylguanidine and respective acids in the molar ratio of 1.0:1.0 are used in the synthesis without further purification. The N,N'-Diphenylguanidine and the corresponding acids were dissolved in water- ethanol (1:1) mixed solvent respectively. The mixture of N,N'-Diphenylguanidine and their respective acid solutions were stirred continuously for six hours at room temperature and allowed for slow evaporation. The obtained crystalline materials were further purified by repeated recrystallization. Optically good quality crystals of DPGTM and DPGP were obtained after a period of 90 days and 40 days and are shown in Fig. 1(a) and 1(b). The grown crystals were subjected to single crystal X-ray

diffraction studies using Enraf Nonius-CAD4 single crystal X-ray diffractometer with MoK $\alpha$  radiation ( $\lambda = 0.7107 \text{ \AA}$ ) to estimate the lattice parameters values. Optically transparent crystals of thickness of 2 mm were used to record the transmission spectrum by employing Varian Carry SE model spectrometer in the range 200 - 800 nm. The powder technique of Kurtz and Perry was used to measure its second harmonic generation (SHG), which is regarded as the simple method to assess the nonlinearities. The laser induced surface damage threshold study for the grown crystal was carried out using Nd:YAG laser.

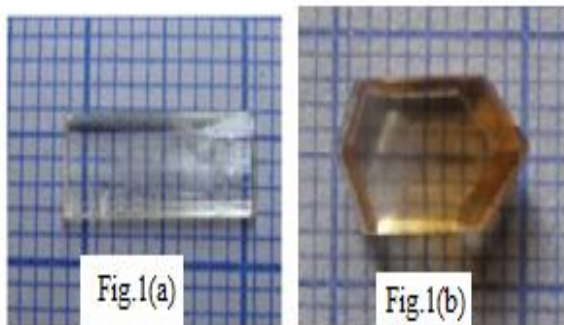


Fig. 1(a) As grown single crystal of DPGTM and  
Fig. 1(b) As grown single crystal of DPGP

### 3. Result and discussion

#### 3.1. Single crystal X-ray diffraction analysis

The grown DPGTM and DPGP were subjected to single crystal X-ray diffraction analysis in order to confirm their structure. It was elucidated from the analysis that both the crystal belong to non-centrosymmetric space group. It is found that the DPGTM belongs to orthorhombic crystal system with P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub> as space group. The obtained cell parameters are,  $a = 7.05 \text{ \AA}$ ,  $b = 14.72 \text{ \AA}$ ,  $c = 18.20 \text{ \AA}$ ,  $V = 1889 \text{ \AA}^3$  and  $\alpha = \beta = \gamma = 90^\circ$ . It was observed that the DPGP belongs to tetragonal crystal system with P4<sub>3</sub> as space group. The obtained cell parameters are,  $a = 10.82 \text{ \AA}$ ,  $b = 10.82 \text{ \AA}$ ,  $c = 12.64 \text{ \AA}$ ,  $V = 1481 \text{ \AA}^3$  and  $\alpha = \beta = \gamma = 90^\circ$ . The obtained parameters were found to be in close agreement with the reported data [7, 8].

#### 3.2. UV-vis-NIR spectral studies

The UV-vis transmission spectrum of DPGTM and DPGP crystal sample were recorded in the range 200 – 800 nm using a polished crystal sample of thickness 2 mm. Title compounds are found to be active in the UV region having a transmittance of about 76% and 71% with the cut-off wavelength of 298 nm and 294 nm for DPGTM and DPGP crystal respectively. The recorded optical transmittance spectrum is shown in Fig.2. It is well known that the parameters, such as optical transmittance range and cutoff region are important to tailor the material for

optical applications. The transmission window in the visible region enables good optical transmission of the second harmonic frequencies of Nd:YAG laser.

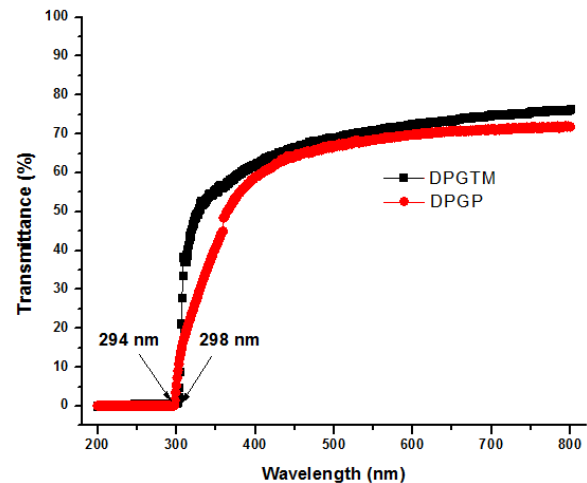


Fig. 2. Transmittance spectra of DPGTM and DPGP crystals

The measured transmittance was used to calculate the absorption coefficient ( $\alpha$ ) using the relation:

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

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 ( $h\nu$ ) [9]

$$(\alpha h\nu)^2 = A(E_g - h\nu) \quad (2)$$

where  $\alpha$  is the absorption coefficient,  $h$  is the Planck's constant,  $A$  is a constant,  $\nu$  is the frequency of the incident photon,  $E_g$  is the optical band gap.

The Tauc's [10] plot between  $(\alpha h\nu)^2$  and the photon energy ( $h\nu$ ) is shown in Fig.3. The band gap of the crystal was evaluated by extrapolation of the linear part of the graph and found to be 4.05 eV and 4.14 eV. Thus, it can be claimed that when the organic acid is replaced by inorganic acid the band gap is found to increase with a value of 0.09 eV. The wide band gap of DPGTM and DPGP crystals confirms the large transmittance in the visible region. The linear behavior of the graph is attributed to the direct band gap transition. As an end result of wide band gap, it is found that N,N'-Diphenylguanidinium compound crystals are more suitable for optoelectronic devices and nonlinear applications [11].

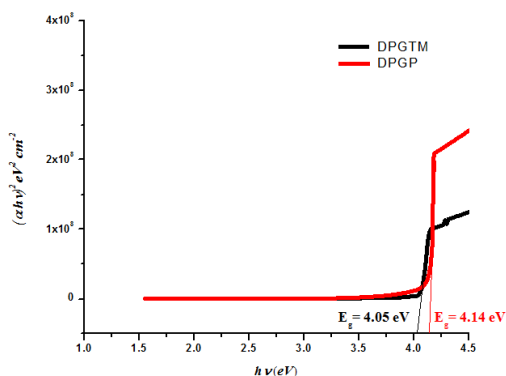


Fig. 3. Tauc's Plot of  $(\alpha h\nu)^2$  vs. photon energy of DPGTM and DPGP crystals

### 3.3 Optical conductivity studies

From the transmittance data, we calculated the optical constants, such as reflectance (R), refractive index (n) and extinction coefficient (k) [12, 13].

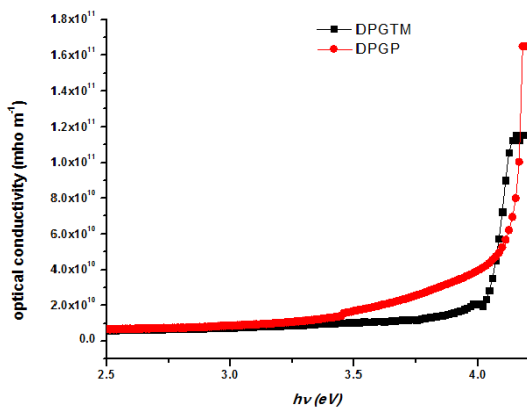


Fig. 4. Plot of optical conductivity vs. photon energy for DPGTM and DPGP crystals

The optical conductivity ( $\sigma$ ) of the crystal was calculated from the well known relation [14, 15],

$$\sigma = \frac{\alpha n c}{4\pi} \quad (3)$$

where  $n$  is the refractive index of the crystal and  $c$  is the velocity of light. The variation of optical conductivity as a function of photon energy ( $E = h\nu$ ) is shown in Fig. 4. It is observed from this figure that the optical conductivity is low at low photon energies and found to reach the maximum value at the corresponding band gap energy values for both the crystals. This maximum conduction is due to electronic excitations of these compounds. Since at frequencies corresponding to band gap energy and beyond the molecules cannot relax and the energy absorbed by atoms is purely exciting electrons to the higher energy levels. This result is an evidence for the optical

conductivity's dependence on band gap in crystals. It is also observed from the Fig. 4, the high energy optical conductivity of DPGP crystal is higher than that of DPGTM crystal. The higher value of optical conductivity of DPGP can be attributed to the substitution of inorganic acid with N,N'-diphenyl guanidine rather than the substitution of organic acid as in the case of DPGTM.

### 3.4. Nonlinear optical studies

The nonlinear optical conversion test was carried out for the grown crystal using Kurtz and Perry technique [16]. It is a popular method to evaluate the SHG of the grown crystal. An optical source of high intensity Nd:YAG laser ( $\lambda = 1064$  nm) is directed on to the powder sample, packed in a micro capillary of uniform bore. The SHG nonlinearity was confirmed from the output of green light emission ( $\lambda = 532$  nm). 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 mV and 5.8 mV was obtained for DPGTM and DPGP powder crystal samples for an input energy of 5 mJ/pulse and 2.7 mJ/pulse, while the standard potassium dihydrogen phosphate (KDP) powder crystal sample produced a SHG signal of 15.4 mV and 5.9 mV for the same above said input energies. It shows that the SHG effective nonlinearity of DPGTM and DPGP is 0.9 and 0.98 times that of standard NLO material KDP.

### 3.5 Laser induced surface damage threshold (LIDT)

Laser damage threshold plays a vital role in deciding the application of crystals for device fabrications. The laser parameters, such as energy, wavelength, pulse duration, longitudinal and traverse mode structure, beam size, location of beam, etc., are the factors on which the laser damage threshold depends upon. Experimentally, a Q-switched diode array side pumped Nd:YAG laser with pulse width of 10 ns with a repetition rate of 10 Hz operating in TEM<sub>00</sub> mode and a fundamental wavelength of 1064 nm Gaussian beam was used to measure the laser damage threshold of DPGTM and DPGP crystals. For single shot experiment, the DPGTM and DPGP crystal samples were mounted on an X-Y translator that facilitates in bringing different areas of the sample for exposure precisely. The onset of damage can be determined by visual damage and audible cracking, the laser beam of 1 mm was focused on the crystal. The sample was placed at the focus of Plano-convex lens of the focal length of 20 cm. An attenuator was used to vary the energy of the laser pulses with a polarizer and a half wave plate. The pulse energy of each shot was measured using the combination of phototube and oscilloscope. The energy fluence is calculated by taking the ratio of input energy and area of the crystal exposed to laser irradiation which is expressed in J cm<sup>-2</sup>. The laser induced damage

threshold of the DPGTM and DPGP crystal is found to be  $13.7 \text{ J cm}^{-2}$  and  $6.5 \text{ J cm}^{-2}$  for single shot (at 1 pulse per second). The laser induced surface damage threshold data obtained for specified pulse duration can be scaled to another pulse duration. For pulse duration of 0.5 ns to 50 ns the below said relation can be used for scaling, where A is the original pulse duration given in nanoseconds (ns). B is the second pulsed duration for which laser induced surface damage threshold is to be calculated.

$$LIDT(B) = LIDT(A) \sqrt{\frac{B}{A}} \quad (4)$$

In this present investigation, we have used a pulsed laser of 10 ns pulse width for which the LIDT is obtained for both the DPGTM and DPGP crystals. If these values are to be scaled for 1 ns then the LIDT values is found to be  $4.33 \text{ J cm}^{-2}$  and  $2.05 \text{ J cm}^{-2}$ . Thus, it can be concluded that the scaling of data suites the above said crystals for nonlinear optical applications.

#### 4. Conclusion

Optically transparent and good quality DPGTM and DPGP crystals were grown using mixed solvent of water-ethanol by slow evaporation technique. The cell parameters were confirmed by single crystal X-ray diffraction. The grown crystals were found to have wide transparency window thus confirming the suitability for optical window applications. The optical band gaps of the grown DPGTM and DPGP crystals were calculated as 4.05 eV and 4.14 eV respectively. The optical conductivity of the grown crystals has been studied. The powder SHG nonlinearity of DPGTM and DPGP crystals are about 0.9 and 0.98 times that of KDP. The laser induced surface damage threshold values are found to be  $13.7 \text{ J cm}^{-2}$  and  $6.5 \text{ J cm}^{-2}$  for DPGTM and DPGP crystals respectively. The scaling of LIDT was done for 1 ns pulse width and it is found to suit the title crystals for nonlinear optical applications. From the above said outcomes, it can be concluded that the band gap of N,N'-Diphenylguanidinium compounds can be engineered and LIDT can be scaled by suitable organic and inorganic acids that can suit for nonlinear and optoelectronic applications.

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