Functional, Optical and Mechanical Studies on Metallo-Organic GNC Crystal Using Density Functional Method

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Abstract - *Semi organic single crystals of Glycine Nickel Chloride (GNC) were grown from an aqueous solution by slow evaporation method at ambient temperature. Supersaturated solution of GNC was prepared in accordance with the solubility data. The chemical composition of the grown crystal was identified by using FT-IR studies. The optimized molecular structure of GNC molecule is calculated by using 6-31G (d, p) basis set. Photoconductivity studies have been carried out to define the negative conductive nature of the material, hence it used in the fabrication of optoelectronic devices.*

*Key Words***: *GNC, FT-IR, DFT, Photoconductivity*

1. INTRODUCTION

Amino acid based semi organic compounds have been recognized as potential candidates for second harmonic generation (SHG) [1-3]. Glycine is the simplest amino acid that cannot force crystal growth into a non-centrosymmetric space group which is solely based on geometry [4-6]. The structure of three non-centrosymmetric glycine coordinated compounds (glycine lithium sulphate, glycine nickel dichloride trihydrate and glycine zinc sulphate trihydrate) was reported by Fleck and Bohaty [7]. The title compound is found to be interesting semi organic non-linear optical (NLO) material which is formed by mixing Glycine and Nickel Chloride. It crystallizes in monoclinic structure with space group of $P2_1$. The aim of our work is to grow Glycine Nickel Chloride crystals and to discuss the results obtained from various studies.

1.1 EXPERIMENTAL DETAILS - Synthesis and Solubility

The synthesis component of Glycine Nickel (II) Chloride was carried out by carefully using Glycine and Nickel (II) Chloride in the molar ratio 2: 1 using double distilled water as a solvent.
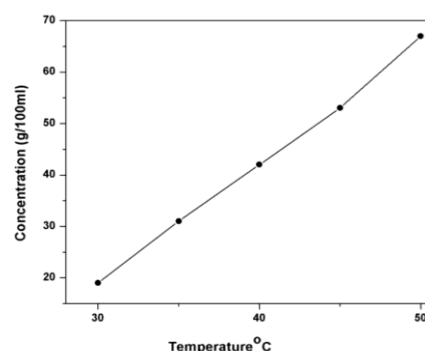

Fig -1: The solubility curve

The solution was stirred well using magnetic stirrer to form a clear solution. The solution was then filtered and allowed to evaporate at room temperature. Optical good quality crystals of GNC were harvested in a span of 6 weeks with dimension 5 mm × 3 mm × 3 mm. The solubility curve and the photograph of the as grown crystals of GNC are shown in Figure 1 and Figure 2 respectively.
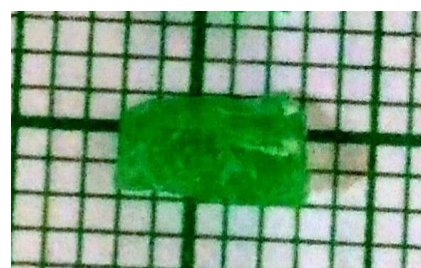

Fig -2: Photograph of grown crystal

2. RESULTS AND DISCUSIONS: Computational Details- Molecular Geometry

The molecular structure optimization of the title compound and corresponding vibrational harmonic frequencies were calculated using the Density Functional Theory with Beckee-3-Lee-Yag-Parr (B3LYP) combined with 6-31G (d, p) basis set. The optimized molecular structure of the isolated GNC molecule is calculated and is shown in Figure 3.
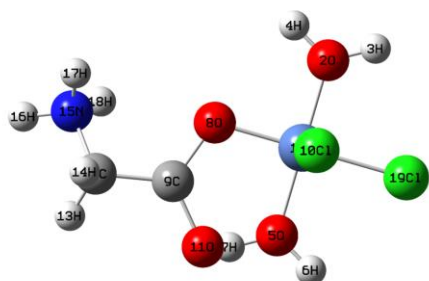
Fig -3: Molecular structure

2.1 FT-IR SPECTROSCOPIC ANALYSIS

The infrared spectral analysis was carried out to understand the chemical bonding and it provided useful information about the molecular structure of the compound. The FT-IR spectrum of GNC was recorded in the wavelength range 500 – 4000 cm^{-1} using Perkin Elmer spectrometer by KBr pellet technique on IFS 66V FT-IR Spectrometer to confirm the presence of functional groups of GNC crystals. The FT-IR spectrum of GNC is shown in Figure 4. The spectrum consists of bands which are formed due to internal vibration of glycine molecule and $NiCl_2$ group. The vibrational frequency of various functional groups of GNC and the frequency assignment are presented in Table 1.
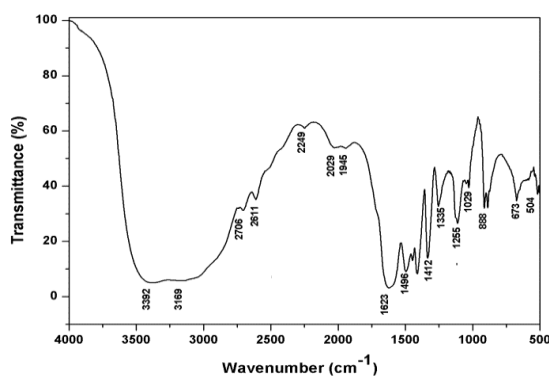

Fig -4: FT-IR Spectrum

C-N vibrations

The C-N ring stretching vibration bands occur in the region 1600 cm^{-1}-1500 cm^{-1}. C-N stretching absorption assigned in the region 1382 cm^{-1}-1266 cm^{-1}. The theoretical and experimental peaks appear at 1500 cm^{-1} and 1496 cm^{-1} respectively [8].

NH$_2$ vibrations

The NH$_2$ asymmetric stretching vibrations give rise to a strong band in the region 3390±60 cm^{-1} and the symmetric NH$_2$ stretching is observed as weak band in the region 3210±60 cm^{-1}. The theoretical asymmetric stretching appears at 3359 cm^{-1} and 3422 cm^{-1} and the experimental value coincides well at 3378 cm^{-1} [9].

C-Cl vibrations

In the lower region, C-Cl stretching vibrations appear at 760-505 cm^{-1} and C-Cl deformation vibrations appear in the region 420-250 cm^{-1}. Compounds with more than one chlorine atom exhibit very strong bands due to the asymmetric and symmetric stretching modes. Vibrational coupling with other groups may results in a shift in the absorption to as high as 840 cm^{-1}. For simple organic chlorine compounds; C-Cl absorption is in the region 750-700 cm^{-1}. The band at 366 and 367cm^{-1} is assigned for C-Cl in-plane bending for FT-IR 144 cm^{-1} and 142 cm^{-1} is for out-of-plane bending vibrations for FT-IR. In the present work the C-Cl stretching vibrations appear at 511 cm^{-1}, 515 cm^{-1}, 558 cm^{-1}, 650 cm^{-1}, 655 cm^{-1}, 691 cm^{-1}, 738 cm^{-1} (theoretical), 516 cm^{-1}, 661 cm^{-1}and 674 cm^{-1} (experimental).

2.2 MECHANICAL STUDIES

Vickers hardness measurements were taken for applied loads varying from 5 to 25 g for an indentation time of 10 s. The experiment was conducted on the well-defined face of the GNC single crystal. Vicker microhardness values were calculated from the relation $H_v = 1.8544p/d^2$ Pascal;

Table -1: Spectral assignments of FT-IR studies

Wavenumber (cm^{-1})		ASSIGNMENTS
Theory	Expt	
3392	3305	OH Stretching
3169	3113	NH^{3+} Stretching
2611	2524	NH^{3+} Stretching
2249	2179	CH asymmetric Stretching
1496	1496	CH$_2$ bending
1447	1447	CH$_2$ Stretching
1335	1325	OCC Stretching

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1412	1409	COO⁻ Symmetric Stretching
1623	1594	COO⁻ Symmetric Stretching
1113	1128	NH_2 deformation
1048	1030	C-N Stretching
888	878	CCN Stretching
673	660	COO⁻ bending
571	574	COO⁻ ROCKING

Where p is the applied load in Newton and d the average diagonal length of the indented impressions in meter. Figure 5 illustrates the Vickers micro hardness profile as a function of the applied test loads. It is evident from the figure that the micro hardness of the crystal decreases with increase in the applied load. The decrease of the micro hardness with increasing load is in agreement with the normal indentation size effect (ISE). The value of work hardening coefficient was found to be 1.51 (Figure 6). Hence, it is concluded that GNC is a hard material [10].
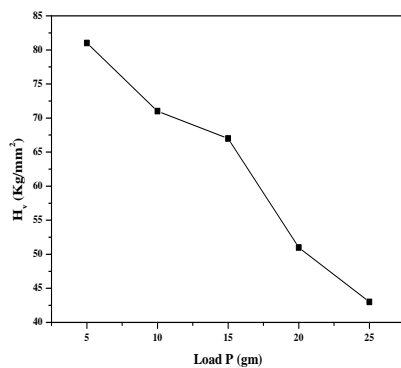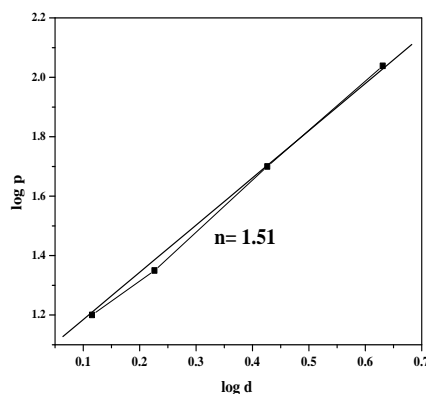

Fig -5: Variation of Vickers hardness number

Fig -6: log d Vs log p

2.3 PHOTOCONDUCTIVITY STUDY

The experiment was performed at room temperature using Keithley 485 Pico ammeter. Dark conductivity of the sample was studied by connecting the sample in series to a DC power supply and a Pico ammeter. Electrical contacts were made at a spacing of about 1.5 mm on the samples using silver paint. The DC input was increased in steps and the corresponding dark currents were noted from the electrometer. For measuring the photo current, the sample was illuminated with a halogen lamp (100 W) by focusing a spot of light on the sample with the help of a convex lens. The variations of photocurrent (I_p) and dark current (I_d) with applied field are shown in Figure 7. Both the photo and dark currents of GNC crystal increase linearly with applied field. It is observed from the plot that the dark current is always greater than the photo current, hence it is concluded that GNC exhibits negative photoconductivity [11].
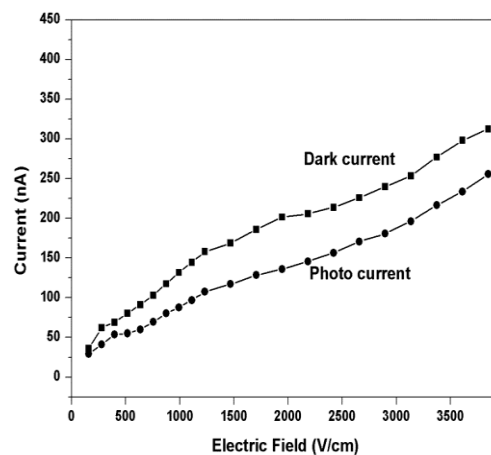

Fig -7: variations of photocurrent (I_p) & dark current (I_d)

3. CONCLUSION

Single crystal of an amino acid based nonlinear optical material GNC was successfully grown by slow evaporation technique. The optimized structure was obtained from Gaussian software. The functional groups were identified using FT-IR analysis and tabulated along with the vibrational frequency obtained from Gaussian. Vickers Hardness measurements reveals that GNC belongs to hard category material Photoconductivity studies reveal the negative photoconductive nature of GNC crystal. Hence, it can be used in the Optoelectronic device fabrications.

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