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Synthesis, Growth and Characterization of semi-organic non-linear optical Triglycine phosphoric acid (TGPA) single crystals

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Abstract
Single crystals of Tri glycine phosphoric acid (TGPA) a semi organic non-linear optical material, has been grown from solution by slow evaporation method at room temperature. The title compound was synthesized and purified by repeated recrystallization process. The growth of crystals was confirmed at pH 2.8. The crystals were characterized by single crystal X-ray diffraction and Fourier transform Infrared Spectroscopic (FTIR) analysis. The formation of TGPA crystal was confirmed by powder XRD analysis. The range and percentage of optical transmission was ascertained by recording UV-vis-NIR spectrum. The second harmonic generation behaviour of TGPA crystal was tested by Kurtz-Perry powder technique and its mechanical hardness was estimated by Vickers microhardness method.
Keywords: Characterization, solution growth, X-ray diffraction, FTIR spectrum, nonlinear optical crystals

Introduction

In our scientific world, the developments of science in different areas have been achieved through the growth of good quality single crystals in order to satisfy the day-to-day technological requirements. But in the recent past the rapid development in the field of optoelectronics greatly increased the demand for newer nonlinear optical (NLO) materials. In this regard, materials scientists discovered new type of materials called semi-organic. Glycine family crystals have been subjected to extensive research by several researchers[1-4] for their efficient NLO properties. The glycine molecule can exist in zwitterionic form and hence it is capable of forming compounds with anionic, cationic and neutral chemical compounds. Thus a large variety of glycine coordinated compounds can be formed. However, only those complexes of glycine, which crystallizes in non-centrosymmetric structure, are expected to exhibit nonlinear optical second harmonic generation. Glycine (NH_2-CH_2-COOH) is one such amino acid that crystallizes in three different forms α, β and γ. It has been reported that glycine combines with H_2SO_4,[5] $CaCl_2$,[6] $BaCl_2$,[7] $CaNO_3$,[8] and $LiNO_3$[9] to form single crystals. The author report in this article on the estimation of solubility and growth of TGPA crystals from aqueous solution by slow evaporation method. These crystals were characterized by single crystal X-ray diffraction, FTIR, UV-vis-NIR transmittance analysis,

Powder XRD, SHG efficiency studies and Vickers microhardness studies.

2. Experimental procedure
2.1 Synthesis, solubility and growth of TGPA single crystals

TGPA salt was synthesized by taking Analar grade glycine and phosphoric acid in the ratio 3:1. The synthesized salt of TGPA was finely powdered and was used for solubility study. The solubility of TGPA was determined for six different temperatures, viz., 30, 35, 40, 45, 50 and 55°C. Solubility at a particular temperature was determined by dissolving the synthesized salt in 100 ml of double distilled water taken in an airtight container maintained at the same temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was estimated gravimetrically. The same procedure was repeated to estimate the solubility at different temperatures. The variation of solubility with temperature is shown in Fig.1. To grow single crystals of TGPA, slow evaporation method was employed. Good quality of crystal with well-defined morphology was grown over a typical growth period of 26 days. The crystals were highly transparent and free from inclusions. The as-grown tri glycine phosphoric acid single crystal is shown in Fig. 2.
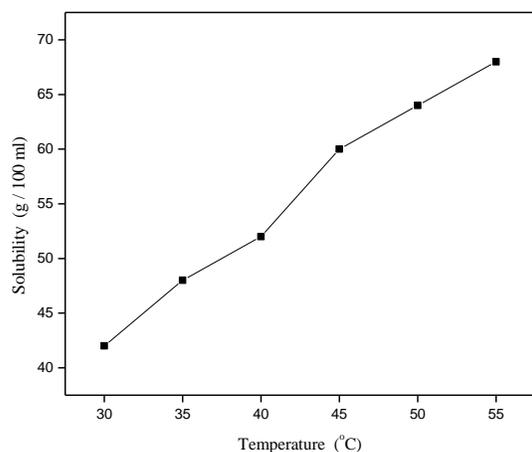
Fig.1. Solubility curve of TGPA

Fig.2.

Photograph of TGPA single crystal

3. Characterization Studies
3.1 Single crystal X-ray diffraction analysis

Single crystal X-ray diffraction was carried out by using ENRAF NONIUS CAD-4 diffractometer to estimate the cell parameters. TGPA belongs to the non-centrosymmetric hexagonal system and the obtained crystallographic parameters are a = 6.985 (8), b = 6.985 (3), c = 5.451 (4), $\alpha = \beta = 90°$, $\gamma = 120°$ and V = 230.32 (6) Å^3.

FTIR studies

Every chemical compound has its own characteristic IR spectrum. The FTIR spectrum contains the entire information about the molecular structure of the investigated sample. In this technique almost all functional groups in a molecule absorb characteristically within a definite range of frequency[10]. In this study, the FTIR spectrum was recorded in the range 400-4000 cm^{-1} for the TGPA single crystal. The FTIR spectrum of TGPA crystal is shown in Fig.3.The peak observed at

3173 cm^{-1} is due to N-H stretching vibration and at 2614 cm^{-1} is due to NH$_3^+$ stretching vibration. The band at 2123 cm^{-1} and 1605 cm^{-1} is due to COO$^-$ stretching vibration. The sharp absorption bands at 1516 cm^{-1} and 1408 cm^{-1} corresponds to NH$_3^+$ asymmetric bending vibration and COO$^-$ stretching vibrations, respectively. The absorption peak at 132 cm^{-1} and 111 cm^{-1} is due to CH$_2$ twisting and NH$_3^+$ rocking.. The peak observed at 1033 cm^{-1}and 893 cm^{-1} is due to CCN asymmetric stretching vibration. The sharp peak at 693cm^{-1} is due to COO$^-$ bending. The Raman band at 505 cm^{-1} is due to COO$^-$ rocking. Thus the FTIR spectrum confirms the formation of TGPA and its characteristic frequencies are observed as mentioned above.
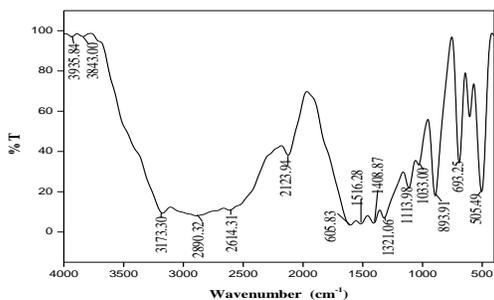

Fig.3. FTIR spectrum of TGPA

3.2 UV-vis-NIR spectral studies

The optical transmittance range and the transparency cut-off are important parameters to tailor the material for specific application. The dependence of optical absorption coefficient with the photon energy helps to study the band structure and the type of transition of electrons[11]. The well polished crystal of 2mm thickness was subjected to transmission measurements using Lambda 35UV-Vis-NIR spectrophotometer in the spectral region of 200-1100 nm. Fig.4 shows the transmission curve, in which the lower cut-off wavelength obtained at 240 nm

and the transparency of the crystal in the entire visible region suggests its suitability for second harmonic generation. Using the formula, Eg = hc/λ, the band gap energy was found to be 4.55eV.
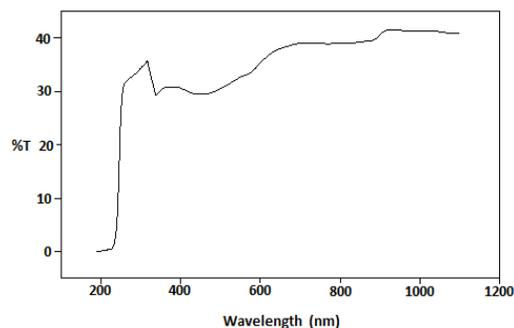
Fig.4. UV-vis-NIR transmittance spectrum of TGPA

3.3 Powder XRD analysis

X-ray powder diffraction was used for the identification of the synthesized crystal. The study was carried out for TGPA crystal using X'PERT PRO Diffractometer with copper (K-Alpha 1) radiation (λ=1.5405600 Å) operating at a voltage of 40KV and a current of 20 mA. The scanning rate was maintained at 1.60/min over a 2θ range of 0-70^0 employing the reflection mode for scanning. The prominent peaks in the XRD pattern have been indexed. The well-defined Bragg's peaks at specific 2θ angles show high crystallinity of TGPA. The recorded spectrum is shown in Fig.5. The differences in the peak amplitude can be attributed to the different sizes and orientation of the powdered grains. Using the value of d, the hkl values of all the reflections were obtained. The peaks observed from the X-ray diffraction spectrum were analysed and the lattice parameters were calculated by the unit cell software program. The calculated lattice parameters are a=7.0861 Å, b=7.0861 Å, c=5.4342 Å and volume =236.30 Å^3.
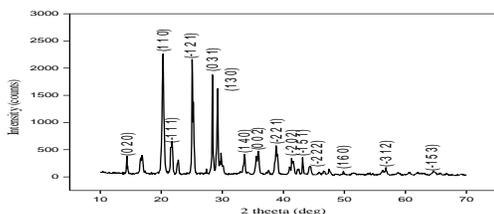
**Fig.5. Powder XRD pattern of TGPA Crystal**

3.5 SHG studies

Kurtz and Perry powder method is an important tool for researchers searching for organic/semi-organic/inorganic NLO material. The experimental setup used in the present investigation was similar to the generic one devised by Kurtz.

Kurtz[12] second harmonic generation (SHG) test was performed to find the NLO property of TGPA crystal. The fundamental beam of 1064nm from Q-switched Nd:YAG laser is used to test the second harmonic generation property of the TGPA crystal by using Kurtz technique. Pulse energy was 4mJ/pulse and pulse width was 10ns.The second harmonic signal generated in the crystal was confirmed from the emission of green radiation of wavelength 532 nm by the crystal which shows that the samples exhibit good NLO property. The SHG efficiency is found to be 0.25 times that of KDP.

3.6. Vickers microhardness studies

Microhardness of a crystal is its capacity to resist indentation. Physically hardness is the resistance offered by a material to the localized deformation caused by stretching or by indentations[13]. The indentation hardness is measured as the ratio of applied load to the surface area of the indentation. Indentations carried out on TGPA crystal using a Vickers microhardness tester fitted with a diamond indentor.

The indentations were made using a Vickers pyramidal indentor for various loads from 25 to 100 g. For each load, several indentations were made and the average value of the diagonal length (d) was used to calculate the microhardness. Vickers microhardness number for TGPA crystal was calculated using the following relation $H_v = 1.8544\ P/d^2$ kg/mm^2,[14] where P is the applied load in kg and d is the diagonal length of indentation impression in millimeter and 1.8544 is a constant of a geometrical factor for the diamond pyramid. The variation of microhardness values with applied load is shown in Fig.6. From the results, it is observed that hardness number increases with load. According to Meyer's law, $P=ad^n$, where 'n' is the Meyer's index and 'a' is an arbitrary constant for a given material. The plot of log P versus log d shown in Fig.7 is a straight line and the slope of the line gives n. From careful observations on various materials Onitsch[15] and Hanneman[16] pointed out that n' lies between 1 and 1.6 for moderately hard materials, and it is more for soft materials. The value of 'n' obtained for grown TGPA crystal was 3.6. Thus TGPA belongs to soft material category.
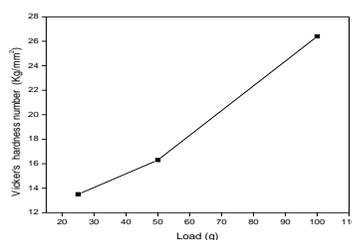
Fig.6. Plot of load versus Hardness number
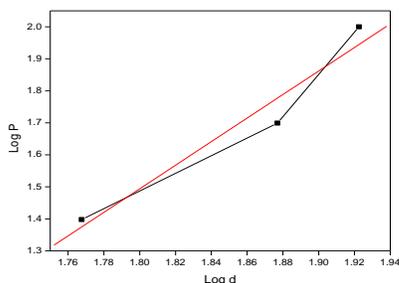
Fig.7. Plot of Log P versus Log d

3.7 Conclusion

  A novel semi-organic crystal TGPA was synthesized. The single crystals of TGPA were grown from solution using water as the solvent. The structure of the grown crystal of TGPA was found by single crystal XRD studies. The formation of TGPA was confirmed by Powder XRD pattern. Functional groups were confirmed by FTIR analysis. From UV-visible spectral studies, the cut-off wavelength was found. The non-linear optical studies confirm the SHG property of the material. From Vickers microhardness studies, it is observed that the hardness number increases with the applied load.

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