Growth and Characterization of Stable β-Polymorphs of L-Glutamic Acid by Slow Evaporation Method

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Abstract: ***Stable β-polymorph of L-glutamic acid was grown from aqueous solution by slow evaporation method. Needle like crystals were obtained from aqueous solution with 110 h. The structural and spectral property of the grown crystal was confirmed by powder X-ray diffraction method and FTIR respectively. Optical property of the grown crystal was studied by UV-Vis-NIR spectroscopy. Thermal property of the grown crystal was studied by TG/DTA. Further it was confirmed by DSC. The SHG efficiency of the grown crystal was confirmed by Kurtz Perry powder method.***

Keywords: Crystal growth from solutions, Powder X-ray diffraction, FTIR, Second harmonic generation.

1. Introduction

A polymorph is defined as "a solid crystalline phase of a given compound resulting from the possibility of at least two crystalline arrangements of the molecules of that compound in the solid state" [1]. Many of the organic compounds and in particular several of the amino acids exhibit polymorphism. One among the 20 amino acids L-glutamic acid, has two known polymorphs; meta stable α and stable β [2]. The β-polymorph has NLO property. Hence effort has been made to grow such crystals by solution growth technique. The structural property was done by powder X-ray diffraction study. Optical property of the crystal was studied by UV-Vis-NIR spectroscopy. The thermal studies were carried out by Thermogravimetric and Differential Thermal Analysis (TG/DTA) and DSC. NLO property is verified by Kurtz Perry method.

2. Experimental Procedure

Commercially available L-glutamic acid was dissolved in deionised water (1.5g /100 ml) at 40°C. The growth process was carried out in aqueous solution and constant stirring is required to make a homogenous mixture. The resulting solution was filtered using Whatmann filter paper and is kept in a beaker. It closed with perforated cover in undisturbed position. After a few days the grown crystals were harvested depending on our required shape and size. The photograph of the grown crystals is shown in Figure1. Grown crystals of β polymorph of L-glutamic acid have been subjected to various characterizations.

Figure 1: Photograph of the grown β-L-glutamic acid

3. Characterizations

3.1 Powder X-Ray Diffraction analysis (PXRD)

In order to confirm the form of crystallization of the grown β crystals of glutamic acid, powder X-ray diffraction spectrum of the grown crystals were recorded. The recorded powder X-ray diffraction pattern of the grown crystals of β polymorph of L-glutamic acid is shown in Figure. 2.

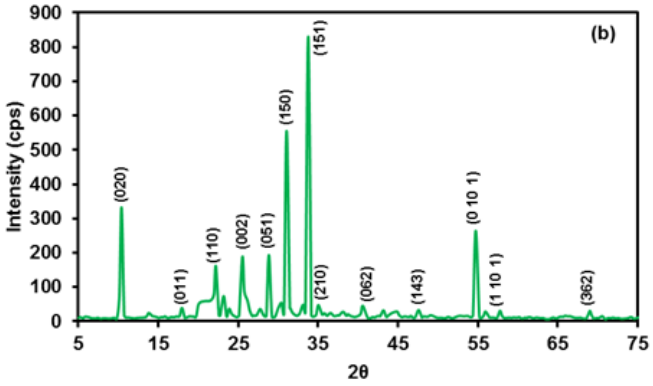

Figure 2: Powder X-ray diffraction pattern of the β-L-glutamic acid

The XRD data obtained from the pattern confirm that the β-L-glutamic acid belong to the orthorhombic crystal system with space group $P2_12_12_1$ and point group 222. The

determined lattice parameters for β polymorph is a=5.183Å, b=17.315Å and c= 6.973Å, and they are in line with the literature values [3, 4-8].

3.2 FTIR spectroscopic analysis

FTIR spectrum of the β-polymorph was recorded and various functional groups present in the crystals were analyzed by identifying their corresponding absorption frequencies. The recorded spectrum of the β polymorph of L-glutamic acid is shown in Figure 3.

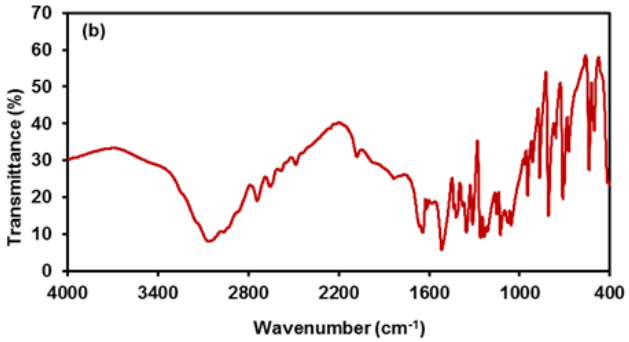

Figure 3: FTIR spectrum of the β-L-glutamic acid

Various absorption peaks present in the recorded FTIR spectra for β crystals are assigned to their corresponding functional groups and are listed in Table 1. In the case of β-L-glutamic acid, the absorption peak observed at 3157 cm^{-1} in the high frequency region corresponds to O-H stretching vibration of the hydroxyl group. The absorption corresponding to the weaker N-H stretching vibration appears as a band at 3092 cm^{-1} in the high frequency region and is due to the primary amines ($-NH_2$). The absorption peak corresponding to the C-H stretching vibration also overlaps with that of the N-H stretching vibration around 2950 cm^{-1}. The absorption corresponding to the C=O stretching vibration is observed as a strong peak at 1679 cm^{-1} and it belongs to the carboxylic acid group of the molecule. The C-O stretching vibration shows an absorption peak at 1130 cm^{-1}. The absorption peak observed at 948 cm^{-1} is corresponding to O-H bending vibration.

Table 1 FTIR functional group assignments of the grown β-L-glutamic acid.

Mode of vibrations	*Standard [16]*	*β-L-glutamic acid*
	Wavenumber (cm^{-1})	*Wavenumber (cm^{-1})*
O-H stretching	3400-2400	3157
N-H stretching	3500-3100	3092
C-H stretching	3000-2850	2950
C=O stretching	1725-1700	1679
N-H bending	1640-1550	1635
C-H bending	1465	1472
C-O stretching	1300-1000	1130
O-H bending	930	948

3.3 Optical Transmittance Study (UV-Vis-NIR)

In order to study the optical transmittance of the grown β polymorph, the UV-Vis-Near IR spectrum of the sample is recorded in the wavelength range from 200 to 2000 nm, and is given in Figure 4. The optical transmittance spectrum is important from the application point of view, as the grown crystal or the device fabricated out of the crystal can only be used in the highly transparent region.

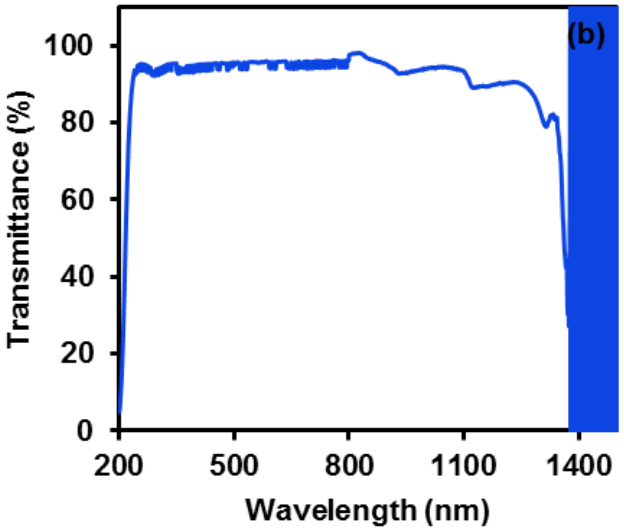

Figure 4: Optical transmittance spectrum of β-L-glutamic acid

The recorded optical transmittance spectrum indicates that the β polymorph has optical transparency in the wavelength region between 226 and 1348 nm. Further, this study indicates that the grown polymorph is highly transparent in the entire visible and near-IR region with UV cut-off well below 300 nm. It is the most desirable characteristics for any optical application, especially for non-linear optical applications such as optical second harmonic generation.

3.4 Thermogravimetric and Differential Thermal Analysis (TG/DTA)

In order to understand the thermal stability of the nucleated polymorph above room temperature, the TG and DTA curve was recorded in the temperature range from ambient to 800 ºC. The recorded TG/DTA thermogram of the β-L-glutamic acid is shown in Figure 5.

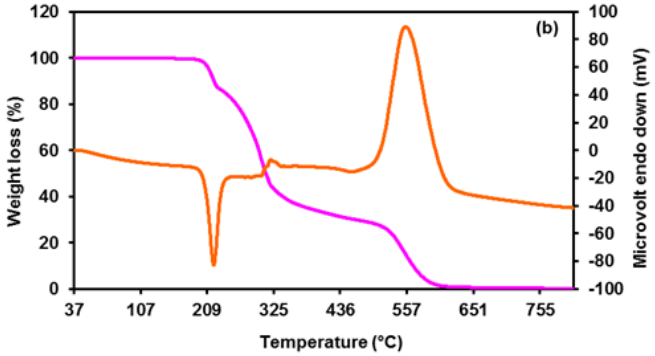

Figure 5: TG/DTA thermogram of the β-L-glutamic acid

In the case of β-L-glutamic acid melting starts at 190.4 °C and ends at 210 °C with a sharp melting band of 19.6 °C. From the TG curve it is observed that the weight loss of 12% occurs between the temperatures 190 °C and 210 °C. This melting indicates that the material is more stable upto the melting. There is no endothermic or exothermic peak observed in the DTA curve below the melting temperature and similarly there is no weight loss observed in TG curve up to the melting temperature. This confirms that the material

does not undergo any phase transformation in this temperature range. A broad exothermic peak is observed in the DTA curve of the grown β-L-glutamic acid microcrystal in the range of 450-630 °C, this may be the cross-linking (cure). After this the material decomposes. Results of this study confirm that β-L-glutamic acid crystals have high thermal stability than that of α-L-glutamic acid crystals.

3.5 Differential Scanning Calorimetry (DSC) analyses

Results obtained from the TG-DTA study was further confirmed by DSC analysis. From the DSC curves, the thermal stability of the grown polymorph was recognized. The recorded DSC thermogram of the grown β polymorph is given in Figure 6.

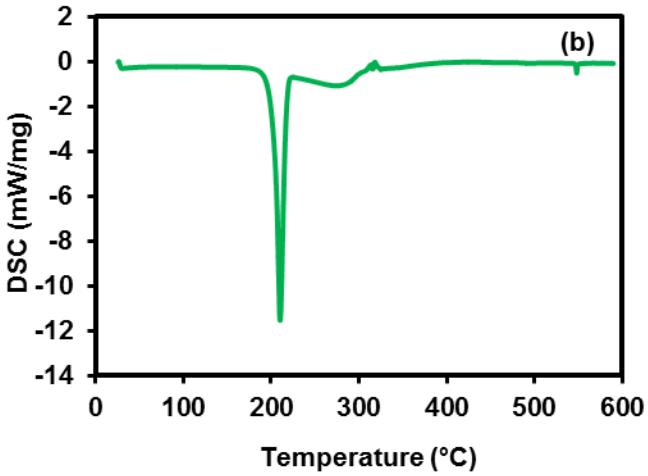

Figure 6: DSC thermogram of the β-L-glutamic acid

The DSC thermogram given in Figure 6 indicates that the grown β polymorph begins its melting at 195.01 °C and ends at 210.24 °C with a sharp melting band of 15.23 °C. From the DSC curve again it is clear that, β-L-glutamic acid polymorph does not have any phase transformation until their melting point and are stable [9].

3.6 Second Harmonic Generation study (SHG)

The second harmonic generation behaviour of the powdered β-L-glutamic acid polymorph was tested by the Kurtz powder technique [10]. Crystalline sample of β polymorphs of L-glutamic acid crystal for which NLO efficiency is to be measured were ground well using mortar and pestle. The ground samples were sieved out for a uniform particle size of 150 µm and used for the experiments. The powder sample is packed in a triangular cell and is kept in a cell holder. The test was carried out using a high-intensity Nd:YAG laser (Quanta-Ray, Spectra physics) source which produces nanosecond pulses (8 ns) of λ =1064 nm light and the energy of the laser pulse was around 350 mJ. Frequency repetition of 10 Hz was passed through the powdered sample. The beam emerging through the sample was focused on to a Czerny-Turner monochromator using a pair of lenses. The SHG behaviour is confirmed from the output of the laser beam having the bright green emission (λ = 532 nm) from the specimen. The detection was carried out using a Hamamatsu R-928 Photomultiplier tube. The signals were captured with an Agilent infiniium digital storage oscilloscope interfaced to a computer. The recorded SHG signal of the grown β polymorph is given in Figure 7.

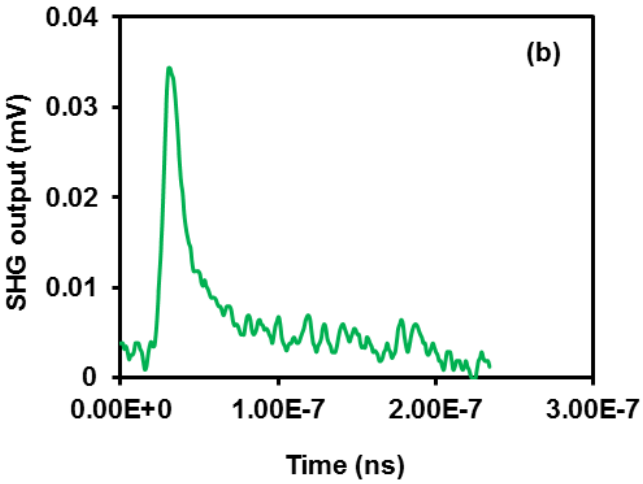

Figure 7: SHG signal of β-L-glutamic acid

The second harmonic signal of about 0.035 mV/pulse was obtained for the crystalline powder of the β-L-glutamic acid (stable form) an input energy of 350 mJ/pulse as shown in Figure 7. This result indicates that the grown β-L-glutamic acid polymorph have the ability to generate SHG for the given laser input. The SHG energy conversion efficiency of β-L-glutamic acid polymorph is less than that of the standard inorganic KDP. The SHG signal of 0.564 mV/pulse was obtained from the standard inorganic KDP crystal for the same input energy.

4. Conclusion

Stable β polymorph of L-glutamic acid was grown by slow evaporation method. The XRD data obtained from the pattern confirm that the polymorph belong to the orthorhombic crystal system with space group $P2_12_12_1$. FTIR spectra of the β-polymorphs were recorded and various functional groups present in the crystals were analyzed by identifying their corresponding absorption frequencies. From UV-Vis-NIR we can confirm the optical transparency of the grown crystal. TG/DTA and DSC analysed the thermal stability of the grown crystals. Second harmonic generation provides an opportunity for the application of crystals in photonic industry for future generation.

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