



Growth and Characterization Studies of 4-Nitrophenol doped Benzoyl Glycine NLO single crystal

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Abstract : Optically good quality single crystals of organic non-linear optical 4-nitrophenol doped benzoyl glycine (4NPBG) were grown by slow evaporation technique. The grown crystals were characterized by Powder XRD, FTIR, UV-vis-NIR spectral analysis and Kurtz-Perry powder test.

Key words : NLO, slow evaporation, 4NPBG, XRPD, FTIR, UV-vis-NIR, Kurtz-Perry powder test.

1. Introduction

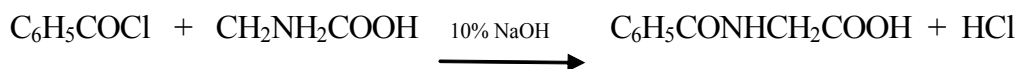
In recent years researchers take effort to develop ultraviolet lasers for photonics, optoelectronics, infrared and medical applications. [1-2]. Properties of individual molecules and their mutual dispositions and organization in the bulk structure are the basic factors that control the attributes of the resulting molecular materials [3-5]. While the molecular

characteristics can be designed and realized to a large extent the control of supra molecular organization continues to be a complex problem, one of the materials properties that are strongly influenced by even small changes in the molecular assembly patterns is the second order nonlinear optical (NLO) susceptibility controlling processes such as second harmonic generation (SHG). An essential condition to realize even order NLO processes in materials is a non-centrosymmetric structure. However optical molecular orientations are required if appreciable effects are to be achieved in molecular materials, organic molecular crystals show a strong predilection towards centrosymmetric organization. Eventhough no direct correlation has been found between the ground state dipole moment of molecules and the preference for centrosymmetric lattice formation, electrostatic interactions could generally promote anti parallel organization of dipolar molecules, while octopolar molecules provide strategy towards non-centrosymmetric crystals. Many approaches have been developed to achieve non-centrosymmetric crystal lattice formation of dipolar NLO-phores. These include utilization of chirality, incorporation of bulky substituents or optimally long alkyl chains and exploitation of H-bond interactions, host –guest complexation and interactions. Even though it does not necessarily produce optimal molecular orientation, chirality is the only approach that guarantees non-centrosymmetric lattice formation for fundamental symmetry reasons. In view of this fact, the general preference of organic molecules towards centrosymmetric assembly of chiral dipolar molecules is a matter of considerable interest especially in the context of developing new materials for quadratic NLO applications systematic analysis of the intermolecular interactions which drive such organizations is an important exercise [6-10]. In this paper we report the results of our work on the growth of 4-nitrophenol substituted benzoyl glycine (4NPBG) NLO single crystals along with the characterization by Powder XRD, FTIR, UV-vis-NIR spectral analyses and Kurtz – Perry SHG test.

2. Experimental Techniques

2.1 Synthesis & Growth

All the starting materials were purchased from E-merck (99.9% pure). Benzoyl chloride, Glycine, sodium hydroxide and 4-nitrophenol were used. Benzoyl Glycine (BG) was synthesized from equimolar ratio of Benzoyl Chloride and Glycine. The reaction formula is as follows



BG was formed in the form of precipitate with little benzoic acid. The as obtained mixture was warmed gently with 100 ml of Carbon tetrachloride and then filtered and pure BG crystalline salt was obtained. From the solubility considerations, dimethyl formamide (DMF) was found to be the best solvent. The Benzoyl Glycine salt was dissolved in DMF. The purity of the salt was obtained by repeated recrystallisation [11]. The solution of benzoyl glycine salt was prepared in a slightly under saturated condition. The solution was stirred well for 4 hours using a magnetic stirrer and then the solution was filtered using whatmann filter paper. Thus obtained solution was mixed with 5 mol% of 4-nitrophenol are kept in 250 ml borosil beaker as such as the spontaneous nucleation takes place and the seed crystals were obtained after 4 weeks. A defect free seed crystal was taken and tied with the thread and it was immersed in the saturated solution containing benzoyl glycine and 4-nitrophenol. Bulk size single crystals of dimension $5 \times 2 \times 3 \text{ mm}^3$ were harvested in a month.

3. Characterization Techniques

The as grown 4-nitrophenol doped benzoyl glycine crystal was subjected to characterization like PXRD, FTIR, UV-vis-NIR spectral analyses and NLO test.

3.1. XRPD analysis

X-ray Powder diffraction technique was used to identify the purity of the as grown 4-nitrophenol doped benzoyl glycine single crystal. The XRPD pattern was recorded for G4NP using a XPERT Powder diffractometer with CuK_α ($\lambda=1.5418 \text{ \AA}$) radiation in the range of 2θ from $10-70^\circ$ at a scanning rate of $1^\circ/\text{min}$. The positions of the powder XRD peaks were found to be in good agreement with the calculated single crystal XRD data. Fig.1 shows XRPD spectrum of 4-nitrophenol doped benzoyl glycine single crystal.

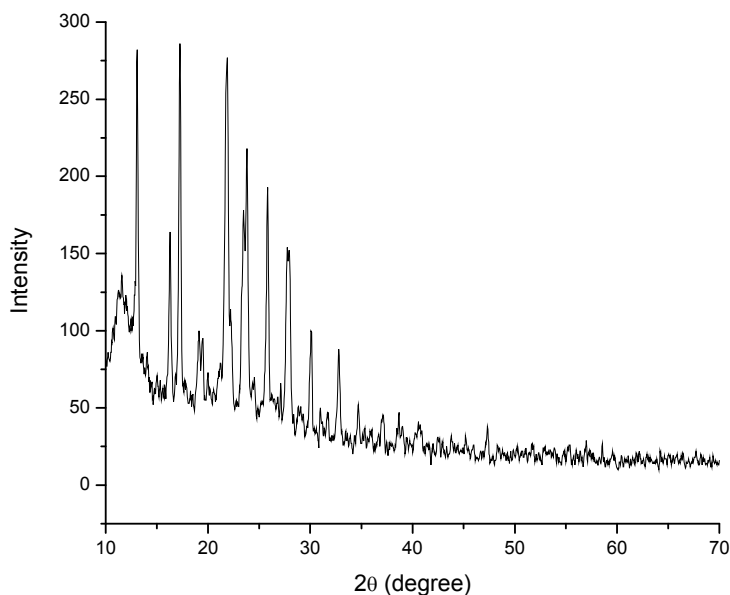


Fig.1. XRPD spectrum of 4NPBG NLO single crystal

3.2. FTIR analysis

FTIR spectroscopy finds application in determining the size of the coordination, the nature of organic ligand bonding as well as in the elucidation of structures of coordination compounds. The FTIR spectrum was recorded in the spectral range 400–4000 cm^{-1} using Perkin-Elmer Lambda-35 FTIR spectrometer, where the 4NPBG crystalline sample was in Pellet form in KBr phase. A peak at 3419 cm^{-1} is due to a sharp N-H stretching vibration mode. The broad envelop surrounding the region 1943 cm^{-1} and 2360 cm^{-1} is due to the hydrogen bonding interaction of –COOH group. A peak at 1640 cm^{-1} is due to the C-O stretching of –COOH group. A peak at 1387 cm^{-1} is due to the C-N stretching of vibration. A peak at 1211 cm^{-1} is due to the C-COO vibration mode. The wavenumber region seen below 100 cm^{-1} is attributed to C-H and O-H bending vibration of aromatic group. The minor peaks appearing in wavenumber region 740 cm^{-1} to 770 cm^{-1} corresponds to the out of plane N-H wagging. Though the spectrum carries the same features as that of previous one, a notable difference is a shift in the O-H stretching of carboxylic acid to higher wavenumber. By 400 cm^{-1} in comparison

to that of pure benzoyl glycine crystal. The peaks are almost resolved as that of previous spectrum. Hence it can be said that the quantity of 4NPBG. The vibrational bands assigned to 1640 cm^{-1} and 1387 cm^{-1} indicate the H-OH bending and NO_2 stretching vibration. The absorption in the region 400 to 500 cm^{-1} are due to the overtones of the fundamental vibrations of 4-nitrophenol. The functional groups present in 4NPBG are compared with 4-nitrophenol and benzoyl glycine. It is also seen that the OH stretching symmetric vibration at 3342 cm^{-1} of benzoyl glycine is shifted to the higher frequency 3419 cm^{-1} in 4NPBG. Hence this will increase the polar character of 4-nitrophenol to a lower order thus concluding the harmonious existence.

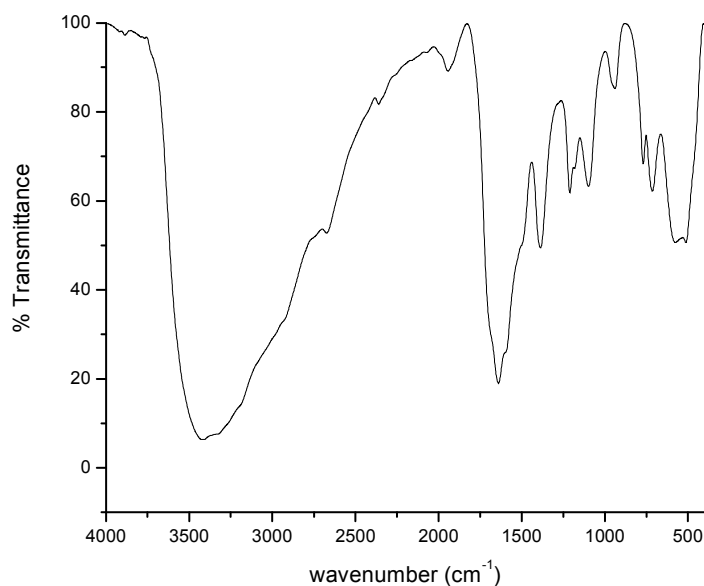


Fig.2. FTIR spectrum of 4NPBG NLO single crystal

3.3. UV-vis-NIR analysis

Fig.3 shows the optical absorption spectrum of 4-nitrophenol doped benzoyl glycine crystal. From the spectrum it is evident that 4-nitrophenol doped benzoyl glycine crystal has a very low cut-off wavelength of 260 nm, along with a large transmission window in the entire visible region and hence it can be utilized for SHG from a laser operating at 1064 nm.

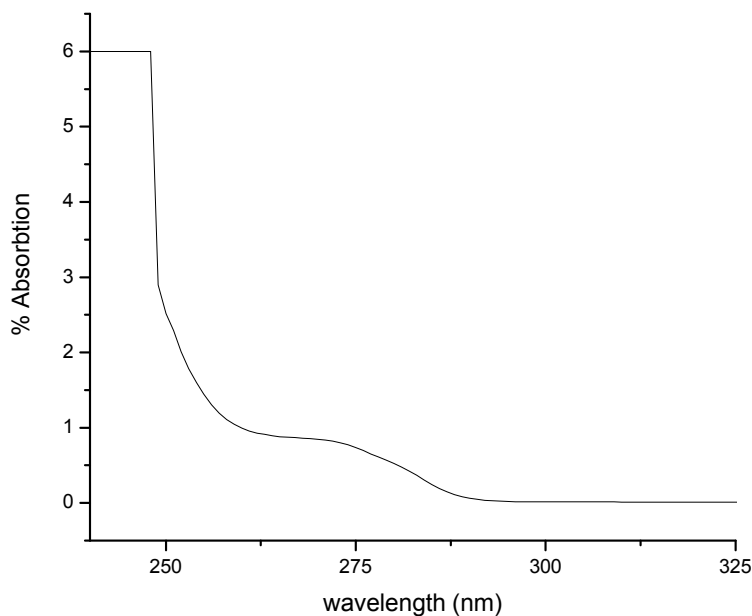


Fig.3. UV-vis-NIR spectrum of 4NPBG NLO single crystal

3.1. SHG Test

The second harmonic generation (SHG) test on 4-nitrophenol doped benzoyl glycine single crystal was performed by Kurtz powder SHG method. The powdered sample of 4-nitrophenol doped benzoyl glycine crystal was illuminated using the fundamental beam of 1064 nm from Q-switched Nd:YAG laser. Pulse energy of 4 mJ/pulse and pulse width of 10 ns and repetition rate of 10 Hz were used. The second harmonic signal generated in the crystalline sample was confirmed from the emission of green radiation of wavelength 532 nm connected a monochromator after separating the 1064 nm pump beam with IR blocking filter.

4. Conclusion

A new NLO crystal of 4-nitrophenol doped benzoyl glycine was grown by slow evaporation method. XRPD analysis confirmed the purity of the crystal. The functional groups in the molecule were identified by FTIR analysis. The cut-off wavelength of the crystal was evaluated from UV-vis-NIR analysis. The Kurtz-Perry powder technique confirmed the SHG property of 4NPBG single crystal.

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References

- [1] Saleh B. E & Teich M. C., Fundamentals of Photonics, (Wiley, New York), 1991.
- [2] Boyd R. W., Nonlinear optics (Academic Press, San Diego), 1992.
- [3] Chemla D. S. & Zyss J (Eds.), Nonlinear optical properties of organic Molecules and Crystals, Vol.: 1 & 2.
- [4] Abraham Rajasekar S et al., Mat. Chem. & Phys., 84 (2004) 157.
- [5] Fedorov V. A. & Kanyev L. G., Sov. Phys. Crystallog 35 (1990) 601-603.
- [6] Maker P.D., Terhune R. W., Nynenoff M & Savage C. M., Phys. Rev. Lett., Vol.:8 (1962) pp.: 21-22
- [7] Hann R. A & Bloor D (eds.), Organic Materials for Non-linear optics (Royal Society of Chemistry), 1989.
- [8] Chemla D. S. & Zyss J, Nonlinear optical properties of organic molecules and crystals, Vol.: 1 & 2, (Academic Press, Orlando), 1987
- [9] Narayan Bhat M & Dharmaprakash S. M., J. Cryst. Growth, 236 (2002) 376.
- [10] Nagaraja H. S. et al., J. Cryst. Growth, 193 (1998) 674.
- [11] D. Prem Anand, S. Selvakumar, K. Ambujam, K. Rajarajan, M. Gulam Mohammed & P. Sagayaraj, Ind. J. Pure & Appl. Phys. 43 (2005) 863-868.

