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Research Article

STUDIES ON GROWTH AND CHARACTERIZATION OF GLYCINE AMMONIUM SULPHATE CRYSTALS

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ABSTRACT

Glycine Ammonium Sulphate (GAS) is one of the potential materials for nonlinear optical (NLO) applications. Single crystals of GAS with high degree of transparency were grown from aqueous solution of glycine and ammonium sulphate at room temperature by slow evaporation technique. Crystalline nature of the crystals has been studied by XRD analysis. Fourier Transform Infrared (FTIR) studies confirm the presence of functional groups in the grown crystals. The relative Second Harmonic Generation (SHG) efficiency of the grown crystals was measured by Kurtz and Perry Powder technique .UV-visible transmittance spectra showed wide transparency window in visible and near IR region. The real and imaginary parts of impedance and electric modulus were investigated for the GAS crystal as a function of frequency and temperature. The hardness values of the grown sample have been found by Vickers microhardness test.

INTRODUCTION

Organic nonlinear materials will be the key elements for future photonic technologies. Aminoacids are interesting class of organic nonlinear materials, which shows nonlinear optical second harmonic conversion efficiency compared to standard potassium dihydrogen phosphate single crystal[1]. Glycine, a simple amino acid has three polymorphic forms viz. α, β and γ forms. Both α and β forms crystallize in centrosymmetric space group $P2_1/c$ [2,3]. γ-glycine crystallizes in non-centrosymmetric space group $P3_1$[4,5] making it a candidate for piezoelectric and NLO applications. It has no asymmetric carbon and is optically inactive. It reacts with a majority of acids and salts forming an important group of electronic materials. New electronic materials of glycine can be synthesized from solutions containing specific ratios of the components. Some complexes of glycine with inorganic salts have already been reported to be promising materials for SHG such as glycine sodium nitrate [7], glycine silver nitrate [8], glycine hydrogen nitrate [9], glycine hydrogen phosphate [6], glycine potassium sulphate[10], glycine lithium sulphate [11], glycine zinc sulphate[12], glycine zinc chloride [13], diglycine manganese chloride[14], triglycine fluoro beryllate [15]etc. In this work, we have made an attempt to combine glycine with ammonium sulphate to form glycine ammonium sulphate (GAS) single crystal. The results obtained are reported herein and discussed.

Growth and Solubility

An aqueous solution of Glycine Ammonium Sulphate (GAS) was prepared by dissolving analytical grade chemicals of glycine and ammonium sulphate in 1:1.5 molar ratio with continuous stirring using a magnetic stirrer for five hours at room temperature. The prepared solution was filtered and kept undisturbed in a constant temperature bath maintained at a temperature of 30 °C. When evaporation takes place slowly, supersaturation is activated. As a result, transparent and

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colourless single crystals of glycine ammonium sulphate (GAS) were formed at room temperature in a period of about 21 days.

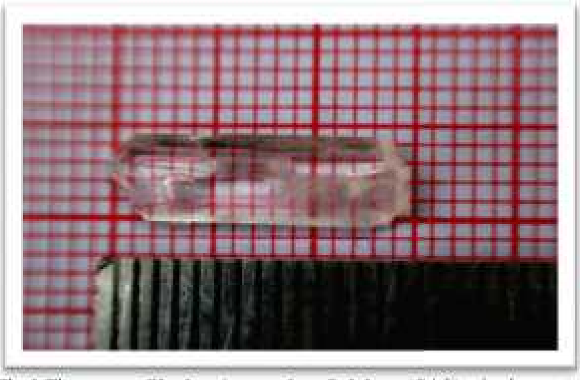


Fig.1 The grown Glycine Ammonium Sulphate (GAS) single crystal

The solubility study of GAS was carried out in a solvent of double distilled water at five different temperatures by gravimetrical method. The solubility was determined by dissolving GAS salt in 100 ml of double distilled water at a constant temperature with continuous stirring. After attaining the saturation, the equilibrium concentration of the solute was estimated gravimetrically. The variation of solubility with temperature is shown in Fig.2. It can be seen that the solubility increases with the increase in temperature. Hence, the sample has positive temperature coefficient of solubility.

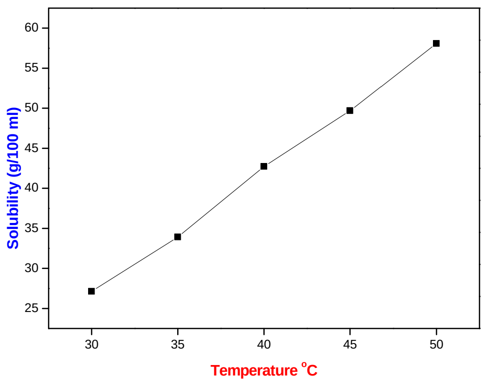


Fig.2 The solubility curve for GAS crystal

RESULTS AND DISCUSSION

Determination of crystal structure

Single crystal XRD data of GAS crystal were collected from a Single-crystal X-ray diffractometer using ENRAF NONIUS CAD-4 X-ray diffractometer with MoK_{α} (λ= 0.71069 Å) radiation and the obtained data are presented in the table 1. From the data is observed that the grown crystals crystallize in the monoclinic system with the space group of $P2_{1/C}$. The density of the crystal is found to be 1.761 g/cc and this value was also checked by floatation method.

Table 1 Single Crystal XRD data for GAS crystal

Unit cell dimensions	**a = 8.262 (3) Å, ~ = 90°** **b = 10.074(2) Å , = 92.66°** **c = 8.632(2) Å, ¥ = 90°**
Volume of the unit cell	717.39 (4) $Å^3$
Z	4
Density	1.761 g/cc
Wavelength	0.71069 Å
Crystal system,	Monoclinic
Space group	$P2_{1/C}$

Optical Transmittance Studies

The determination of optical transmission range and cutoff wavelength are important for any NLO material because a nonlinear optical material can be of any practical use if it has a wide transparency window. In the present study, we have recorded the UV-Vis NIR transmission spectrum in the range of 190 nm-1100 nm using the LAMBDA-35 UV-Vis-Spectrophotometer. The transmission spectrum of GAS crystal is shown in the Fig.3. It can be seen from the transmission curve that the lower cutoff wavelength is obtained at 198 nm. The material is found to be transparent to all radiations in the wavelength range 210 nm-1100 nm. The absence of absorption in the visible region clearly indicates that GAS crystals can be used as window material in optical instruments [16]. Using the formula E_g=1240 / λ (nm), the bandgap is calculated to be 6.263 eV.

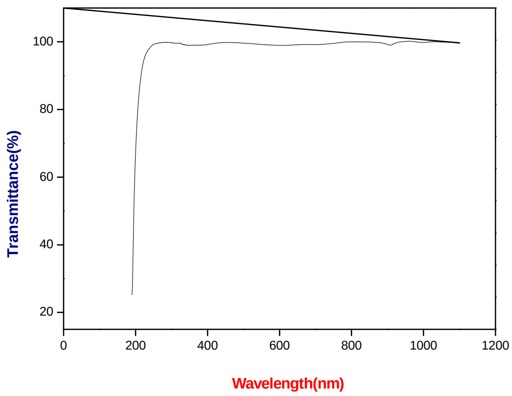


Fig.3 UV-Vis-NIR transmittance spectrum of GAS crystal

Ftir Spectrum

Fourier transform infrared (FTIR) spectrum was recorded by the KBr pellet method for the grown GAS crystal in the wave number of 400-4000 cm^{-1} by using a SHIMADZU spectrometer. The FTIR spectra of GAS crystal is shown in the Fig.4.The absorption peaks observed at 504 and 695 cm^{-1} are attributed to carboxylate groups, while the peaks observed at 1509, 1102 cm^{-1} are attributed to NH_3^+group. Thus the carboxyl group present as carboxylate ion and amino group exists as ammonium ion. The absorption at 1337 cm^{-1} is due to CH_2 twisting mode. The COO^- asymmetric stretching and COO^- symmetric stretching vibrations are observed at 1611 cm^{-1} and 1401 cm^{-1}. The presence of various functional groups of the grown crystal is in good agreement with those reported in the literature [17].

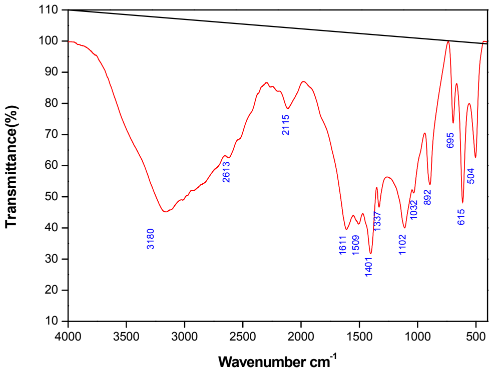


Fig.4 FTIR spectrum of GAS crystal

Table 2 Observed FTIR vibrational assignments for GAS crystals

Wave number (cm^{-1})	Assignments*
3180	NH_3^+ stretching
2613	Combination band
2115	Combination band
1611	COO^- asymmetric stretching
1509	NH_3^+ bending
1401	COO^- symmetric stretching
1337	CH_2 twist
1102	NH_3^+ rocking, $\gamma_{sy}SO_4^{2-}$
1032	CCN asymmetric stretching
892	CCN symmetric stretching
695	O-C-C deformation
615	COO^- wagging
504	COO^- rocking

EDS analysis

Energy dispersive spectroscopy (EDS) is an analytical technique used for the elemental analysis of a sample. It is one of the variants of X-ray fluorescence spectroscopy which relies on the investigation of a sample through interactions between electromagnetic radiation and matter, analyzing X-rays emitted by the matter in response to being hit with charged particles. The EDS detector measures the relative abundance of emitted X-rays versus energy. The detector is typically lithium drifted silicon solid state device. EDS studies were performed using the EDS detector (Oxford Instruments, INCA Penta FETx3). The recorded EDS spectrum for the grown GPS crystal is shown in the figure 5. From the spectrum, it is clear that the elements such as C, S, O were detected in the crystal.

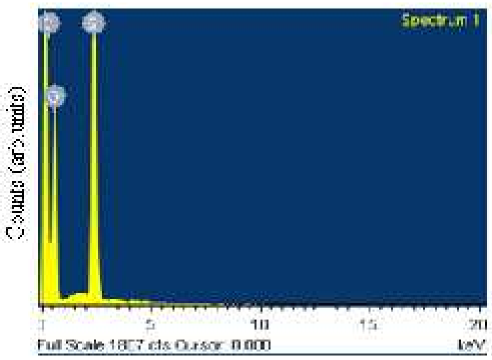


Fig.5 EDS spectrum of the grown GAS Crystal

Second Harmonic Generation

The NLO property of the grown crystal was tested by passing the output of Nd-YAG Quanta ray laser with fundamental radiation of wavelength 1064 nm through the crystalline powder GAS sample by Kurtz and Perry method [18]. The emission of green radiation from the sample confirms the second harmonic generation in the crystal. SHG output from the sample was compared with that from KDP crystal. The SHG relative efficiency of GAS crystal is about 0.90 times that of KDP.

Impedance Studies

Impedance spectroscopy is a powerful technique for the characterization of electrical behavior of NLO materials and defined as the frequency domain ratio of the voltage to the current and it is the opposition of the flow of alternating current (AC) in a complex system [19,20]. The frequency dependent properties of a material are often represented as complex impedance Z^* and which is related as $Z^*(\omega) = Z' - jZ''$ where Z' and Z'' are the real and imaginary components of impedance. The variations of real part of impedance (Z') and imaginary part of impedance (Z'') with frequencies at temperatures are shown in the figures 6 and 7. From the result it is observed that the real and imaginary part of impedance decreases with the increase in temperature and frequency. This decrease of impedance gives an indication of negative temperature coefficient of resistance behavior like that of an insulator. The high value of impedance at low frequency indicates low ionic mobility in the grown GAS crystal.

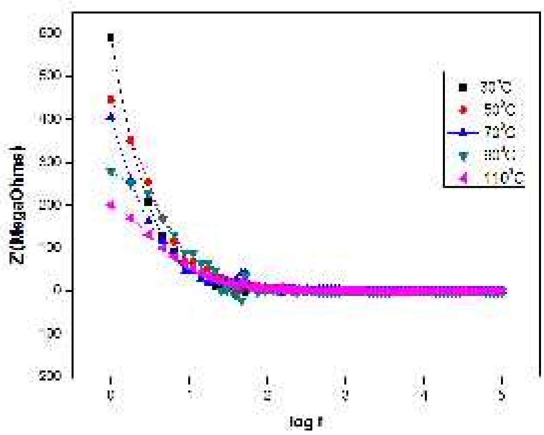


Fig.6 Frequency dependence of real part of impedance for GAS crystal at different temperatures

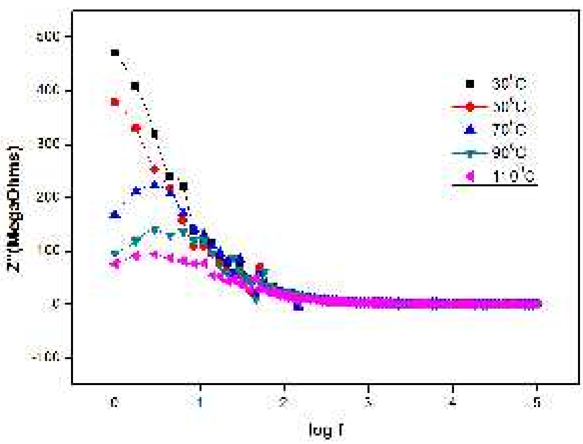
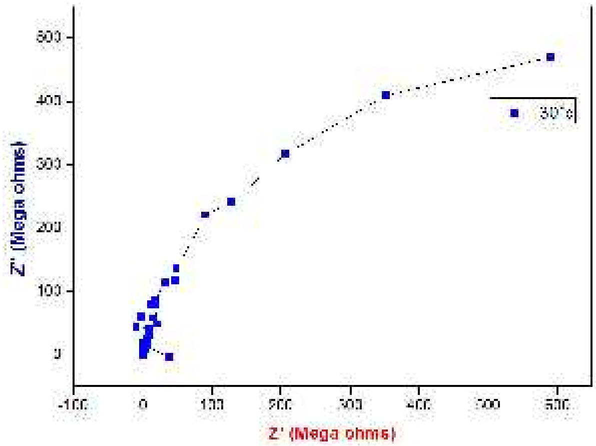
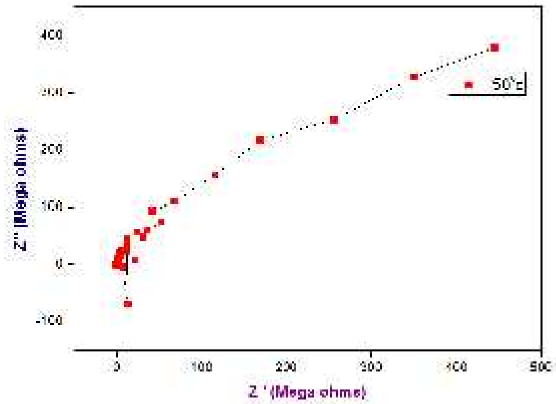


Fig.7 Frequency dependence of imaginary part of impedance for GAS crystal at different temperatures

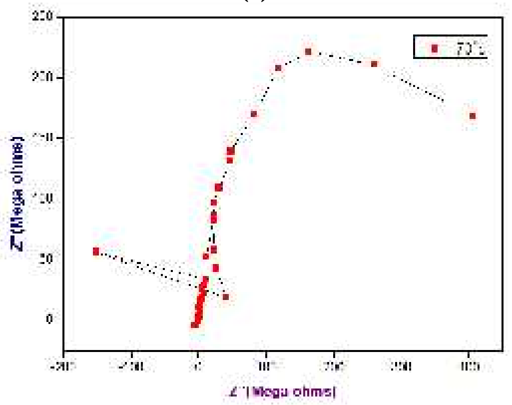
The peaks in the plots of impedance versus frequency are corresponding to relaxation process and the peak frequency is equal to relaxation frequency. Nyquist plots of the grown sample show the transport response function characteristically, one semicircular arcs and spikes and these plots reveal the presence of bulk effect and grain boundary effect of the sample. The Nyquist's plots for the grown GAS crystal have been drawn between real part and imaginary part of impedance at different temperatures and they are presented in figures 8 (i-iv). Semicircles at low frequencies are considered due to the grain boundary whereas the semicircles at higher frequencies depict the bulk effect. The bulk effect arises due to the parallel combination of bulk resistance and bulk capacitance of the sample [21,22].



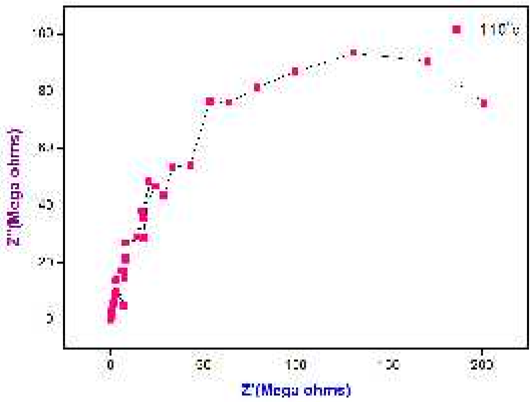
(i)



(ii)



(iii)



(iv)

Fig.8 Nyquist's plots for GPS at (i) 30 °C, (ii) at 50 °C, (iii) at 70 °C and (iv) at 110 °C

Hardness Test

Hardness testing has been widely used to study the strength and deformation in the materials. The method of measuring hardness is not dependent on a single physical property but may involve both the elastic and plastic deformation characteristics such as work hardening coefficient, stiffness constant, yield strength and elastic modulus etc. A good quality crystal was placed on the platform of the Vickers microhardness tester and loads of different magnitudes were applied for a fixed interval of 10 seconds. The hardness number was calculated using the equation $H_v = 1.8544\ P/d^2$ kg /mm^2 where P is the applied load in kg and d is the diagonal length of the indentation in millimeter. The variation of hardness number with applied load for GAS crystal is shown in the figure 9. It is observed that Vickers hardness number of the grown crystal increases gradually with increase in load due to the reverse indentation size effect[23].Cracks start develop in the crystal when a load of more than 100 g is applied.

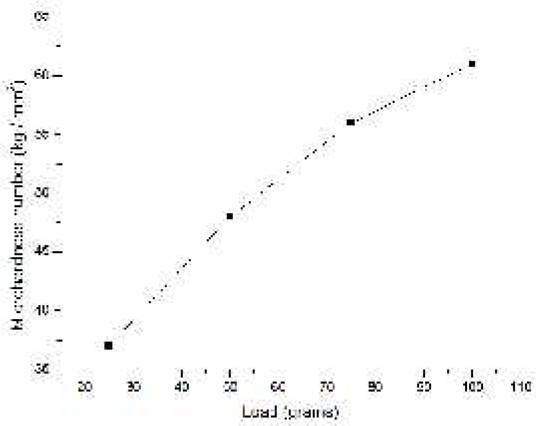


Fig.9 Variation of microhardness number with the applied load for GAS crystal

CONCLUSION

Transparent good quality single crystal of Glycine Ammonium Sulphate was grown by slow evaporation technique from a mixture of aqueous solution of Glycine and Ammonium Sulphate at constant temperature of 30 °C. The lattice parameters were found by single crystal XRD method. The FTIR spectrum was recorded for the sample and functional groups were identified. Optical transmittance spectrum confirms that the grown crystal of GAS is suitable for NLO applications because it has high transparency and high optical band gap. The SHG efficiency of the grown crystal is about 0.9 times that of Potassium dihydrogen Phospahte (KDP). The electrical properties such as real part and imaginary part of impedance for GAS crystal were analyzed at different frequencies and temperatures. EDS method was used to check the presence of various elements in GAS crystal. From hardness studies, it is understood that the grown crystal of GAS has moderate hardness and it has reverse indentation size effect.

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