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ChemTech

International Journal of ChemTech Research
CODEN (USA): IJCRGG ISSN : 0974-4290
Vol.6, No.3, pp 1548-1551, May-June 2014

ICMCT-2014 [10th – 12th March 2014]
International Conference on Materials and Characterization Techniques

Synthesis, Structural, Spectral, Linear and Nonlinear optical properties, Laser damage threshold and Thermal studies of Gamma-Glycine from a new additive

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Abstract: The good quality crystal of non-centrosymmetric Gamma Glycine (GG) was grown by slow evaporation technique from aqueous solution in the presence of a new additive sodium nitrite. Single crystal X-ray diffraction and powder X-ray diffraction studies were carried out in order to confirm the structure and crystalline nature of GG crystal. The FT-IR spectrum confirms the expected functional groups of the title compound. The second harmonic generation (SHG) nonlinearity was confirmed by Kurtz and Perry powder technique. The laser induced surface damage threshold for the grown crystal has been measured using Nd:YAG laser. The thermal behavior of the grown crystal has been analyzed by Thermogravemetric and Differential thermal analyses (TG-DTA).
Key Words: Gamma glycine, Non-Centrosymmetric, Laser damage, SHG.

1. Introduction and Experimental Procedure

Great efforts have been made to the research and design of highly efficient non-linear optical (NLO) materials due to their widespread applications, such as high speed information processing, optical communication and optical data storage [1]. Glycine is one of the family members of amino acids which are well known to have polymorphism. The polymorphs are namely α-glycine, β-glycine and γ-glycine of which the first two crystallizes in centrosymmetric structure and the third crystallizes as non-centrosymmetric structure. The crystallization depends on several factors, such as variations in crystallization environment, solvent, temperature, use of additives and concentration, which can cause the same molecules to pack differently and form different crystal lattices or polymorphs. Herein, we report the growth and characterizations of gamma glycine grown using a new additive.

1.1 Material synthesis and Crystal growth

The starting materials Glycine (Qualigens) and Sodium nitrite (Merck) were taken in 2:1 ratio. Initially the calculated amount of glycine was dissolved in double distilled water, to this aqueous solution calculated

quantity of sodium nitrite was added and the mixture was stirred for 8 hours in order to achieve homogeneity. The solution was filtered and kept undisturbed. Optically transparent good quality Gamma glycine single crystals were harvested after a time span of 28 days. The photograph of as grown GG crystal is shown as inset in Fig.1 (a).

2. Results and Discussions

2.1 Single Crystal X-ray and Powder X-ray diffraction analyses

In order to confirm the cell parameters of GG it was subjected to single crystal X-ray diffraction analysis. It is observed that GG belongs to hexagonal crystal system with non-centrosymmetric space group $P3_1$ and the cell parameters were found to be, a = b = 7.02 Å, c = 5.47 Å and V = 233.8 $Å^3$ which are found to be in good agreement with the reported data [2]. From the observed cell parameters it can be concluded that the sodium nitrite has not been incorporated into the lattice of the grown crystal but its presence in the aqueous solution yielded gamma glycine. The powder X-ray diffractogram of GG is shown in Fig. 1 (b). The characteristic peak at 25.39^o (2θ) and the presence of (1 0 0), (1 1 0), (1 0 1), (1 1 1) and (2 0 1) planes in the powder X-ray diffraction spectrum strongly confirms the structure of GG. The appearance of sharp and strong peaks confirms the good crystallinity of the grown sample.

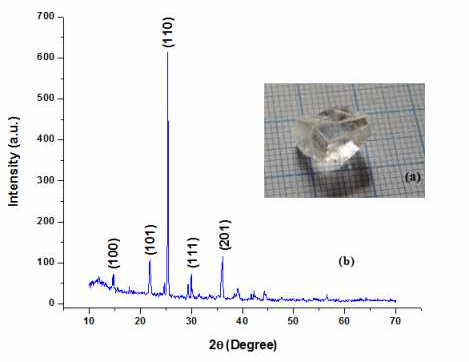

Fig.1. (a) As grown GG crystal
(b) Powder X-ray diffractogram of GG

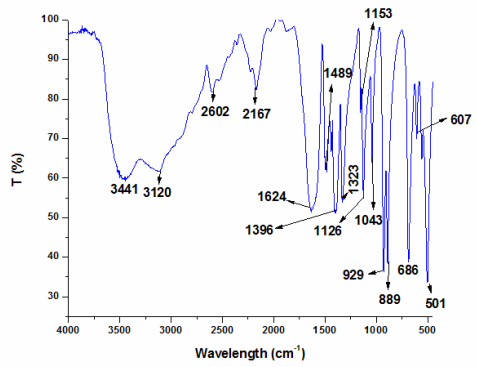

Fig.2. FT-IR Spectrum of GG

2.2 FT-IR Spectral analysis

In order to reveal the presence of characteristic vibrations of the functional groups of GG the FT-IR spectrum was recorded in the range of 4000 – 400 cm^{-1} and is shown in Fig.2. The bands observed at 501, 607 and 686 cm^{-1} are attributed to carboxylate groups while the peaks observed at 1489 and 1126 cm^{-1} are attributed to NH_3^+ group. The peaks at 1043 and 889 cm^{-1} are assigned to C-N stretching vibration and C-C stretching vibration, respectively. The bending vibration of C-H group appears at 929 cm^{-1}. The peak at 1323 cm^{-1} is assigned to CH_2 wagging vibration [3]. The high wave number region 2167 – 2598 cm^{-1} and 2794- 3441 cm^{-1} consists of band due to CH_2 and NH_3^+ stretching vibration.

2.3 UV-vis spectral analysis

The optical transmission spectrum of gamma glycine crystal was recorded in the range 200 – 800 nm. The UV–vis spectrum recorded with the optically transparent single crystal of GG is shown in Fig.3. As the UV cut-off of GG occur at 302 nm with a transmittance of nearly 82%, makes it suitable for the SHG of laser radiation 1064 nm. It is seen from the spectrum that the crystal is transparent in the entire range without any absorption peak, which is an essential parameter for NLO crystals.

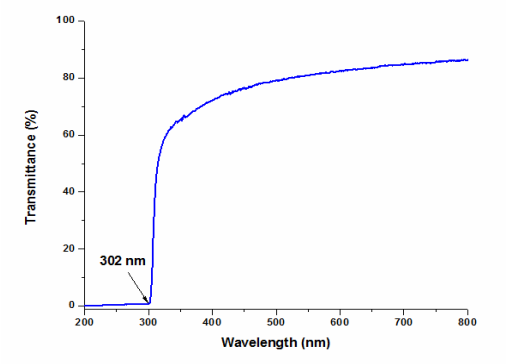

Fig.3. Optical Transmittance spectrum of GG crystal

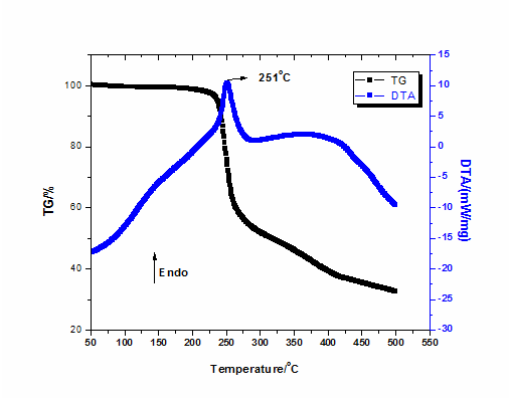

Fig.4. TG-DTA Thermogram of GG

2.4 Nonlinear optical study

A fundamental beam of wavelength 1064 nm with a pulse duration of 8 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 second harmonic signal of 22.8 mV was obtained for GG powdered crystal sample for an input energy of 5 mJ/pulse, while the standard potassium dihydrogen phosphate (KDP) powdered crystal sample gave a SHG signal of 15.4 mV for the same input energy. It shows that the SHG effective nonlinearity of GG is 1.48 times that of standard NLO material KDP.

2.5 Laser Damage threshold study

The multiple shot surface laser damage threshold is the most important parameter for NLO applications. The surface damage threshold of the GG crystal was calculated using the expression:

Power density, $P_d = \frac{E}{\tau \pi r^2}$ (1)

where E is the energy in (mJ), τ is the pulse width (ns) and r is the radius of the spot (mm). Based on multiple shot methods, the surface damage threshold of GG crystal is found to be 0.8 GW/cm^2.

2.6 Thermal analysis

The TG – DTA studies were carried out simultaneously in the temperature range of 50–500 ^{o}C and the thermogram is depicted in Fig.4. From TG curve, it is noticed that there is no weight loss up to 235 ^{o}C and there is a maximum weight loss in the temperature range 240 – 500 ^{o}C. The endothermic peak at 251 ^{o}C in DTA curve in association with the weight loss in TG confirms the decomposition of the GG at 235 ^{o}C. It shows that the GG crystal is thermally stable till 235 ^{o}C.

2.7 Conclusions

We have grown single crystal of gamma glycine by solvent evaporation technique from a mixture of aqueous solutions of glycine and sodium nitrite at ambient temperature. The sodium nitrite acts as an additive and thereby crystallizes alpha glycine as gamma glycine. The crystal structure and the crystalline nature of the GG were studied by single crystal and powder X-ray diffraction analyses. The presence of expected functional groups and molecular vibrations has been verified by FT-IR technique. The GG crystal have good transparency window in the UV – Vis region. The good second harmonic generation nonlinearity and laser damage threshold value indicates the use of GG crystals for application in nonlinear optical devices. The thermal stability of gamma glycine has been analyzed by simultaneous TG-DTA studies and it reveals that the title compound can be used for NLO applications till 235°C.

3. References

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