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Growth of N-Glycyl-L-Valine (GV) single crystal and its spectral, thermal and optical characterization

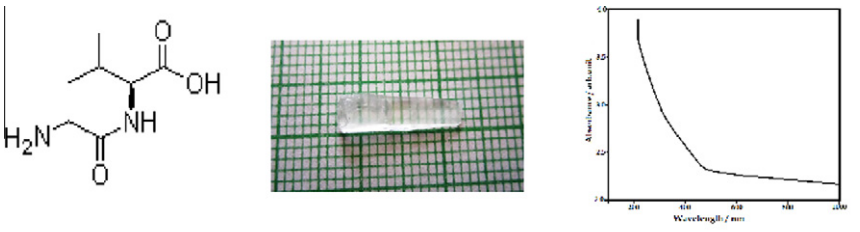
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HIGHLIGHTS

- N-Glycyl-L-Valine (GV) single crystals were grown by slow evaporation solution growth method.
- The FTIR and ^{1}H NMR spectral studies conducted on the GV confirms the functional groups and position of protons.
- The UV–Vis–NIR spectral study done reveals that GV crystal has a good optical transparency.
- The TG–DTA analyses reveals that GV crystal is thermally stable up to 246 °C.
- The Kurtz–Perry test done on the GV crystal reveals that the grown crystals has nonlinear optical (NLO) properties.

GRAPHICAL ABSTRACT



N-Glycyl-L-Valine (GV) | As grown crystal GV | UV-Vis –NIR spectrum of GV

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ABSTRACT

A nonlinear optical crystal of N-Glycyl-L-Valine (GV) single crystals was grown by slow evaporation solution growth technique from an aqueous solution. The unit cell parameters and the crystal structure were determined by single crystal X-ray diffraction study. The Fourier transform infrared (FTIR) and proton nuclear magnetic resonance (^{1}H NMR) spectral studies were carried out to identify the functional groups of the grown crystals. The ultraviolet visible near infrared (UV–Vis–NIR) spectrum was recorded to study the optical transparency of the grown crystal. The thermogravimetric (TG) and differential thermal (DTA) analyses revealed the thermal stability of the sample. The presence of second harmonic generation (SHG) for the grown crystal was confirmed by Kurtz–Perry powder technique.

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Introduction

Extensive research has been conducted over the past two decades on the growth of non-linear optical (NLO) crystals. The NLO property of the materials is playing a major role in emerging photonic and optoelectronic technologies. New NLO frequency conversion materials have a significant impact on laser technology and optical data storage [1]. The focus of the recent researchers is on developing new semiorganic NLO materials, as they have the advantages of being both organic and inorganic materials. The origin of NLO property in these materials is due to the presence of delocalized

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π electrons. Many natural amino acids individually exhibit the NLO properties [2] because they have a donor NH_2 and an acceptor COOH leading to the possibility for intermolecular charge transfer.

Glycine is the simplest amino acid and it forms several new compounds with other organic as well as inorganic materials. Recently, several complexes of glycine have been reported, viz., diglycine picrate [3], glycine sodium nitrate [4], glycine lithium sulphate [5], etc. In particular, semi-organic systems provide many interesting structure and bonding schemes for the molecular engineering of highly efficient new NLO materials. In this article, we report the growth of single crystals of N-Glycyl-L-Valine a new semiorganic NLO material by slow evaporation method and its characterization by, XRD, spectral, and optical analyses. Second harmonic generation (SHG) test and the thermal studies augmented the capability of the crystal as potential NLO material for a commendable temperature range.

Materials and methods

Crystal growth

In the present study, GV crystals were grown by low temperature solution growth using slow evaporation technique. The commercially available N-Glycyl-L-Valine (AR grade) was purified by repeated crystallization process before the actual growth as the quality of single crystals depends on the purity of the used materials. Since, the growth process and the quality of the crystals significantly depend on supersaturation, appropriate selection of solvent for the growth of the material is very important in crystal growth process. Deionized water at 35 °C was found to be the suitable solvent for preparing the growth solution. The super saturated solution was filtered by whatmann filter paper and allowed to evaporate slowly at room temperature over a period of three weeks, which yielded optically good quality crystals as shown in Fig. 1. A large size crystal can be obtained by taking large quantity of starting material.

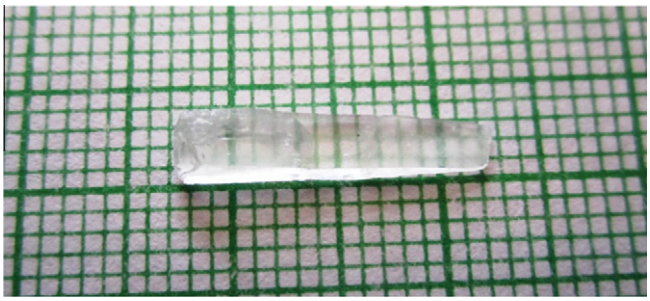


Fig. 1. As grown crystal GV.

X-ray diffraction study

In order to confirm the cell parameters of the grown GV crystals, the sample was subjected to single crystal XRD studies. The single crystal XRD study of GV single crystals was carried out using ENRAF NONIUS CAD4-F single X-ray diffractometer with Mo kα (λ = 0.7170 Å) radiation. Reflections from a finite number of planes were collected. The study revealed that grown GV crystal belongs to orthorhombic system with the following cell parameters, a = 5.452 Å, b = 26.601 Å, c = 43.872 Å and V = 6362.697 (Å)^3. These values have a very close agreement with reported values [6].

FTIR spectral analysis

The functional groups of GV were confirmed by recording the FTIR spectrum in the range of 400–4000 cm^{-1} (Fig. 2) using BRUKER IFS – 66 V spectrometer by KBr pellet technique to confirm the presence of amino acid in the sample qualitatively. A sharp band at 1693 cm^{-1} is due to the amide carboxyl group and weak band at 1627 cm^{-1} is due to the carboxylic acid carbonyl group. Similarly the peaks at 1548 and 3074 cm^{-1} is due to the N—H stretching and bending vibration of amide and free —NH_2 groups. A sharp signal at 3240 cm^{-1} is due to the hydroxyl group in carboxyl acid and the peak at 2958 cm^{-1} is due to the presence of alkyl stretching vibration. A signal at 2653 cm^{-1} is due to the intermolecular hydrogen bonding present in between two carboxylic acid groups.

Proton NMR spectral studies

Identification of compounds is an important task and is very much accomplished by techniques like NMR spectral analysis [7]. The proton NMR spectrum was recorded for the crystal dissolved in deuterated water (D_2O) using JOEL GSX 400 NB FT NMR spectrometer, 400 MHz. The ^{1}H NMR spectrum of GV is shown in Fig. 3. A sharp singlet at 0.91 ppm is due to the six protons of dimethyl group. A multiplet at 1.90 ppm corresponds to H—C, β-to —COOH group. The sharp doublet at 4.25 ppm is assigned to C—H attached α-to —COOH group. The two singlets at 8.03 and 11.0 ppm are attributed to the carboxylic acid proton —COOH and amide proton —NH—C=O— of the GV respectively. The two sharp singlets at 1.53 and 3.54 ppm correspond to free amide protons —NH_2 and carbonyl group —CH_2 attached in between to the free amide and carbonyl group.

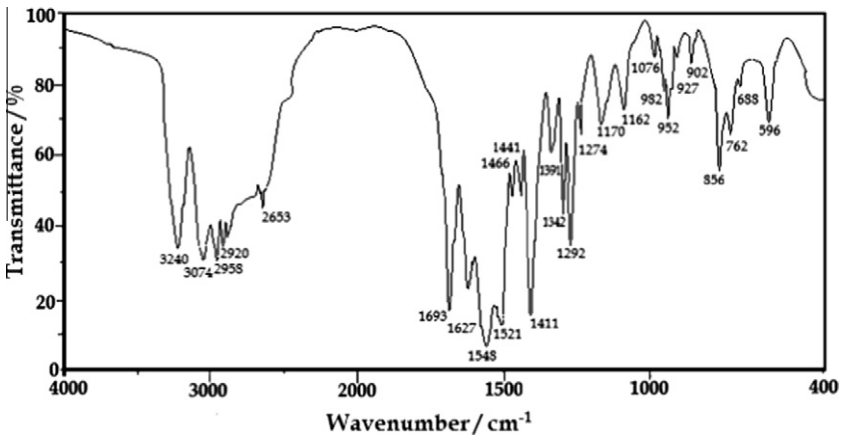


Fig. 2. FTIR spectrum of GV.

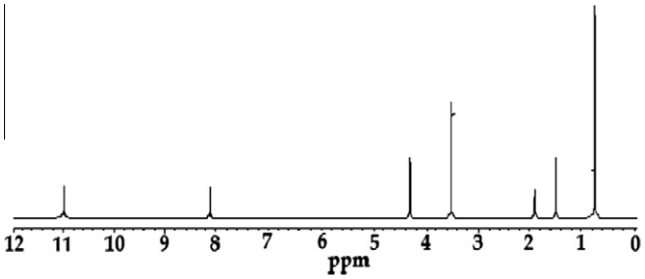


Fig. 3. ^{1}H NMR spectrum of GV.

UV–Vis–NIR spectral analysis

The transparent nature of GV crystal was examined by the UV–Vis–NIR spectral analysis in the region between 200 and 1000 nm using VARIAN CARY 5E UV–Vis–NIR spectrophotometer. From the spectrum (Fig. 4), it is evident that the GV has a good transmittance as its lower cutoff wave length is below 300 nm. The large transmission in the entire visible region enables it to be a good candidate for optoelectronic applications.

Thermal analysis

Thermogravimetric and differential thermal analyses give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal [8]. The thermo gravimetric analysis deals with the change in the mass of the substance, which is continuously monitored as a function of temperature when it is heated. The thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of the crystal was done using the instrument NETZSCH STA 409 °C at a heating rate of 20 °C min^{-1} in the temperature range of 20–800 °C and the thermogram is shown in Fig. 5. The sample is found to be thermally stable up to 246 °C. The TGA curve shows sharp melting endotherm at 246 °C followed by a weak exotherm at 380 °C, the later being clearer in the DTA curve. The DTA measurements are in close agreement with the TGA analysis in the experimental limits. The sharpness of the melting curve is an indication of purity of the sample.

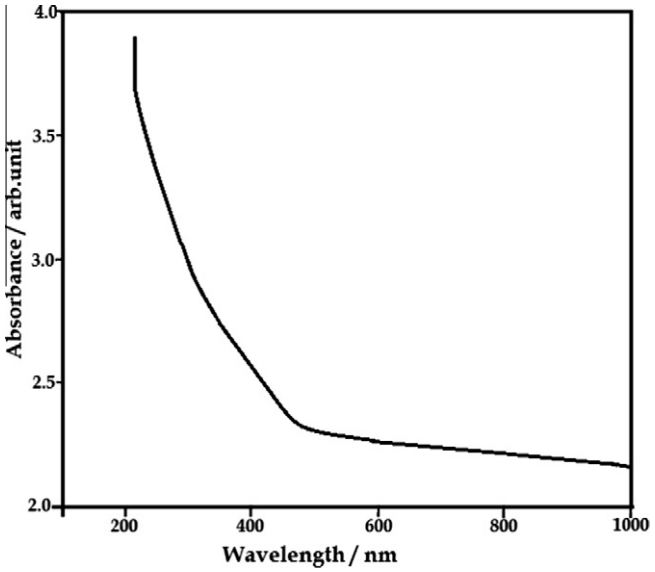


Fig. 4. UV–Vis–NIR spectrum of GV.

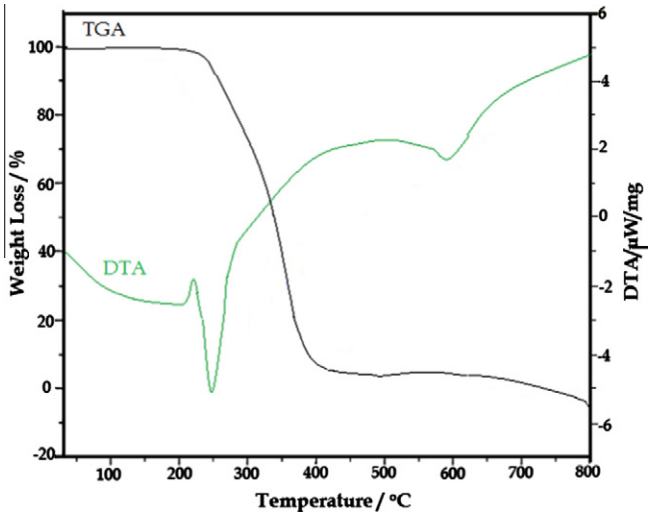


Fig. 5. TG–DTA curves of GV.

Nonlinear optical test

Second harmonic generation (SHG) test for GV crystal was carried out using the Nd-YAG laser of wavelength of 1064 nm using Kurtz and Perry powder technique [9]. The input laser beam was passed through an IR reflector and was then directed on the microcrystalline powder sample packed in a capillary tube. Photodiode detector and an oscilloscope assembly detected the light emitted by the sample. The emission of green light (532 nm) confirmed the SHG of the crystal.

Conclusion

The single crystals of N-Glycyl-L-Valine (GV) were grown by slow evaporation technique. The single crystal X-ray diffraction analyses confirm the lattice parameters of GV crystals which were in accordance with the literature values. FTIR and ^{1}H NMR spectral studies supported the structure and purity of GV. The UV–Vis–NIR spectrum showed that it has a good optical transmittance in the entire visible region and it is a potential candidate for optoelectronics. The thermogravimetric analysis showed that the grown crystal is thermally stable up to the temperature of 246 °C. The SHG property was experimentlly verified. Hence, the aforesaid results make GV crystals a valid candidate for the NLO applications.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.saa.2012.10.078.

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