Studies on the Structural, Thermal, Fluorescence and Linear–Non-linear Optical Properties of Glycine Sodium Acetate Single Crystal for Electro-Optic Device Applications

N.N. Shejwal, S.S. Hussaini, Ramesh B. Kamble, Mohd Anis and M.D. Shirsat

Abstract In the present communication, glycine sodium acetate (GSA) single crystal is grown by the slow evaporation method at room temperature. The cell parameters are confirmed by powder X-ray diffraction technique. This research paper focuses on structural, thermal, second harmonic generation, photoluminescence, linear and non-linear optical properties of glycine sodium acetate single crystals. The Kurtz-Perry powder technique confirmed the second harmonic generation efficiency of the grown crystal is 1.7 times more than that of the standard potassium dihydrogen phosphate (KDP) crystal. The high optical transparency (88 %) of the grown crystal is determined by employing UV-visible studies. The optical band gap of grown crystal is found to be 5.12 eV. The transmittance data is used to evaluate the potential optical constants viz. optical conductivity, refractive index, extinction coefficient and complex dielectric constant. The different functional groups are identified using Fourier transform infrared (FT-IR) spectral analysis. The thermal stability of the grown crystal is found to be 176 °C by means of thermo gravimetric analysis. The presence of sodium element is also confirmed by atomic absorption spectroscopy technique. The photoluminescence study of grown crystal is investigated in the range of 300–900 nm and confirms the near infrared emission in the electromagnetic spectrum.

N.N. Shejwal · M.D. Shirsat (✉)
Intelligent Materials Research Lab, Department of Physics, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad 431004, Maharashtra, India
e-mail: mdshirsat@gmail.com

S.S. Hussaini · M. Anis
Crystal Growth Laboratory, Department of Physics, Milliya Arts, Science and Management Science College, Beed 431122, Maharashtra, India

R.B. Kamble
Department of Physics, Indian Institute of Science, Bangalore 560012, Karnataka, India

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1 Introduction

The advances in nonlinear optical materials are resulted in distinguished progress in optical modulation which leads to the diversified applications such as fiber optical communication system, holography, optoelectronic devices and laser industries [1]. In the current year, the investigation on amino acid designed nonlinear optical (NLO) materials is stimulated as a forefront candidate for photonic devices due to a new and unique zwitterionic nature and charge transfer ability through acceptor-donor groups. The coordination through amino acceptor-donor groups with semi organic metal complexes mainly offer excellent second harmonic generation (SHG) coefficient, enriched transparency, wide optical band gap and higher thermal stability [2, 3]. A variety of amino acids mixed organometallic complexes have already been reported in earlier literature [4–6]. The gamma glycine single crystal in presence of sodium acetate was reported by [7]. The L-Arginine acetate single crystal was grown and studied by [8]. The L-Threonine zinc acetate single crystal studies have been reported as a promising NLO material by [9]. Glycine is a simple colorless organic compound commonly found in proteins, containing zwitterionic structure which is responsible for its optical activity. It exhibits large second order susceptibility, good transmission in UV as well as visible region and good thermal stability is required for NLO applications [10]. The physicochemical properties of organometallic compound are enhanced due to the addition of amino acids and also alter the cento symmetry. The literature survey reveals that the linear and nonlinear optical performance of glycine sodium acetate materials is not reported. Hence, the present communication is focuses on the growth and characterization of glycine sodium acetate single crystal through different techniques in order to know its applicability in photonic devices.

2 Experimental

2.1 Material Synthesis and Crystal Growth

Stoichiometric amounts of Glycine and sodium acetate taken in 1:1 and ratio was dissolved in deionized water for the synthesis of glycine sodium acetate (GSA). The homogenous solution is obtained by constant stirring of 6 h using magnetic stirrer. The clear transparent solution of glycine sodium acetate was filtered well by using Whatman filter paper in large sized beaker which was covered with transparent film to avoid the external impurities. The solution was allowed to crystallize by slow evaporation process at room temperature. In the period of 15 days, good quality transparent crystals with optimum dimensions were obtained. The grown glycine sodium acetate crystals are shown in Fig. 1a.

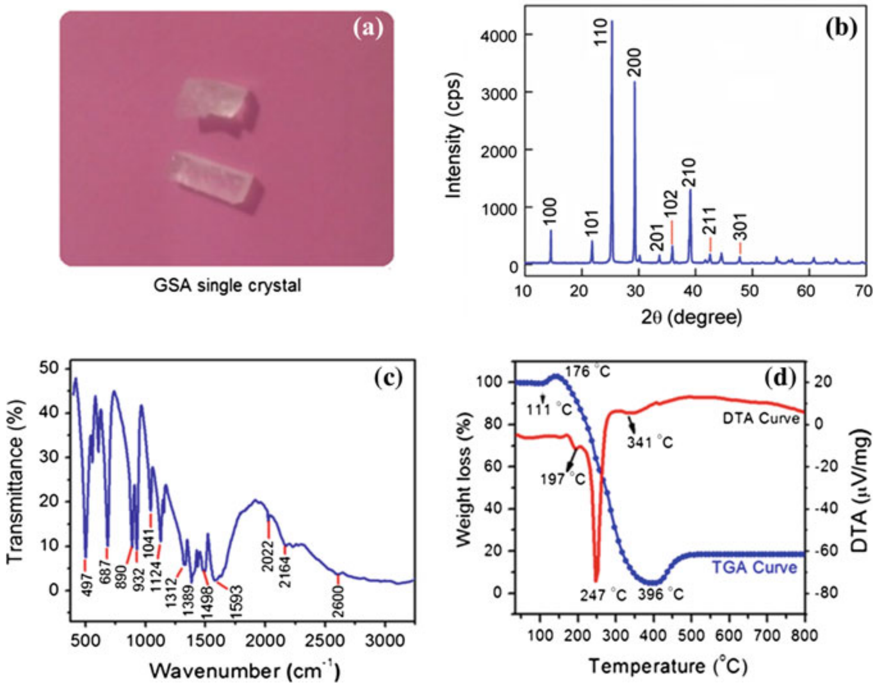

Fig. 1 **a** Single crystal image, **b** powder XRD pattern, **c** FT-IR spectra, and **d** TG/DTA curves of GSA crystal

2.2 Analysis Techniques

The grown crystal is subjected to various characterizations techniques in order to investigate its suitability in the field of NLO applications. The powder X-ray diffraction is carried out to confirm the crystal structure and cell dimension with the help of XPERT-PRO diffractometer system using Bruker AXS D8 advance Cu wavelength (1.5406 Å). The presence of sodium metal in the grown crystals was confirmed by atomic absorption spectrometer. The functional group is confirmed by using PERKIN ELMER RX1 Fourier transform infrared spectrometer. The thermal analysis studies are carried out by using Perkin Elmer Diamond thermal analyzer instruments. The Cary Eclipse Win FLR EL07073870 Instrument was employed to record the photoluminescence emission spectrum of grown crystal. The optical parameters are identified with the help of Shimadzu UV-2450 spectrophotometer. The Kurtz and Perry powder technique has been employed to test the non-linear optical nature of grown crystal.

3 Results and Discussions

3.1 Powder X-ray Diffraction Studies

The powder X-ray diffraction technique is employed to determine the crystal structure. The sharp X-ray diffraction pattern of glycine sodium acetate (GSA) crystal shows the well-defined peak at a specific position (2θ) with intensity variation. It indicates the purity of glycine sodium acetate (GSA) crystal as shown in Fig. 1b. The calculated lattice parameter of GSA crystal are, a = 7.17 Å, b = 7.17 Å, and c = 5.58 Å, whereas the angles are $\alpha = 90°$, $\beta = 90°$ and $\gamma = 120°$ and volume (V) = 286.86 $Å^3$ which agreed with the reported literature [7, 11].

3.2 FT-IR Studies

The infrared spectroscopy is an effective and most popular technique used for identifying molecules and the chemical functional group of the sample. Fourier transform infrared radiation spectrum is a plot of transmission of IR radiation as a function of wavelength is shown in Fig. 1c. The NH_3^+ asymmetric stretching vibrations are observed at peak 2602 cm^{-1}. The peak at 1593 cm^{-1} corresponds to strong asymmetric COO^- stretching vibration. The peak observed at 687 cm^{-1} is attributed to COO^- bending vibrations. In the mid energy region of the spectrum, the peak at 1312 cm^{-1} corresponds to CH_2 twisting vibrations in GSA crystal. The absorption peak at 1398 cm^{-1} is attributed to symmetric stretching vibrations of COO^-. The peak found at 1041 cm^{-1} is due to the CCN asymmetric stretching vibration. The absorptions due to the carboxyl group of free glycine are observed at around 497 cm^{-1}. The large shifting in frequencies of carboxyl group and NH^{3+} and functional group analysis confirmed that, the glycine molecule would be coordinated with sodium ion through its carboxyl and amine group due to zwitterions nature [7, 12].

3.3 Thermal Studies

The thermo gravimetric and differential thermal analyses (TG-DTA) of GSA crystal were carried out between the temperatures of 30–400 °C in the nitrogen atmosphere to determine the thermal stability of the grown crystal. The TG/DTA curves of glycine sodium acetate crystal are illustrated in Fig. 1d. From the DTA curve, the melting point is confirmed by a sharp endothermic peak appeared at 247 °C followed by second minor endothermic transition takes place at 341 °C. The thermo gravimetric analysis does not show any kind of phase transition till the melting of glycine sodium acetate crystal. The absence of phase transition improves the temperature range for the applicability of the crystal for photonic applications. The absence of weight loss around 100 °C confirmed that the water molecules are absent in the crystalline structure of grown crystal. The TGA curve shows that grown crystals exhibit a sharp single weight loss starts at 176 °C which ends at 396 °C. There is no weight loss observed in TGA curve below 176 °C temperature. Differential thermal analysis (DTA) reveals a minor endothermic peak around 197 °C of sample which may be due to conversion of γ-glycine into α-glycine [11]. The decomposition process continues at higher temperature accompanied by weight loss of material.

3.4 Atomic Absorption Studies

The quantitative determination of metal element in the grown crystal is confirmed by using atomic absorption spectroscopy (AAS) technique which is a spectro analytical procedure employing the absorption of optical radiation by free atom in the gaseous state. The sodium (Na) element is found to be 9.3 ppm in the grown crystal. The presence of single sodium metal confirmed the purity of the grown crystal. The coordination of glycine with sodium element in the mixture leads to the formation of resultant non-centrosymmetric structure.

3.5 Photoluminescence

The photoluminescence studies furnished the quality information regarding the electronic states of the material, influence of intrinsic impurities on the material emission spectra etc. The glycine sodium acetate crystal is photo excited with the energy wavelength of 260 nm and the emission spectrum is recorded in the range of 300–900 nm as shown in Fig. 2. The stable single peak is observed in the range from 787 to 812 nm at room temperature. The single peak maxima at 799 nm, indicates that GSA crystal has infrared emission. The GSA materials with near infrared emission might be of suitable for NIR optical imaging and sensing determination of biological targets [13, 14].

3.6 UV Spectral Studies

The significant optical parameters such as transmission, optical dielectric constant, optical band gap, extinction coefficient of the grown crystals has been investigated by using Shimadzu UV-2450 spectrophotometer in the range of 200–900 nm. The transmission studies assist to examine the behaviour of electron in two different energy states due to the absorption of UV and visible light. The recorded

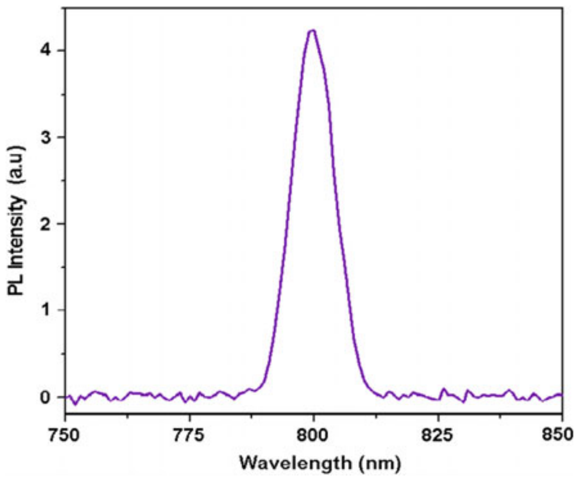

Fig. 2 Photoluminescence (PL) curve of GSA

transmission spectrum of GSA crystal is depicted in Fig. 3a. The glycine sodium acetate crystal exhibits high transmittance (88 %) with lower cut off wavelength at 240 nm. The enriched transparency window and lower cut off wavelength of GSA crystal indicates its suitability for SHG device applications [15]. The very low absorption in the visible region clearly indicates that the grown crystal can be used for photonics and optoelectronic applications. The optical absorption coefficient (α) is determined using the equation $\alpha = 2.303 \log (1/T)/t$. The optical band gap ($E_g$) was determined from the relation [15] given as follows,

$$(\alpha h\nu)^2 = A\left(h\nu - E_g\right) \tag{1}$$

where, A is a constant, E_g is the optical band gap and $h\nu$ is the incident photon energy. The optical band gap of GSA crystal is determined using the Tauc's graph depicted in Fig. 3b. The optical band gap of GSA is found to be 5.12 eV. The crystal with wide optical band gap reveals its suitability for the design and fabrication of UV tunable lasers and optoelectronic devices [16]. The extinction coefficient is evaluated using the relation,

$$K = \lambda\alpha/2\pi \tag{2}$$

The variation of extinction coefficient (K) as shown in Fig. 3c within the material medium indicates that the loss of optical energy is due to the absorption and scattering of light within the material medium. The high transmittance, low absorption and reflectance of GSA crystal urge its applicability for antireflection coating in the solar thermal devices [17]. The variation of optical conductivity (σ_{op}) with photon energy is shown in Fig. 3d. The GSA exhibits lowered extinction coefficient and higher optical conductivity which make it excellent material for high speed information processing and computing devices [17]. The complex dielectric

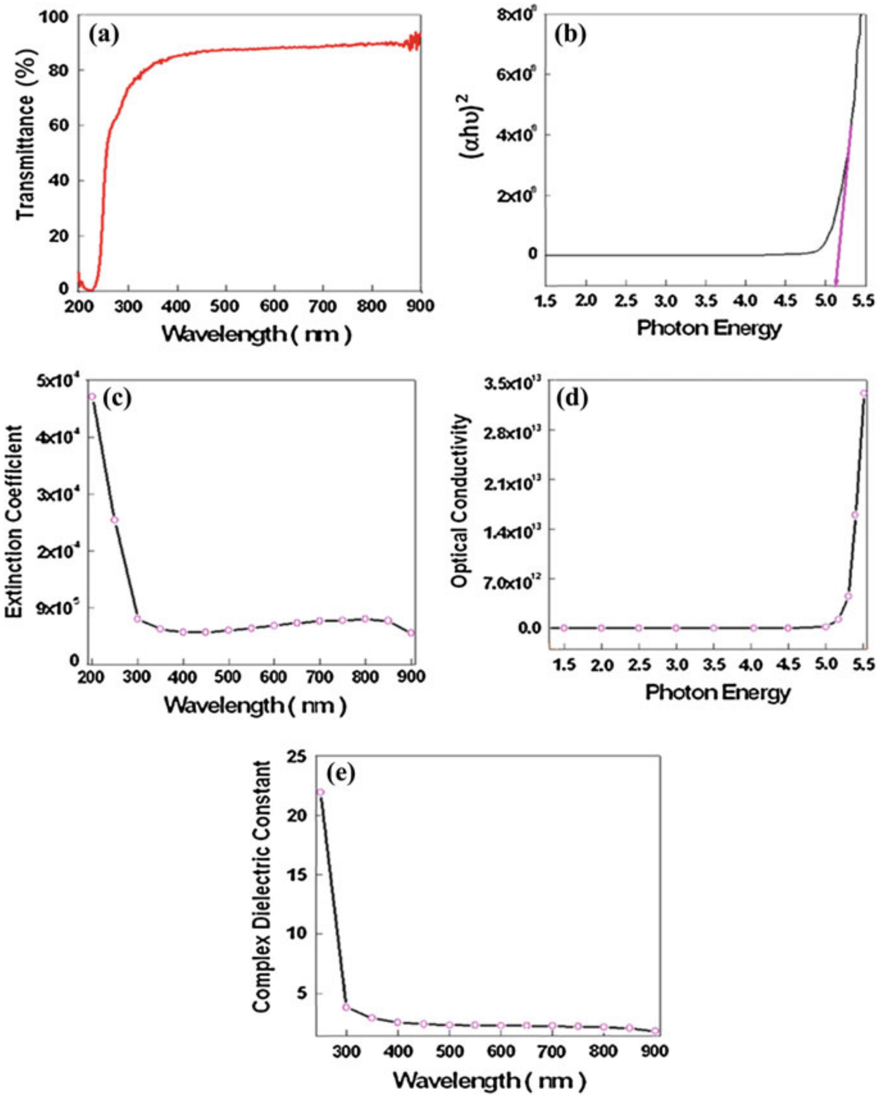

Fig. 3 **a** UV transmittance, **b** optical band gap, **c** extinction coefficient, **d** optical conductivity, **e** complex dielectric constant for GSA single crystal

constant ($\varepsilon = \varepsilon_r + \varepsilon_i$) characterizes the optical properties of the grown crystals is shown in Fig. 3e. The lower value of dielectric constant with wide band gap of GSA crystal suggests the suitability of optoelectronic devices. The GSA crystal with promising optical properties emphasizes it's prominence for distinct electro-optic applications.

3.7 Non-linear Optical Studies

The second harmonic generation (SHG) conversion efficiency of glycine sodium acetate is measured by Kurtz-Perry powder technique. The crystal was grounded into a fine powder and densely packed into capillary tube. An actively Q switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm with energy 3.5 mJ/pulse of width 8 ns was incident on the capillary tube. The green optical emission (532 nm) was detected by photomultiplier tube detector and output voltage was recorded on cathode ray oscilloscope as 18 mV. The SHG output signal of standard KDP material was found to be 11 mV. In the present analysis, the SHG conversion efficiency of glycine sodium acetate is found to be 1.7 times more than that of KDP. The coordination of sodium with hydrogen bond in asymmetric nature may be the reason for NLO efficiency enhancement. The higher SHG efficiency of glycine sodium acetate crystal is most desirable for designing of NLO devices.

4 Conclusion

The optically good quality single crystal of glycine sodium acetate (GSA) was grown by slow evaporation technique at room temperature. The crystalline nature was determined by powder X-ray diffraction technique. The Kurtz-Perry powder technique confirmed the SHG efficiency of the grown crystal to be 1.7 times more than that of standard KDP. The high optical transparency (88 %) of the grown crystal with lower cutoff wavelength of 240 nm was determined employing UV-visible studies. The optical band gap of grown crystal was found to be 5.12 eV. The transmittance data is used to evaluate the potential optical constants viz. reflectance, refractive index, extinction coefficient and complex dielectric constant. The different functional groups were identified by using Fourier transform infrared (FT-IR) spectral analysis. The thermal stability of the grown crystal was found to be 176 °C. The presence of sodium element is also confirmed by atomic absorption spectroscopy technique. The photoluminescence study of grown crystal is investigated in the range of 300–900 nm and confirmed the infra-red emission in the electromagnetic spectrum. The high optical transparency, lower extinction coefficient, cut-off wavelength, and wide optical band gap make GSA crystal, very suitable for fabrication of NLO devices.

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