Structural and Dielectric Properties of Picric Acid-Doped Glycine Lithium Sulphate Single Crystals

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Abstract

Here we report the growth of picric acid ($C_6H_2(NO_2)_3OH$) doped Glycine Lithium Sulphate ($C_2H_5Li_2NO_6S$ - GLS) single crystal by solution growth with slow evaporation method at normal temperature. Single crystal XRD (X – Ray Diffraction) studies, powder XRD studies, FTIR (Fourier Transform Infrared Spectroscopy) spectra analysis, Z scan analysis and micro hardness studies were performed. Collect FTIR spectrum to search for functional group information. The XRD spectrum reveals that, low angle boundaries of the internal structure. The mechanical stability of the growing concrete was tested using a Vickers microhardness tester and the work hardening coefficient of the plant material was estimated. Third order nonlinear optics analyzed by using the Z-scan technique and determines the nonlinear refractive index (n_2), nonlinear magnetic susceptibility and nonlinear absorption coefficient (β) of the sample. Dielectric constant has been observed that, it such studies decreases with increasing frequency. When picric acid is added to pure GLS crystals, the dielectric constant increases with increasing doping concentration.

Keywords: Dielectric Constant, Glycine Lithium Sulphate Crystals, NLO Properties, Single Crystals, XRD studies.

1. INTRODUCTION

Many attempts to grow organic nonlinear optical (NLO) was held, it have many applications in optoelectronic devices [1]. The advantage of using organic plant material is that it allows tuning of the chemical structure and properties required for nonlinear optical applications [2]. They also have greater optical sensitivity and an inherently ultra-fast response time compared to inorganic crystals. The discovery of new crystals for many optical applications has become a new science in recent years [3]. Non-linear optical crystals are attracting the attention of many technologists today due to their important technologies in optical communication, laser spectroscopy, optical systems and electronic devices, photonics, optoelectronics, sensors and electronic devices in color displays [4]. Optical applications depend on many physical properties such as optical properties, thermal stability and physicochemical properties. The development of new optical materials with good chemical and physical properties is important in photonics, optoelectronics and many other applications. Optoelectronics inspired the search for nonlinear optical devices for efficient operation [5].

It has been reported that crystals of many amino acids and their complexes exhibit unusual optical properties and the ability to form secondary harmonics, due to the fact that they have cells without a center of symmetry [6]. Glycine molecules can appear as zwitterions and thus form compounds with anionic, cationic and neutral compounds [7]. Glycine lithium sulphate (GLS) is a semi-organic NLO crystal composed of a combination of glycine and lithium sulphate. The aim of this project is to growth single crystal and various studies of picric acid doped glycine lithium sulphate (GLS) crystals.

2. METRIALS AND METHODS

2.1. Synthesis and growth of picric acid doped GLS

From Fig. 1. shows a GLS single crystal, it was grown by solution growth method from a solution of (AR grade) glycine and lithium sulphate in a molar ratio of 1:1 M at room temperature. The solution was evaporated to yield GLS crystals. To obtain picric acid doped GLS, add 1% M of picric acid to the GLS solution. One of the most important factors for the growth of single crystals is the correct choice of solvent [8]. The solubility test was done gravimetrically to find the appropriate solvent [9] was performed and it was found that the suitable solvent for crystal growth was water. Once saturation is reached, the stability of the glue can be determined. Solubility graph for pure and picric acid doped GLS samples were prepared as shown in Fig. 2. The solubility of both samples was found to increase with temperature. When picric acid is doped into the GLS crystals we see an increase in solubility.

Fig. 1. Picric acid doped GLS

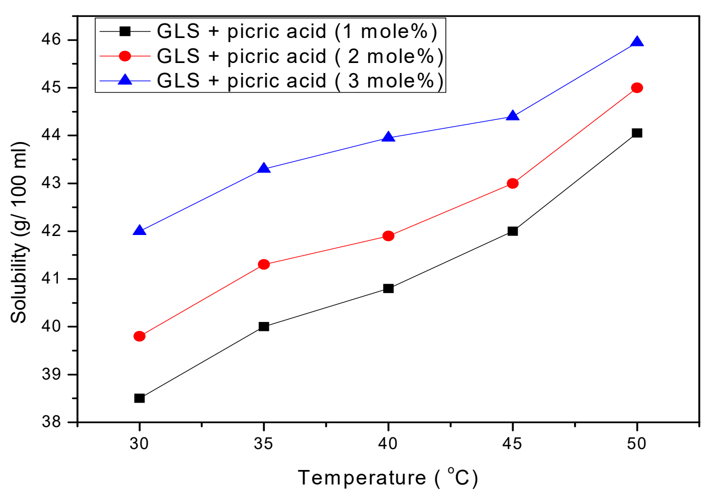

Fig. 2. Solubility curves for picric acid doped GLS

2.2. Determination of solutbility and nucleation kinetic parameters

From the results, it is seen that nucleation parameters such as Gibbs free energy variation, critical radius and critical nucleus of the molecule decrease with increasing super saturation. Fig. 2. Shows the nucleation rate as a function of super saturation. From the results, it is seen that the nucleation rate decreased when picric acid was added to the GLS sample, and the nucleation rate increased with the increase of super saturation (Fig. 3).

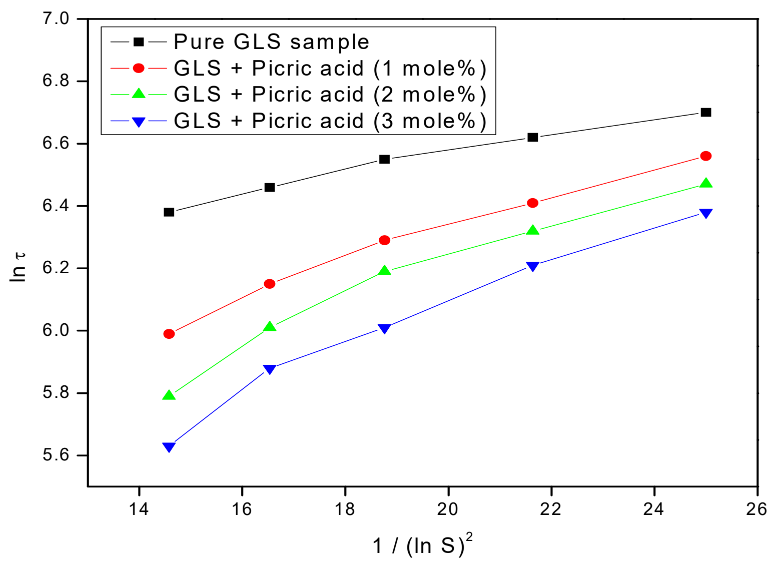

Fig. 3. Variation of induction period with supersaturation ratio for picric acid doped GLS

3. RESULTS AND DISSCUSION

3.1. Single Crystal XRD analysis

This data of unopened and picric acid-doped GLS were collected with a single-crystal XRD. It with graphite monochromatized MoKα radiation [10]. Crystallographic data from GLS single crystal and picric acid doped GLS single crystals a = 5.027 Ǻ, b = 7.632 Ǻ, c = 16.394 Ǻ, a = 90°, b = 90° c = 90 °, and a = 5.052 Ǻ, b=7.6292 Ǻ, c = 16.534 Ǻ, a = 90°, b= 90°, c=90°. As can be seen from the data, both grown crystals crystallized in the orthorhombic system. Both crystals from this study have 4 molecules per unit cell (Z). The change in the lattice is not due to the incorporation of picric acid into the lattice of the GLS. The presence of additives in GLS can cause lattice strain leading to changes in cell parameters in picric acid-doped GLS samples.

3.2. Powder XRD analysis

The recorded powder XRD patterns for the samples are shown in the fig. 4. Indexing of a powder XRD pattern consists of the assignment of Miller indices (hkl) to each reflection peak. Pure and picric acid GLS crystals belong to the orthorhombic structure. Hence, the following relation for the orthorhombic structure was used for indexing the diffraction patterns. It is noticed that the crystal parameters obtained from the powder XRD method are the almost same as those obtained from single crystals XRD method.

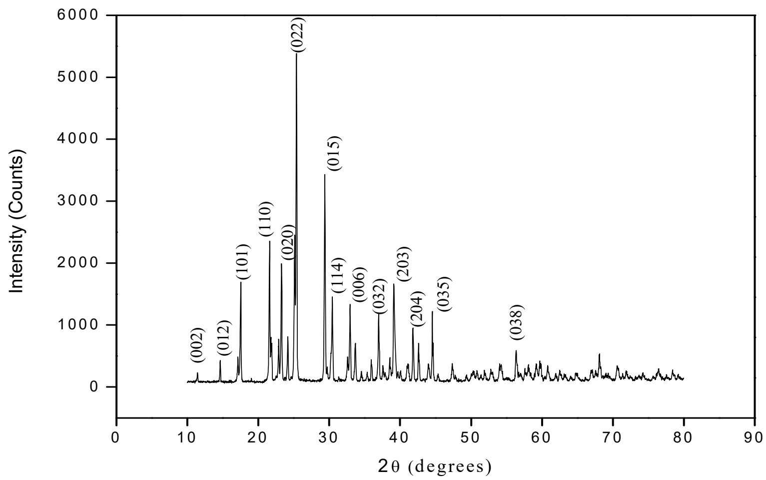

Fig. 4. Powder XRD pattern for 3 mole% of picric acid doped GLS sample

3.3. FTIR studies

The recorded FTIR spectra of the picric acid doped GLS samples are shown in Fig. 5. The peak at 3455 cm^{-1} in the spectrum is assigned to the O-H stretching vibration of the COOH group. [11]. A very strong peak appears at 3155 cm^{-1} due to NH stretching vibrations. The weak IR band at 1700 cm^{-1} clearly indicates the presence of the zwitterionic form of the COO ion. The peak at 1664 cm^{-1} is attributed to the C=O stretch of the COOH group. The peak at 1557 cm^{-1} is assigned to NH_2 in the planar deformation of the sample. The peaks observed at 1376-1557 cm^{-1} and 2745-3155 cm^{-1} are characteristic peaks of glycine. The COO vibration shows its characteristic peak at 1415 cm-1. Additional peaks at 1330 and 1320 cm^{-1} are due to changes in the CH_2 group of the crystal structure. The methyl group also has a strong absorption at 1376 cm^{-1}.The torsional vibration of NH_2 is well known since its peak is 1170 cm^{-1}. the absorption from the C-N peaks is found at 1058 and 1035 cm^{-1}, respectively. COO-(781 cm^{-1}), COO-scissors (679 cm^{-1}) plane deformations, COO^-(551 cm^{-1}) oscillation vibrations were observed [12].

Third order nonlinear optics analyzed by using the Z-scan method [13]. It is a standard procedure to determine the non-linear refractive index (n_2), non-linear magnetic susceptibility and non-linear absorption coefficient (β) of the sample. The aperture normalized permeability of the open and closed pores and the sample position Z were measured for GLS crystals doped with picric acid (3mol%), and the curves are shown in Figures 6 and 7 . The third-order nonlinear refractive index (n2) 0.65×10^{-10} cm^2/W indicates that the model has self-focusing power [9]. The β of the crystal sample is 0.19×10^{-4} cm/W, indicating the two-photon absorption process in this sample. The absolute value of the non-linear magnetic field of the GLS crystal doped with picric acid (3 mol%) is 0.803 x 10^{-6}esu, indicating the III order NLO of the crystal.

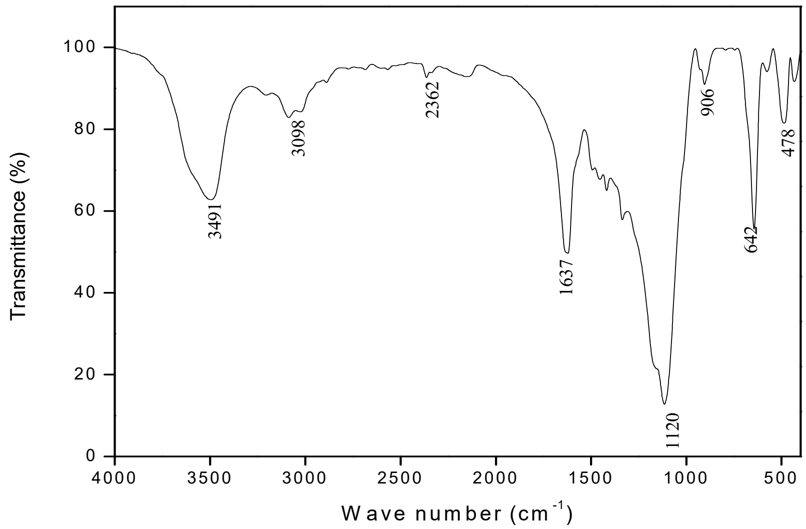

Fig. 5. FTIR spectrum of GLS doped with picric acid (3 mole%)

3.4. Third-order NLO parameters by Z-scan method

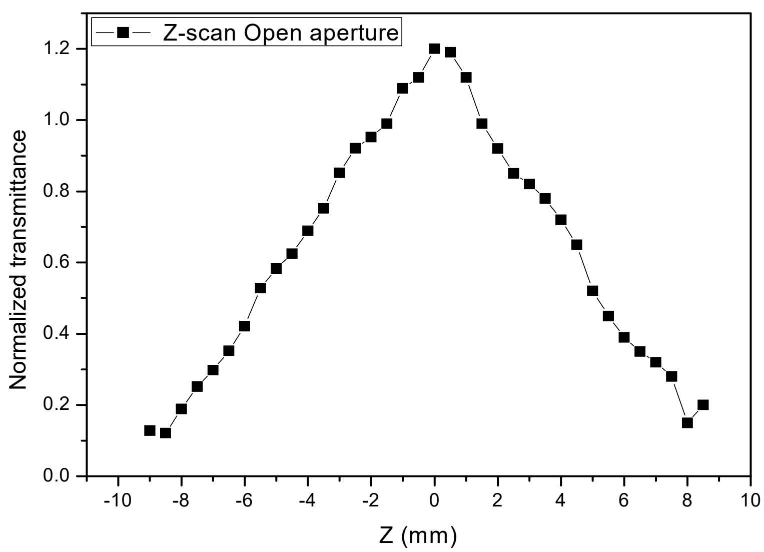

Fig. 6. Z-scan pattern for the sample in open aperture

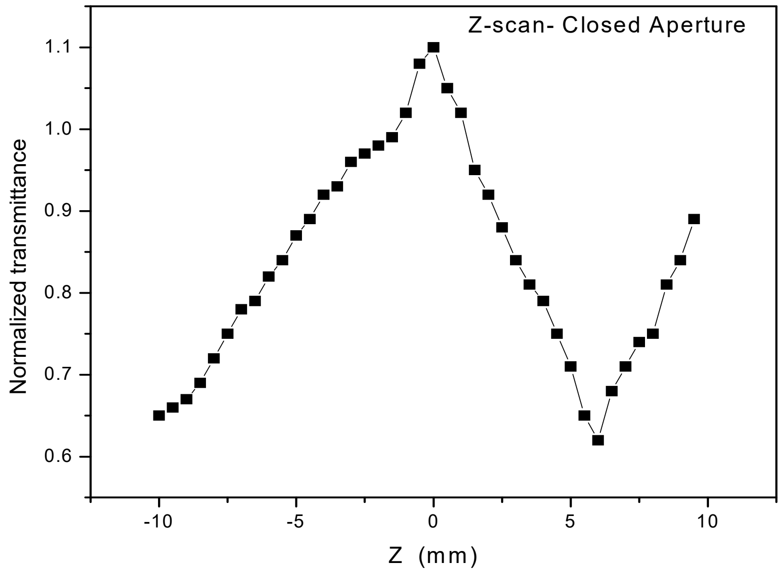

Fig. 7. Z-scan pattern for the sample in closed aperture

3.5. Dielectric analysis

It has been measured that the dielectric constant of such studies decreases with increasing frequency. When picric acid is added to pure GLS crystals, the dielectric constant increases with increasing dopant concentration [14]. For samples, the dielectric constant and dielectric loss decrease with increasing frequency. This indicates that pure and doped crystals tend to contain molecules with different relaxation times. The dielectric constant increases with increasing impurity concentration. From the measurement of the dielectric constant and fig. 8 and 9 the following observations can be made. Because the crystals grown in this process have low dielectric loss at high frequency, this model improved the quality of the eye and the defect. This is an important parameter for nonlinear optical materials in their applications [15]. The low dielectric loss value indicates the quality of pure and doped GLS crystals.

3.6. Vickers Micro hardness analysis

Micro hardness instruments were made using a Vickers micro hardness indentation (Leitz Weitzier Maju tester). In this study, pure GLS and doped GLS were subjected to three weights of 25, 50 and 100 g, respectively, and given an indentation time of 10 sec. Several indentations were made for each load and the average diagonal length (d) was used to calculate the micro hardness value "Hv" using the relationship Hv = 1.8544 P / d2 kg mm^{-2} [16]. P is the applied load in kg and d is the diagonal length of the indentation in mm.

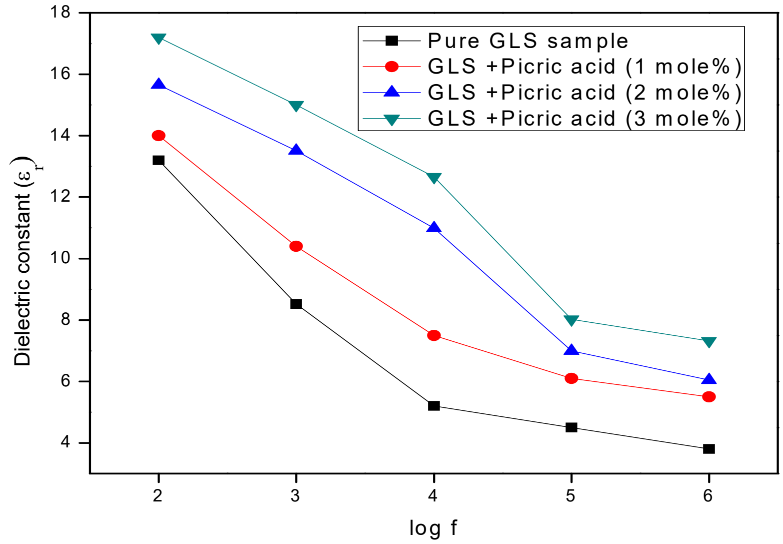

Fig. 8. Variation of dielectric constant with frequency of pure and picric acid doped GLS at 30 ℃

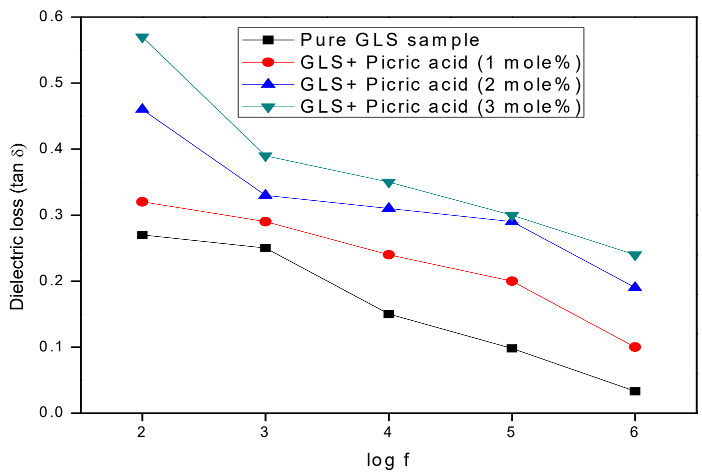

Fig. 9. Variation of dielectric loss with frequency of pure and picric acid doped GLS crystals at 30 ℃

The hardness values for the pure GLS crystal and the doped GLS crystal are plotted against the corresponding properties and are presented in Fig. 10. From the results, it can be seen that the hardness value increases with the increase in load patterns. It was found that the hardness values increased with increasing dopant concentration in the GLS crystal lattice. The plot of wheel P versus wheel d is a straight line as shown in Fig. 11. The slope n of the straight line in the figure gives the work hardening coefficient (n). An n-value of 5.62 was obtained for the picric acid doped GLS crystal.

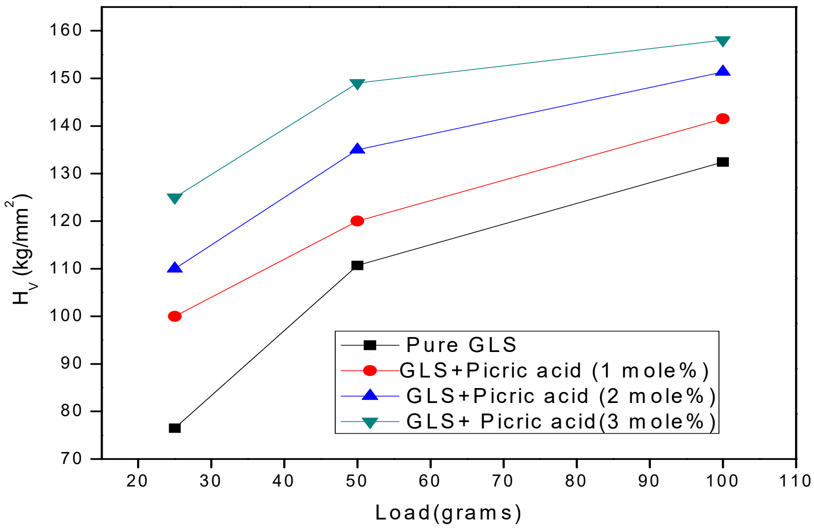

Fig. 10. Variation of Vickers hardness number with load for picric acid doped GLS.

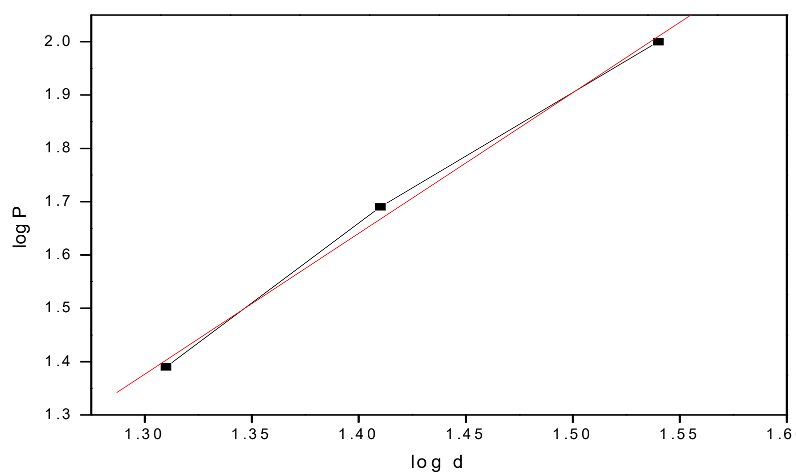

Fig. 11. Variation of log d with log P for 3 mole% of picric acid added GLS crystal

4. CONCLUSION

It was found that the picric acid doped GLS crystals were slightly yellow, the undoped GLS crystals were colorless, and both crystals were transparent and non-hygroscopic. The two stones of this work crystallize in an orthorhombic structure with a center-unsymmetrical cluster. The optical properties of the samples were found at wavelengths of light sources commonly used for nonlinear optics, showing that these samples are very good materials for nonlinear optics applications. Micro hardness studies have shown that picric acid doped GLS crystals are harder than undoped GLS crystals. The dielectric constant and loss factor values are found to be more in the case of doped samples compared to that of undoped samples of GLS and gamma-glycine. The increase of dielectric loss gives an indication of presence of dopants of in the case of doped GLS and gamma-glycine samples.

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