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Studies on the growth and properties of an organic nonlinear optical crystal benzoyl glycine (BG)

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ABSTRACT

Benzoyl Glycine (BG) an organic nonlinear optical crystal was synthesized and grown by slow evaporation method at room temperature. Single crystal X-ray diffraction study reveals that the crystal belongs to orthorhombic system and crystallizes in the non centro symmetric space group $P2_12_12_1$. Powder X-ray diffraction was recorded and the peaks were indexed. Absorption spectrum shows that the crystal is transparent in the entire visible region. The functional groups present in the material were interpreted by FTIR spectral analysis. TG-DTA was performed to study the thermal stability of the crystal. Microhardness and etching studies were also carried out. The SHG efficiency of BG was 2.5 times higher than that of KDP.

Introduction

The design and synthesis of new and highly efficient organic nonlinear optical materials is still a dynamic area of contemporary materials research in view of its impact on laser technology, optical communication and optical data storage technology [1-2]. A number of such organic materials have been reported in literature [3-4]. Benzoyl Glycine is one of the organic nonlinear optical materials having good second harmonic generation [5]. The structure of Benzoyl glycine was reported [6]. The metastable zone width, induction period and interfacial energy of the BG were determined [7]. In the present investigation we report the growth of benzoyl glycine in mixed solvents such as acetone-water and N, N- Dimethyl Formamide (DMF)-water for different pH values. The grown crystals from N, N- Dimethyl Formamide (DMF)-water were characterized by singe crystal and powder X-ray diffraction, morphology, optical absorption, FTIR analysis, thermal behavior, microhardness and second harmonic generation (SHG) test.

Experimental

Synthesis and solubility

The required amount of benzoyl glycine was dissolved in a mixed solvent of acetone and water. The prepared solution was allowed to evaporate at room temperature. The synthesized material was re-crystallized successively to minimize the impurities. Transparent needle shaped crystals were obtained in a period of 6 days..

Solvent of moderate solubility has to be considered for growing good quality crystals. An attempt was made to grow benzoyl glycine in a mixed solvent of N, N- Dimethyl Formamide (DMF) and water (1:1) which yield transparent crystals. Solubility of BG was carried out in a mixed solvent of DMF and water (1:1) and in a mixed solvent of acetone and water (1:1) for temperatures 30ºC, 35ºC, 40ºC, 45ºC, and 50ºC by gravimetric analysis as shown in Fig.1. It was observed that in a mixed solvent of DMF and water, BG shows moderate solubility and that mixture was considered as the right solvent to grow BG.

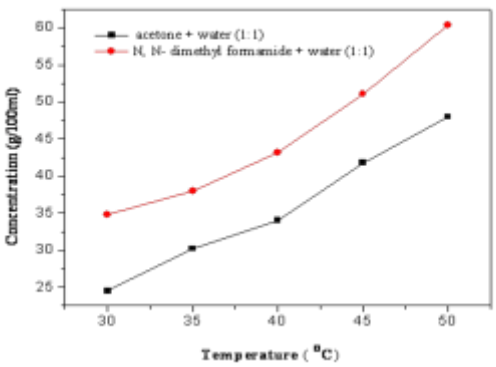

Fig.1. Solubility of BG

Crystal Growth

The growth rate of a crystal depends on temperature, degree of supersaturation, pH and concentration expressed by the functional relation as R=F (T,S,pH,C). Benzoyl Glycine was dissolved in a mixed solvent of acetone and water (1:1). Transparent needle shaped crystals were obtained by spontaneous nucleation in a period of 8 days as shown in Fig. 2(a). The required amount of BG as per solubility data was dissolved in a mixed solvent of N, N-Dimethyl Formamide and water (1:1). The solution was transferred to a clean petri dish and allowed to evaporate. The influence of pH on the growth rate affects crystal morphology [8]. Benzoyl glycine crystals were grown for various pH values 3.0, 3.5, 4.0 and 5.0 by slow evaporation technique as shown in Fig. 2(b). The growth period of the crystals for different pH values is listed in Table 1. It was

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observed that the crystals grown at pH 3.0 are optically good compared to the crystals grown from pH values 4.0 and 5.0.

The transparent seed crystal obtained from the solution of pH 3.0 was employed for bulk growth by the slow cooling technique. The growth was carried out in a constant temperature bath with an accuracy of ± 0.01K. The temperature was reduced at the rate of 0.2 K per day as the growth progressed. An optical quality crystal of dimension 16 x 6 x 3 mm^3 was grown over a growth period of 15 days as shown in Fig. 2(c).

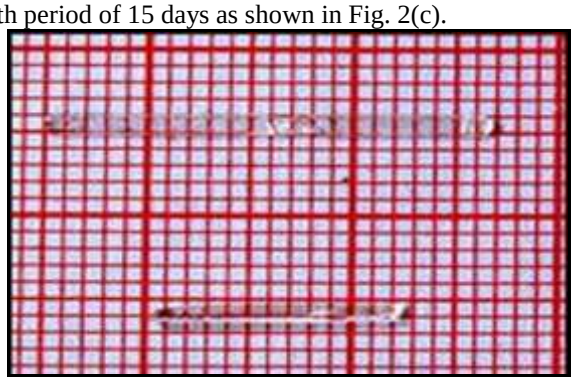

Fig. 2 (a) Single Crystals of BG in a mixed solvent of acetone and water (1:1)

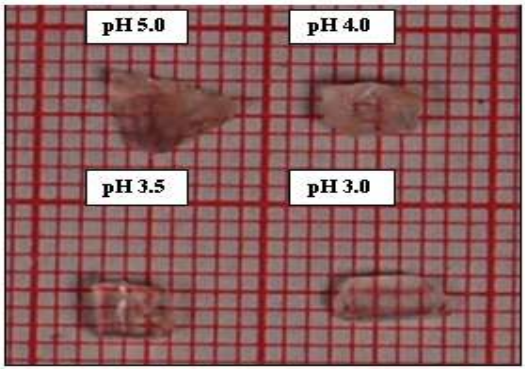

Fig.2 (b) As grown crystals of BG in a mixed solvent of N, N-Dimethyl Formamide and water (1:1) for various pH values

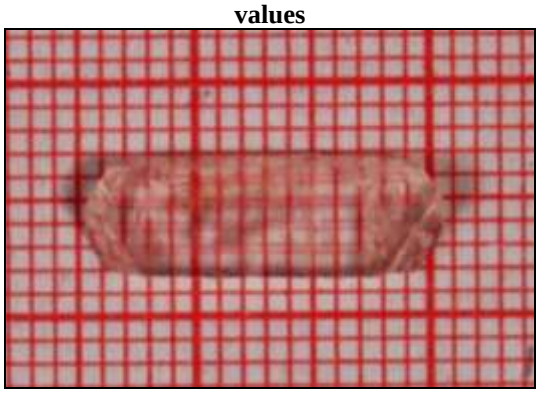

Fig. 2(c) Single crystal of BG in a mixed solvent of N, N-Dimethyl Formamide and water (1:1) at pH 3.0 by slow cooling

Results and discussion

Single crystal x-ray diffraction

The single crystal X-ray diffraction BG crystal has been carried out using Enraf-Nanious CAD-4 diffractometer. From the study, it was found that the crystal belongs to orthorhombic system with a non-centro symmetric space group $P2_12_12_1$. The cell parameters are, a= 8.86 Å, b= 9.08 Å, c=10.55 Å and volume V = 849 $Å^3$.

Powder x-ray diffraction

Powder X-ray diffraction was carried out using a Reich-Seifert X-ray diffractometer with Cu Kα (λ =1.5405 Å) radiation. The sample was scanned over the range 10°–60° at a rate of 1º/min. The X-ray diffraction pattern of BG is shown in Fig.3. The X-ray diffraction peaks were indexed for the lattice parameters and the prominent peaks obtained from powder X-ray diffraction confirm the crystallinity of the grown crystal. The peak corresponds to (122) has maximum intensity per second.

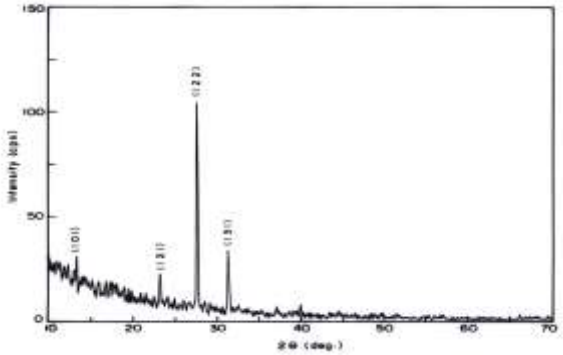

Fig.3 X-ray diffraction pattern of BG

Morphology studies

The morphology of the Benzoyl Glycine crystal grown from the mixed solvent of acetone-water is shown in Fig .4(a). The developed prominent planes are ((010), (0 -10), (-10-1), (101), (10-1), and (-101). The plane (101) is the most prominent among the other well developed planes. From the morphology studies, it was observed that the crystal grows faster along the 'b' direction.

The morphology of the BG grown from the mixed solvent of N, N- Dimethyl Formamide (DMF)-water at pH 3.0 is shown in Fig.4 (b). The planes are (100), (-100), (-111), (1-1-1), (111), (1-11) and (-11-1). The plane (111) is the most prominent plane compared to the other planes which dominate the crystal morphology.

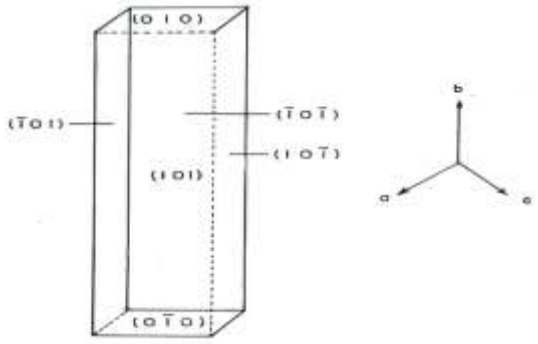

Fig. 4 (a) Morphology of BG crystal grown from mixed solvent of acetone and water

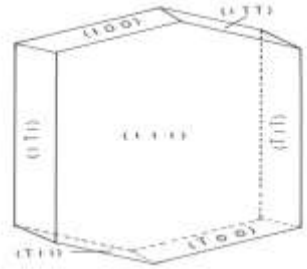

Fig. 4 (b) Morphology of BG crystal grown from mixed solvent of N, N- Dimethyl Formamide and water

UV-Vis-NIR absorption spectrum

The absorption spectrum of BG was recorded using Shimadzu UV–Vis spectrophotometer in the range from 200–1000 nm is shown in Fig.5. There was no absorption of light in the entire visible and near-IR region. It was observed that the crystal has a lower cut off at 340 nm. The crystal is found to be transparent in the entire visible region.

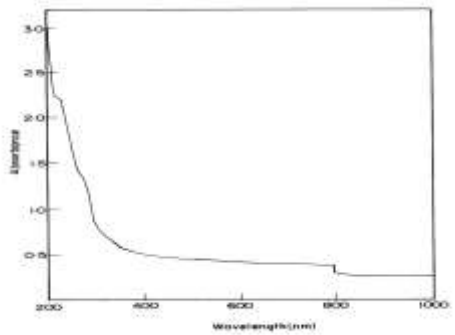

Fig.5. Optical absorption spectrum of BG

FTIR Analysis

The Fourier transform infrared analysis of BG was carried out using BRUKER IFS 66V model spectrophotometer by KBr pellet method in the wave number range from 4000 to 450 cm^{-1}. The recorded FTIR spectrum of BG is shown in Fig.6. The absorption peaks due to the vibrations of various functional groups present in the material was interpreted. The sharp peak at 3341 cm^{-1} is assigned to N–H symmetric stretching vibration. The peaks at 3086 cm^{-1} and 2937 $cm^{-1}$are attributed to the C–H symmetric stretching mode vibrations. The peak at 1740 cm^{-1} is due to C=O symmetric stretch. The C-C symmetric stretching are observed at 1600 cm^{-1} , 1491 cm^{-1} and 1416 cm^{-1}.The peaks at 1317 cm^{-1} and 1257 cm^{-1} corresponds to C-N symmetric stretching vibration. The C-O symmetric stretching is observed at 1189, 1079, and 1000 cm^{-1}. The bands observed at 850 cm^{-1},723 cm^{-1}, and 660 cm^{-1} are due to C-H bending vibration.

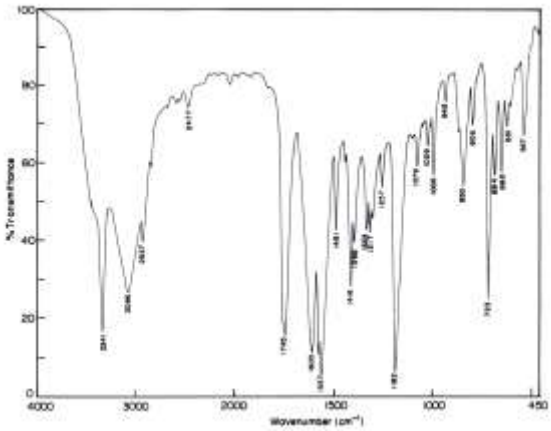

Fig.6. FTIR spectrum of BG

Thermal behavior

The thermal behavior of BG was studied using ZETZSCH – Geratebau GmbH thermal analyzer and the TG-DTA thermogram is shown in Fig.7. From the DTA graph, it was observed that the material is thermally stable upto 174.0º C. TGA graph shows that there is a sharp weight loss at 271.5ºC. In the DTA curve, the exothermic peak at 272.5ºC corresponds to the melting point of the substance.

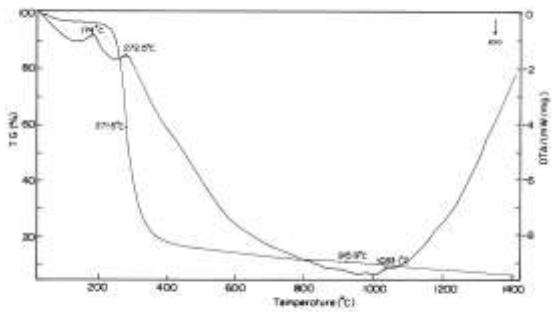

Fig. 6. TG-DTA of BG

Vickers micro hardness test

Microhardness measurement for the grown crystal was made using a Ultra micro hardness tester fitted with a Vicker's diamond pyramidal indentor attached to an incident light microscope. The static indentations were made at room temperature by varying the load from 5g to 60g. The plot of hardness (*H*v) versus load is shown in Fig. 8. From the study, it was observed that there is an increase in hardness with load, which can be attributed to the work hardening of the surface layer. Beyond the load of 50 g, significant cracking occurs, which may be due to the release of internal stresses generated with indentation.

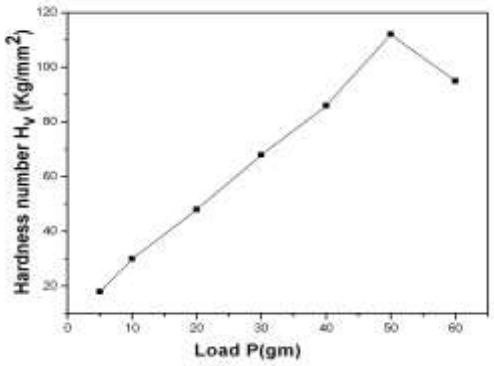

Fig. 8. Hardness behaviour of BG

Etching studies

Growth features and etches pits reveal reciprocity [9]. The presence of dislocation in crystals is usually inferred from the etch pits observation [10]. There is correlation between structural properties and surface features. The etching experiment was carried out on the single crystals of BG using mixed etchant of N, N- Dimethyl Formamide (DMF) and water. Fig.9 (a) shows the surface features of the BG single crystal before etching. Rectangular etch patterns are observed for an etching time of 20s is shown in Fig.9 (b). The observed etch pits, due to layer growth, confirmed the two-dimensional nucleation mechanism with less dislocations.

Fig .9. Etch pit observed on BG single crystal for a mixed etchant of N, N- Dimethyl Formamide (DMF) and water (a) before etching (b) 20s.

NLO studies

The NLO property of the crystal was confirmed by the Kurtz and Perry powder technique [11]. A fundamental beam of 1064 nm with pulse energy of 2.9 mJ and pulse width of 10 ns was passed through the sample. The emission of green light from the sample confirms the NLO property of the crystal. KDP sample was used as the reference material and the SHG efficiency of BG was found to be 2.5 times higher than that of KDP.

Conclusion

Single crystal of Benzoyl Glycine was grown by slow cooling technique. X-ray diffraction studies reveal that the crystal belongs to orthorhombic system. Absorption spectrum shows lower cut off at 340 nm. The FTIR analysis confirms the presence of functional groups in the grown crystals. Thermal behavior shows that the material is thermally stable up to 174.0ºC. The microhardness test reveals that the hardness increases with an increase in the load. Etching study showed that the crystal has adopted the two dimensional layer mechanisms with less dislocation. The relative second harmonic generation efficiency of BG crystal was found to be 2.5 times higher than that of KDP.

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