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PHYSICS

GROWTH AND CHARACTERIZATION OF GAMMA GLYCINE SINGLE CRYSTAL FROM AMMONIUM SULFATE AS SOLVENT

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Abstract

Single crystals of γ-glycine, an organic nonlinear optical material were grown by low temperature solution growth methods from aqueous solutions of glycine and ammonium sulfate. Powder X-ray diffraction of the grown crystal was recorded and indexed. The γ-phase of glycine is confirmed by powder XRD and FTIR spectroscopy.CHN analysis shows the non-existence of ammonium sulfate species in the grown γ-glycine single crystals .Optical transmittance spectrum was recorded in the range from 200 to 1100nm.Thermal properties of the grown crystal have been investigated using differential thermal analysis. The NLO property of the crystal was confirmed by Kurtz and Perry technique.

Keywords: Single crystal Growth; Characterization; X- ray diffraction; Nucleation; Growth from solutions: Non-linear optical Materials

Introduction

The nonlinear optical (NLO) properties of large organic molecules and polymers have been the subject of extensive theoretical and experimental investigations during the past two decades [1]. The organic NLO materials play an important role in second-harmonic generation (SHG), Frequency mixing, electro-optic modulation, optical parametric oscillation, optical bistability, etc [2]. Recently, an extremely large number of organic compounds with nonlocalized π-electron systems and a large dipole moment have been synthesized to realize the nonlinear susceptibilities far larger than the inorganic optical materials [3].Aminoacids are interesting class of organic nonlinear materials, which shows nonlinear optical second harmonic conversion efficiency compared to standard potassium dihydrogen phosphate single crystal (KDP)[4-5], Glycine is well known aminoacid crystallizes from its aqueous solution in different polymorphic forms. So far, there were three different polymorphic forms reported for glycine; the metastable α,unstable β and the stable γ at ambient conditions. The polymorphs of α– and β-glycine crystallize in centrosymmetric space group $P2_1/c$ while γ-glycine crystallizes in trigonal space group with cell parameters $a=b=7.037A^0$, $c=5.483\ A^0$, $\alpha=\beta=90^0$ and $\gamma=120^0$; thus, making it suitable for piezoelectric and nonlinear optical (NLO) applications [6].In this work, we report a detailed study about the growth, structural, vibrational, thermal and optical properties of γ-glycine from aqueous solution of glycine and ammonium sulfate for the first time.

Experimental

All starting materials were of AR grade and the growth process was carried out in aqueous solution. Single crystal of γ-glycine is grown by slow evaporation technique at room temperature using water – ammonium sulfate as solvent. The starting materials glycine and ammonium sulfate were taken in the equimolar ratio (1:1). The calculated amount of salts were dissolved in double dissolved water at ambient conditions. The solution stirred well for about 4h using a magnetic stirrer to obtain a homogenous mixture. The saturated solution was filtered using whatman (41) filter paper. The filtered solution was taken in a beaker and it is kept at room temperature in a dust free compartment for slow evaporation .The induction period for γ nucleation is 2 days. The nucleated crystals were allowed for further growth and it is harvested. A colorless, transparent crystal are obtained. The transparent crystal become opaque after two weeks. The photograph of the as-grown crystal is presented in Fig.1.

Fig.1.Photograph of γ-glycine single crystal

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Results and discussion

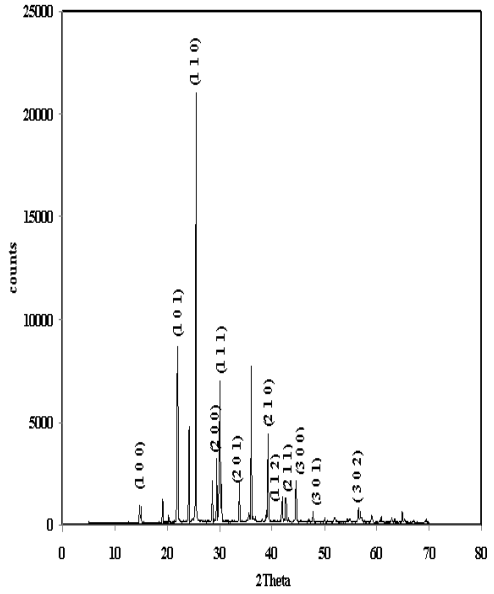
CHN analysis

The CHN analysis was carried out for γ-glycine single crystal using Elemental vario EL III elemental analyzer. The result of the elemental analysis shows that the powdered sample contain the following percentage of elements:C=32.324% (32.00), H=6.975 (6.714) and N=18.869% (18.659). The microanalysis of the powdered sample shows good agreement with the calculated values given in parenthesis .

Powder X-ray diffraction analysis

The grown crystals were characterized by Powder X-ray diffraction using a Bruker D8 Advance, Germany instrument with CuK_α radiation (1.5406 A^0).The sample was scanned in the range 5^0 to 70^0 at a scan rate of 1^0 min^{-1}.The indexed powder X-ray diffraction pattern is shown in Fig.2.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=b=7.014A^0(7.037 A^0), c=5.454A^0 (5.483A^0) and volume=232.3 $Å^3$ (235.1 $Å^3$).These values compare well with the literature values reported by litaka [7] given in parenthesis which confirms that the grown crystal is in the γ-phase and belongs to the hexagonal system .Further, it is evident that ammonium sulfate is not incorporated in to the grown crystal but its presence in the solution inhibit the growth of γ-glycine.

Fig.2.Indexed Powder XRD pattern of γ-glycine crystal



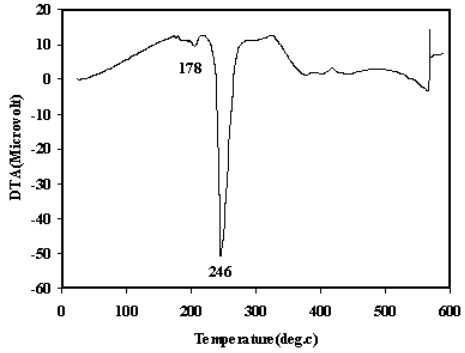
FTIR analysis

The FTIR spectrum of γ-glycine single crystal is recorded in the range of 400-4000cm^{-1} using Perkin Elmer grating Infrared spectrophotometer. The absorption peaks observed at 506.34, and 682.08cm^{-1} are attributed to carboxylate groups, while the peaks observed at 2610.29 1497.48 and 1121.13cm^{-1} are attributed to NH_3^+ group. Thus, the carboxyl group is present as carboxylate ion and amino group exists as ammonium ion in γ-glycine.The C-C-N asymmetric and C-C-N symmetric stretching vibration are observed at 1037.78 and 890.64 cm^{-1} .The absorption at 1328.89 cm^{-1} is due to CH_2 twisting mode. The COO^- asymmetric stretching and COO^-symmetric stretching vibration are observed at 1404.16 cm^{-1} and 1632.84 cm^{-1}.The absorption peak at 3434.84cm^{-1} is due to N-H asymmetric stretching vibration. The broad band centered around 3300cm^{-1} is due to C-H stretching. The prominent band near 2166.25cm^{-1} may be attributed to the combination of the asymmetrical NH_3^+ bending vibration and the torsional oscillations of the NH_3^+ group. The absorption peaks of γ-glycine single crystals are inline with the literature values [8, 9, and10].

Thermal analysis

The DTA thermogram of γ-glycine crystal were carried out by employing Perkin Elmer Diamond DTA .The recorded DTA thermogram is shown in Fig.3.A platinum crucible was used for heating the sample and analyses were carried out in the atmosphere of nitrogen at a heating rate of 10^0 c min^{-1} in the temperature range 30-600^0c.The first endothermic peak in DTA at 178^0c corresponds to the phase transition from γ-phase to α-phase .Perlovich et al.[11] reported that the transition temperature between γ to α can range between 165 and 201^0c .The melting point of the grown crystal is 246^0c. Thus in the present work, γ-glycine crystal grown from a mixture of glycine and ammonium sulfate is structurally stable up to 178^0c.

Fig.3.DTA curve of γ-glycine crystal

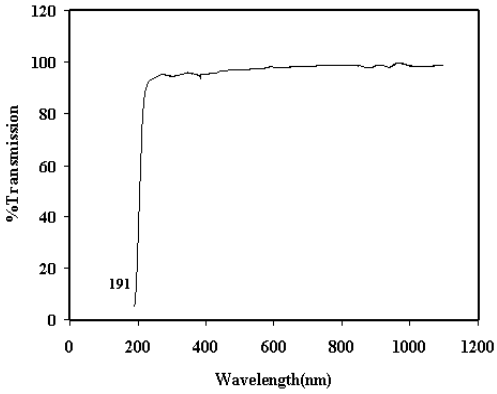


Optical transmittance studies

The optical transmittance spectrum of grown crystal is recorded using Perkin Elmer Lamda Spectrophotometer in the region 190nm-1100nm (Fig.4) .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. The lower cut off region is obtained at 191 nm and there is a good transmittance in the visible region .The absence of absorption of light in the visible range of the electromagnetic spectrum is an intrinsic property of all the aminoacids .Using the formula E_g=1240/λ (nm); the band gap is calculated to be 6.49eV.The observed spectral and bandgap value are closely agree with the reported values.

Fig.4.UV-Vis-NIR spectrum of γ-glycine crystal



Nonlinear optical test

Nonlinear optical property of the γ-glycine single crystal was performed by Kurtz and Perry SHG test [12].The crystal was ground in to powder and densely packed between two transparent glass slides .An Nd:YAG laser beam of wavelength 1064nm was made to fall normally on the sample cell .The emission of green radiation from the sample confirms the second harmonic generation in the crystal .Potassium dihydrogen orthophosphate (KDP) crystal was powdered to the identical size and was used as reference material in the SHG measurement .The SHG output obtained from the grown powdered crystalline sample showed a signal of 0.650mV/pulse with an input energy of 370 mJ/pulse ,while the standard KDP crystal gave a signal of 0.452mV/pulse for the same input energy .Thus SHG relative efficiency of γ-glycine single crystal was found to be 1.43 times higher than that of KDP.

Conclusion

Single crystals of γ-glycine from a mixture of water- ammonium sulfate as solvent has been grown in solution growth technique for the first time .The lattice parameters were found by Powder XRD spectrum.CHN analysis showed that absence of entry of ammonium sulfate in to the crystal lattice during the growth process .The FTIR spectrum confirms the presence of various functional group of γ-glycine .The DTA thermogram reveals that phase transformation from γ- to α-glycine at about 178^0c.Optical transmittance spectrum confirms that this crystal is suitable for NLO applications. The SHG efficiency of the grown crystal is about 1.43 times that of Potassium dihydrogen phosphate (KDP).

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