Growth, Spectral, Thermal and Dielectric Properties of Triglycine Phosphate Non Linear Optical Crystal

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Abstract

Single crystals of Triglycine Phosphate (TGP) were grown from aqueous solution by slow evaporation technique. Good optical quality single crystals with dimensions 14X10X4 mm³ were obtained. Single crystal X-ray diffraction analysis reveals that TGP crystals belong to monoclinic system. Various diffracting planes of the grown crystal were identified from the powder X-ray diffraction study. The functional groups present in the structure of the grown crystal are identified by using FTIR spectral analysis. The UV-visible absorption spectra have been recorded to study the optical transmittance in the range from 200 nm to 800 nm. Thermal stability and melting point of the grown crystal were found by thermal analysis. Dielectric constant and dielectric loss measurements were carried out for different temperatures and frequencies.

Keywords: Single Crystal; Slow Evaporation Technique; Single Crystal X-ray Diffraction; FT-IR; TGA/DTA

Introduction

Today's technology is seeing a rapid change and its reflection on materials is splendid. The technological development to a larger extent is dependent on the development of crystal growth. Hence the growth of single crystals has become inevitable for any further development in materials science research. In recent years, emphasis has been centred on materials exhibiting large second-order NLO response because of the potential application in telecommunications, optical computing, optical signal processing, laser technology, data storage and image processing [1, 2]. The development of photonic and optoelectronic technologies rely heavily on the growth of NLO materials with high nonlinear optical responses and the development of novel and more efficient materials [3]. Many NLO crystals grown by mixing amino acids with various organic and inorganic acids have been reported in the literature [4-6]. Amino acids are interesting materials for NLO application as they contain proton donor carboxyl acid (-COO) group and the proton acceptor amino (NH₂) group in them [7]. Glycine is the smallest among the amino acids, which are found in proteins, and is of special interest as a model for theoretical and experimental studies [8]. The present investigation deals with the growth of Triglycine

Phosphate single crystal by slow solvent evaporation technique and to characterize the grown crystal. The grown crystals were characterized by single crystal and powder X-ray analysis, FTIR and UV spectral analysis, TG/DTA and dielectric measurements. The results of these studies have been discussed.

Experimental

Triglycine phosphate was obtained by mixing glycine and phosphoric acid in the stoichiometric ratio 3:1 at a constant temperature of 30°C. The fully reacted solution was filtered and crystalline TGP was obtained by evaporation of filtered solution. Transparent crystals were obtained within a period of 2-3 weeks. Photograph of the grown crystal is as shown in Fig 1

Figure 1: Grown pure TGP crystal.

Figure 2: Structure of Triglycine Phosphate crystal.

Result and Discussion

Single Crystal XRD Measurement

Grown TGP crystal is subjected to single crystal XRD to determine the unit cell dimensions and cell volume. A good quality crystal of dimension about $5 \times 4 \times 4$ mm³ was selected for the X-ray diffraction studies. Single crystal XRD using a computer controlled Enraf Nonius- CAD4 single crystal diffractometer. Structure of Triglycine Phosphate crystal as shown in Fig 2. Unit cell dimensions determined by single crystal X-ray diffraction analysis are presented in Table 1.

Powder XRD analysis.

The powdered sample of the grown crystal was also subjected to powder X-ray diffraction analysis using XPert PRO powder X-ray diffractometer. The peaks observed in the X-ray diffraction spectrum were analysed and the lattice parameters were calculated by the least square fit method. The data obtained by the powder X-ray diffraction analysis is in accordance with the single crystal X-ray diffraction data. It is clear that for the crystal $a \neq b \neq c$, $\alpha = \gamma = 90^\circ$ and $\beta \neq 90^\circ$, which ensures that the grown TGP crystal is of monoclinic structure [9]. The indexed powder X-ray diffraction pattern is shown in Fig. 3.

FT-IR Spectral Analysis

FT-IR spectra of TGP crystal shown in figure 4. The FT-IR spectra of pure and doped TGP crystals were recorded in the region 400- 4000 cm⁻¹ using Perkin-Elmer Spectrum-one FT-IR spectrometer. The fundamental modes have been qualitatively assigned, Figure 4.

The functional groups present in the grown crystal were confirmed with the FT-IR spectral analysis. The bands at 3778 cm⁻¹ are assignable to symmetric NH₂ deformation mode. Asymmetric stretching vibration of NH₂⁺ was observed at 3111 cm⁻¹ within the allowed region as the protonation of NH₂ group can shift in band position towards the range 3300–3100 cm⁻¹ for asymmetric stretching in amino acid derivatives [10]. The band observed at 2962.97 cm⁻¹ and 2890.02 cm⁻¹ are assignable to CH₂ stretching mode. The band at 2230.28 cm⁻¹ is assigned to asymmetric NCO stretching mode. NH₃ symmetric and degenerate modes of deformation at 1490.73 cm⁻¹ and 1590.40 cm⁻¹. P = O stretching was in 1326.85 cm⁻¹ and P – O stretching was in 1041.83 cm⁻¹. The results are matching with the reported value [11]. The peak at 926.73 cm⁻¹ are assignable C-OH plane mode. The peak at 887.92 cm⁻¹ is due to C-C stretching mode. The deformation vibrations of the carboxylate ion are due to the band observed at 682.95 cm⁻¹. The peak at 607.79 cm⁻¹ is due to C-N bending mode. Deformation of COO⁻ at 501.99 cm⁻¹.

UV-Vis Spectral Analysis

Optical transmittance range and transparency cut-off wavelength are the main requirements for device applications. Grown crystals were optically characterised by UV-Vis spectral analysis and is shown in figure 4. The UV-Vis spectra was recorded in the range of 190-1200 nm by using Lambda 35 Spectromete. Figure 5.

The absorbance was evident below 204 nm. A complete transparency between 230 and 800 nm is interesting, as it is very much required for NLO applications of this crystal [12].

Thermal Analysis

Thermal stability of the grown crystal was identified by Thermo Gravimetric (TG) and differential thermal analysis (DTA). The thermal analysis was carried out simultaneously employing Perkin Elmer thermo gravimetric and differential analyser (Mode: PYRIS DIAMOND) in nitrogen atmosphere heated from 400 to 7300 with a heating rate of 100 C to understand thermal behaviour. The TG/DTA patterns obtained in the present work is shown in Fig.6.

Table 1: Single crystal XRD data of TGP crystal

Chemical Formula	(NH ₂ CH ₂ COOH) ₃ H ₃ PO ₄	Crystal system	monoclinic
Wavelength	0.71073 Å	Space Group	Pcc2
a	5.094 Å	α	90°
b	11.984 Å	β	111.70°
c	5.453 Å	γ	90°
cell volume	309.3(4) Å ³		

Figure 3: Indexed powder XRD pattern of TGP.

Figure 4: FT-IR spectrum of TGP.

The TG curve shows no change in weight up to 235°C, which eliminate the possibility of hydrate or solvate formation of crystals. The major weight loss around 235–285°C and minor weight loss in the temperature range 285–385°C could be attributed to the sublimation and decomposition of the glycine resulting in the release of CO and NH₃ molecules [13]. The peak at 252.86°C in DTA curve indicated the decomposition of the glycine. Thereafter residue remains up to of 800 °C. It is clear that the crystal is thermally stable up to 235°C.

Dielectric studies

Dielectric study of the grown crystal was carried out to an accuracy of $\pm 2^\circ\text{C}$ using an LCR meter with five different frequencies, viz. 100 Hz, 1 KHz, 10 KHz, 100 KHz and 1 MHz at various temperatures ranging from 30°C to 220°C. A sample of having silver coating on the opposite faces was placed between the two copper electrodes and a parallel plate capacitor was thus formed.

Variation of dielectric constant (ϵ_r) with frequency and temperature is shown in figure 7. In the present work, ϵ_r was found to increase with increase in temperature and decrease with increase in frequency. The increase in dielectric constant with temperature is essentially due to the temperature variation of ionic polarizability. Variation of dielectric loss factor with frequency and temperature is shown in figure 8. Value of $\tan \delta$ shows systematic variation with temperature. Variation of σ_{ac} with frequency and temperature is shown in figure 9. σ_{ac} values found to increase with the increase in temperature, indicating that the grown crystal is normal dielectric material.

Conclusion

Triglycine phosphate was grown using slow evaporation technique from an aqueous solution

Single crystal of The Singe crystal and Powder XRD analysis confirmed the monoclinic structure of the crystal. Various functional groups have been identified by the FTIR spectral analysis. The wide range of transparency in UV and visible region enables that the grown crystal is to be a good candidate

Figure 5: UV-Vis Spectrum of TGP.

Figure 6:

Figure 7: TG/DTA plot of TGP crystal.

Figure 8: Variation of dielectric constant (ϵ_r) with frequency and temperature.

Figure 9: Variation of dielectric loss factor with frequency and temperature.

for optoelectronic applications. The thermo gravimetric analysis confirms the thermal stability of the grown TGP crystal up to 235 °C. Variations of ϵ_r , $\tan \delta$, and σ_{ac} values with frequency and temperature shows that the grown crystal is normal dielectric material.

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