# GROWTH AND CHARACTERIZATION OF AN ORGANIC NLO SINGLE CRYSTAL GUANIDINIUM META-NITROBENZOATE FOR PHOTONIC APPLICATIONS

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**Abstract**

**Good quality single crystals of guanidinium meta-nitrobenzoate (GMNB) was grown by slow evaporation technique using a mixed solvent of water + methanol in 1:1 ratio. The grown crystal was subjected to single crystal X-ray diffraction analysis in order to reveal its crystal structure and unit cell parameters. The FT-IR spectral analysis was carried out in order to confirm the presence of expected functional groups. The UV-vis analysis was done for GMNB single crystals to determine the optical transparency. Simultaneous TG-DTA analysis was employed to understand the thermal and physio-chemical stability of the title compound. The mechanical stability of GMNB single crystal was studied using Vicker's micro hardness test on prominent plane at different temperature to reveal the anisotropic nature. The laser stability was analyzed laser induced damage threshold study using Nd:YAG laser. The existence of second harmonic generation (SHG) of GMNB was confirmed by Kurtz-Perry powder technique and was compared with standard reference material potassium dihydrogen phosphate (KDP). The particle size dependency of GMNB powder sample was studied in order to reveal its phase matching behavior.**

**Index Terms: Crystal growth, Second harmonic generation (SHG), laser damage threshold (LDT), Phase matching.**

## I. INTRODUCTION

In the last few decades crystals have been grown by several researchers to quest and discover new nonlinear optical materials for several applications. Nonlinear optical (NLO) materials have proven to be interesting candidates for a number of applications such as second harmonic generation, frequency mixing, electro-optic modulation, etc. [1]. The preparation of crystalline materials for second harmonic generation (SHG) requires establishing of a non-centrosymetric arrangement of the crystal structure. As non-centrosymmetric space group is one of the major requirement for the existence of second harmonic generation activity. Organic NLO materials offer the potential of relatively low-power laser driven nonlinear optical system due to their optical properties, such as fast optical response time, non-resonant susceptibility and high second harmonic generation (SHG) nonlinearity compared to inorganic materials [2]. Most of these organic molecules shows large nonlinear optical responses compared with inorganic counterparts, due to presence of the electron-donor and electron-acceptor groups located at the extreme of a system involving correlated and high delocalized π electron states. The preparation of perfect single crystals of preferred dimensions is found to be difficult when compared with its inorganic counterparts due to the effect of organic solvents on the growth and the habit of these highly polar materials is very significant [3]. Organic solvents often yield crystals with various habits from needles to prismatic crystals depending on the factors such as, chemical nature, solubility, polarity, evaporation rate and other properties [4]. This effect is mainly because of the interaction of these solvent molecules on the surface of the growing crystal.

Also, the chemical nature of the solvent decides the quality of the growth in most of the cases. The primary condition for the selection of suitable solvent for the growth of a particular material is its solute solubility in the crystallization temperature range [5]. Guanidine is a simple organic chemical compound, whose structure is related to those of amides and proteins and its specific planar configuration makes this cation as a potential H-donor in hydrogen bonds [6]. Due to the efficient solvation by water molecules guanidine is a highly stable cation in aqueous solution with pKa of 13.6 meaning that guanidine is a very strong base there by guanidine cation readily forms compound with several acids. In this present communication, we are reporting on the growth of GMNB single crystals from a mixed solvent with well settled facets and investigations on the characterization of guanidinium meta-nitrobenzoate single crystals with a special emphasis on exploring their structural, spectral, optical, laser stability, thermal and nonlinear optical properties. We are also reporting, the temperature dependent mechanical properties and particle size dependency of the title material with a detailed discussions.

## II. EXPERIMENT

### *A. Material synthesis*

Single crystals of title compound was synthesized by the chemical reaction of commercially available, Guanidine carbonate (HI-MEDIA, AR grade) and Meta-nitrobenzoic acid (SRL-CHEM, AR grade) in a mixed solvent of water + methanol (1:1) in 1:2 ratio. The raw materials for the synthesis were used as such without further purification. The calculated quantity of meta-nitrobenzoic acid was first dissolved in methanol (300mL), to which the calculated quantity of guanidine carbonate was added with continuous stirring. Upon addition of guanidine carbonate the solution was precipitated with effervescence thereby indicating the compound formation. The precipitate was further dissolved by adding distilled water (300 mL). The collected salt was used for the further growth process.

### *B. Crystal Growth*

The synthesized product was purified by further recrystallization process. The recrystallized salt was slowly added to the mixed solvent of water + methanol (1:1) ratio. The resultant solution was colorless. The solution was stirred continuously at room temperature with an immersible magnetic pedal for nearly 8 hours in order to achieve homogeneity. The solution was then filtered and kept at undisturbed. Care was taken to cover the beaker with an aluminum foil in order to prevent the evaporation of the solvent during the entire process. Good quality single crystal of GMNB was harvested after a period of 27 days by slow evaporation technique and is shown in Fig. 1.

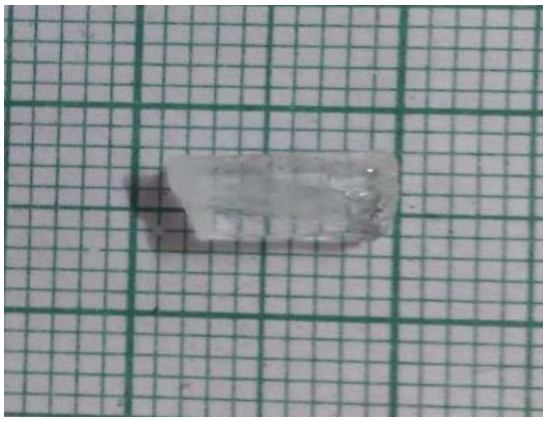

Figure 1. Photograph of as grown GMNB crystal

### *C. Characterization Techniques*

Single crystal X-ray diffraction data of GMNB was elucidated using ENRAF NONIUS CAD-4 single crystal X-ray diffractometer. FT-IR spectrum was recorded to interpret the chemical bonding and modes of vibration of GMNB in the range 4000–400 $cm^{-1}$ by PERKIN–ELMER spectrometer using KBr pellet technique with a resolution of 1.0 $cm^{-1}$. The UV-vis transmission spectrum of GMNB crystal was recorded in the wavelength range 200–800 nm using Varian Carry SE model spectrometer. The laser induced surface damage threshold study was carried out for the grown crystal using Nd:YAG laser. Thermo gravimetric and differential thermal analyses were 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 30–500 $^{o}$C. Microhardness analysis of GMNB crystals were examined by using Leitz–Weitzler hardness tester at different temperature. The second harmonic generation (SHG) efficiency was measured using the Kurtz

and Perry technique. The particle size dependency of GMNB powder sample was studied in order to understand the phase matching property.

## III. RESULTS AND DISCUSSION

### *A. Single Crystal X-ray Diffraction study*

Single crystal X-ray diffraction analysis was carried using the good quality single crystal of GMNB in order to reveal the unit cell parameters, space group and crystal system. It is revealed from the analysis that the GMNB crystal belongs to orthorhombic crystal system with $P2_12_12_1$ non-centrosymmetric space group. The unit cell parameters are found to be, a = 7.36 (4) Å, b = 10.10 (9) Å, c = 13.65 (7) Å, V = 1015 $Å^3$ and is found to be in good agreement with the reported data [7].

### *B. Spectral Analysis*

The chemical bonding and modes of vibration of the grown compound was analyzed by recording FT-IR spectrum. The molecular structure of GMNB is shown in Fig. 2.

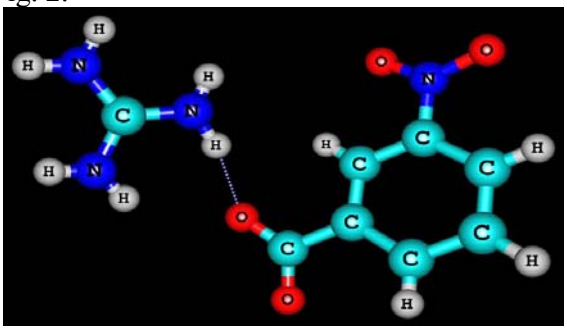

Figure 2. Molecular structure of GMNB

The spectral analyses of GMNB was carried out on the characteristic vibrations of guanidinium cation and meta-nitrobenzoate anion. FT-IR spectrum of GMNB is presented in Fig. 3.

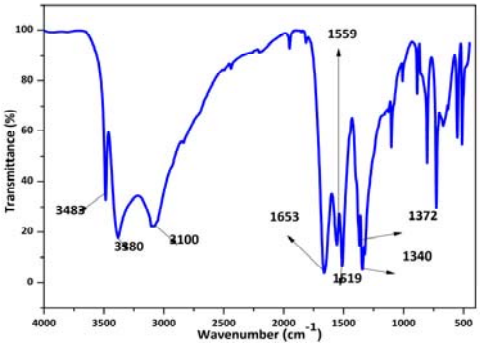


Figure 3. *FT-IR spectrum of GMNB*

The intense band in the high-energy region shows the $NH_2$ asymmetric and symmetric stretching vibrations at 3483 and 3380 $cm^{-1}$ respectively. The broad absorption band at 3100 $cm^{-1}$corresponds to aromatic ring carbon hydrogen (C-OH) stretching. The peak corresponding to this mode of vibration is broadened due to the intermolecular hydrogen bonding of $NH_2$ groups. The sharp intense peak at 1653 $cm^{-1}$ corresponds to C=O stretching vibration of carboxylate group of meta-nitrobenzoate.

The peaks at 1559, 1519 and 1372 $cm^{-1}$are due to aromatic skeletal vibrations. The symmetric and asymmetric stretching vibrations of $NO_2$ groups occur at 1519 and 1340 $cm^{-1}$. The groups of peaks below 1000 $cm^{-1}$ are due to CH bending vibrations. Hence, the spectrum carries all the vibrations due to the title compound.

### C. Optical Analysis

The optical transparency and cut-off wavelength are the most important optical parameters to tailor the materials for various applications. NLO materials can be placed widely in the applications if only it has a good transparency range. As polishing of crystal plays a major role in enhancing the transparency of optical materials, the as grown crystal was subjected to polishing using alumina powder and polishing sheet. The cut and polished GMNB crystal of thickness 1.5 mm was used for UV–vis spectral study and the transmission spectrum is shown in Fig. 4. It is clear from Fig.4, that GMNB single crystal has good transmittance of about 75% with cut- off wavelength 255 nm. The absence of significant absorption in the region between 255 nm and 800 nm shows that the GMNB crystal may be exploited for nonlinear optical applications.

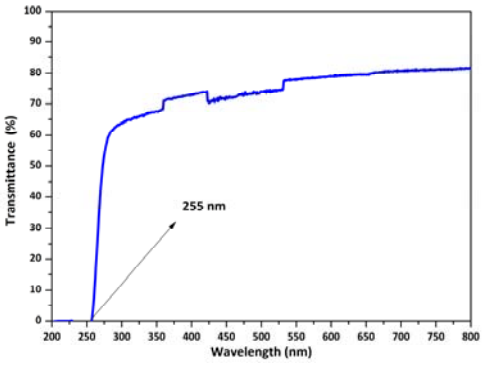


Figure 4. Transmission spectrum of GMNB crystal

D. Laser Damage Threshold (LDT) study

One of the decisive and important criteria for a NLO crystal to perform as a device is its resistance to laser damage. Laser damage threshold plays a vital role in deciding the application of crystals for device fabrication. 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. In order to evaluate the laser damage stability of GMNB crystal it was subjected to LDT with multiple shots experiment. Good optical quality cut and polished sample was used for the study. A fundamental beam of 1064 nm, repetition rate of 10 Hz and pulse width 10 ns of Q-switched Nd:YAG laser was used to measure the LDT of GMNB. The input energy was raised from 5 mJ/pulse until damage was observed. The spot size of the beam was measured to be 1 mm. The laser damage threshold of the crystal was calculated using the expression:

$$\text{Power density} = E / \tau\pi r^2 \ (GW/cm^2)$$

where, 'E' the input energy (mJ), 'τ' the pulse width (ns), 'r' the radius of the circular spot (mm).

The Laser damage threshold value of GMNB was found to be 0.58 GW/cm$^2$ which is found to be slightly greater than that of standard reference material KDP (0.20 GW/cm$^2$). It is also evident and clear from the earlier report [8], that in the long-pulse regime ($\tau > 100$ ps), the damage is controlled by the rate of thermal conduction through the atomic lattice and in the short-pulse regime ($\tau < 100$ ps), it is due to optical break down and various nonlinear ionization mechanism. Hence, thermal effect becomes important for the pulse width that are nanosecond and longer. The local heating caused by macroscopic inclusion is also a more severe problem in the high intensity short-pulse system than in low-intensity long-pulse. In the present work we have used 10 ns pulses.

E. Thermal Analysis

The thermal behavior of GMNB crystalline sample was studied by thermo gravimetric (TG) analysis and differential thermal analysis (DTA) analysis using GMNB crystalline sample of 5.28 mg. A thermal analyzer was employed at a heating rate of 10 °C/min in nitrogen atmosphere. The TG and DTA thermo gram were recorded in the temperature range 30 - 500 °C. The TG-DTA thermogram of GMNB is depicted in Fig. 5. It is evident from Fig. 5., that GMNB crystals are thermally stable up to 160 °C and it is free from moisture. There are two stages of weight losses, where first stage weight loss occurs from 146 – 164 °C. The second stage of weight loss occurs from 273 – 323 °C. During the first stage of weight loss it is evident that around 65% of the title material is eliminated and given out as gaseous volatile substances such as $NH_2$, $NO_2$ and $CO_2$ etc., from the title material. The sharpness of the endothermic peak at 153 °C shows good, natural crystalline formation. The residual mass of about 14 % at 500 °C is attributed to the residual mass of carbon atoms. Therefore, from the above inference it is claimed that GMNB material first decomposes and then melts and it can be exploited for further applications with a temperature stability of 160 °C.

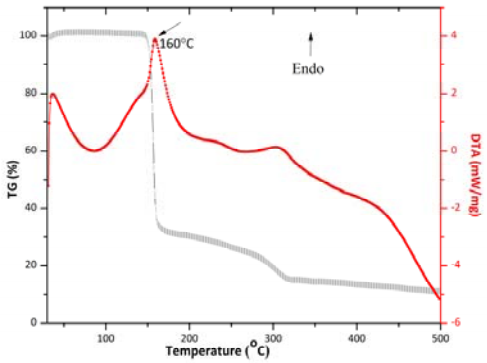


Figure 5. TG-DTA curve of GMNB

F. Mechanical analysis

Measurement of hardness is a useful nondestructive testing method used to determine the applicability of the crystal in the device fabrication. Microhardness study was carried out on GMNB single crystal using a Vickers microhardness tester fitted with a Vickers diamond pyramidal indenter in order to evaluate its mechanical stability. The static indentations were made at room temperature and 333 K with a constant indentation time of 5 s for all indentations. A cut and polished sample of GMNB was used for the study. The indentation marks were made on the flat, smooth and prominent faces by varying the load from 10 to 40 g at room temperature and 333 K. Since the GMNB crystal melts at 160 °C the crystal was heat treated up to 60 °C. The Vicker's

Microhardness number of the title crystal was calculated using the relation,

$$H_V = 1.8544 \left(P/d^2\right) \text{ (kg/mm}^2\text{)}$$

Where, '$H_v$' is the Vickers hardness number, 'P' is the applied load and 'd' is the average diagonal length of the indentation mark.

Plots between hardness number and load for GMNB single crystals at room temperature and 333 K is depicted in Fig. 6. It is clear that the microhardness number increases with increasing load. It is evident from the above plot that the microhardness number of the crystal increases with increase in load which is in agreement with the reverse indentation size effect (ISE) [9] and also decreases with increase in temperature. The decrease in the value of hardness number with respect to increase in temperature can be attributed to the fact that, when the temperature increases, the average inter atomic distance becomes greater than that at room temperature due to lattice vibration. This leads to more and more lattice phonon interactions which causes the breaking of bond as well reduce the hardness value [10]. The maximum value of hardness number observed for GMNB, crystal is 37 kg/mm$^2$ at 40 g (room temperature) respectively. The load above these values develops multiple cracks on the crystal surface due to the release of internal stresses generated locally by indentation.

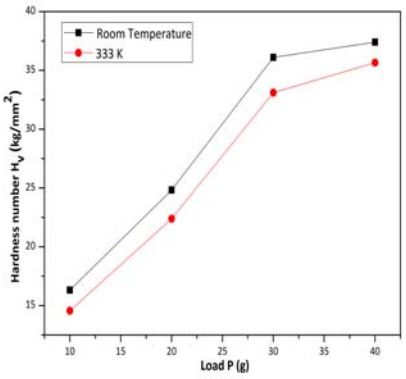


Figure 6. Plot of hardness number vs. load for GMNB single crystal

G. Nonlinear optical study

The second harmonic generation efficiency was studied by employing the Kurtz and Perry powder technique [11] which remains a valuable tool for the initial screening materials for SHG property. Q-switched Nd:YAG laser with the fundamental beam of 1064 nm, repetition rate of 10 Hz and pulse width 10 ns was used to measure the SHG efficiency of GMNB. The standard reference material potassium dihydrogen phosphate (KDP) was used to compare the SHG efficiency. The grown single crystal of GMNB was crushed into powder with a uniform particle size and then packed in a micro-capillary tube of uniform pore size (125 – 150 μm) and exposed to laser radiation. The SHG output was converted into electrical signal and was displayed on a digital storage oscilloscope. The optical signal incident on photo multiplier tube was converted in to voltage output. The SHG output signal intensity of 44 mV was measured for GMNB crystalline powder while that for standard KDP crystalline sample was 30 mV for an input energy of 30 mJ/pulse. Thus it is clear that the SHG efficiency of GMNB was found to be 1.46 times than that of standard reference material KDP.

H. Particle size-dependency of SHG

Particle size dependency of SHG is used as an initial screening methodology to identify the materials with the capability for phase matching. The SHG nonlinearity have been shown to depend strongly on the particle size [12]. Materials which exhibits phase matching behavior are grown into large size single crystals for NLO applications [13]. The continuous increase of SHG signal and its saturation with increase of particle size confirms the phase matching behavior of the material. The variation of particle size with respect to SHG intensity was studied in order to shed light in to the existence of phase matching property. The particle size dependency of SHG was carried out by sieving the GMNB powdered crystalline sample into various microcapillary tubes of sieve sizes ranging from 65-500 μm. Measuring SHG as a function of particle size provides clear information about type of phase matching condition. The increase in SHG nonlinearity value with increase in particle size and saturation at a maximum value is denoted as type-1 phase-matching occurs. Single crystal of GMNB was grounded and sieved into distinct particle size ranges, below 65, 65–125, 125–250, 250–350, 350- 500 μm. A Q-switched Nd:YAG laser operating at 1064 nm and 10 ns pulse width with an input

repetition rate of 10 Hz and energy 21 mJ/pulse was used for this study. As the particle size increases the SHG output signal voltage increases almost linearly up to 125–250 μm. The SHG output voltage deviates from the linearity above 250 μm and gains saturation. The particle size dependency of SHG output for GMNB crystals is depicted in Fig. 7. It is also evident from Fig. 7, that GMNB exhibits type-1 phase matching as the SHG nonlinearity increases with the particle size and saturates at a maximum value. Therefore GMNB crystal can be used as an efficient candidate for frequency doubler and optical parametric oscillator.

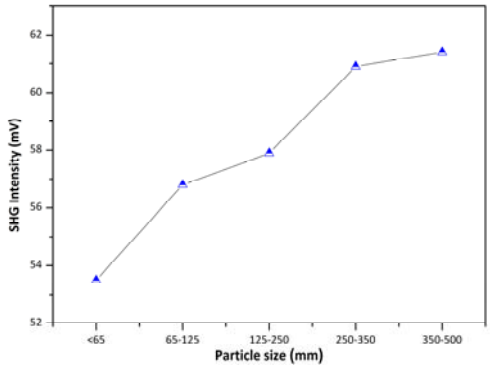


Figure 7. Particle size dependency of SHG

## IV. CONCLUSION

Optically good quality single crystal of GMNB was grown by slow evaporation technique. A prismatic habit of GMNB single crystal was grown using a mixed solvent of water + methanol (1:1). The cell parameters were identified using single crystal X-ray diffraction analysis. The presence of functional groups and modes of vibrations for GMNB was interpreted using FT-IR. From the UV-vis analysis it was confirmed that GMNB crystals has a wide transparency in the range 255 - 800 nm. Laser Damage Threshold (LDT) of GMNB was found to 0.58 GW/cm$^2$ by multiple shots experiment. The TG-DTA analysis was done in order to find the melting point and thermal stability of GMNB. It is found that the title material is stable up to 160 $^o$C. Vicker's microhardness studies were performed in order to evaluate the mechanical stability at room temperature and 333 K and it is concluded that the title compound is stable till 40 g load. It is also evident from the microhardness study that the hardness value decreases with increase in temperature. The presence of second harmonic generation (SHG) in the title compound was confirmed by powder Kurtz-Perry technique. The particle size dependency of SHG was done to have a clear picture about the type of phase matching. Indeed, the promising crystal growth, crystal habit, characterizations, high SHG, LDT and phase matching property employs the title material as a potential candidate for further device fabrication and other nonlinear optical applications.

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