INVESTIGATION ON GROWTH AND CHARACTERIZATION OF NONLINEAR OPTICAL DICHLORO-DIGLYCINE ZINC II SINGLE CRYSTAL

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Abstract: *The study of amino acid based nonlinear optical (NLO) materials with optimum physical properties is an important area due to their practical applications such as optical communication, optical computing, optical information processing, optical disk data storage, laser fusion reactions, laser remote sensing, colour display, medical diagnostics, etc. Also, microelectronic industries require crystals which possess low dielectric constant at higher frequency. Keeping this in view, attempts have been made to grow nonlinear optical crystals and study their optical, electrical and mechanical properties. Nonlinear optical single crystals of dichloro-diglycine zinc II have been grown by slow evaporation method. The grown crystals were characterized using single crystal X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), UV-VIS-NIR spectrum, thermal, mechanical and dielectric studies. The results of characterization studies have been discussed in detail to understand their properties. The grown crystals have better thermal stability and sufficient mechanical strength. They are capable of inducing polarization due to dielectric behaviour when powerful laser beam is incident on them. The various characterization studies suggest that the grown crystals are promising materials for optoelectronic and nonlinear optical applications.*

Keywords: *Single X-ray diffraction, UV-Visible spectroscopy, NLO, SHG, Dielectric constant, Dielectric loss studies.*

1. INTRODUCTION

In the current day technological society, nonlinear optical (NLO) materials are mainly useful in the area of optical data storage, lasers, optical signal processing, second harmonic generation etc. Even though varieties of nonlinear optical materials exist, its applications are restricted due to physical and chemical properties. Broad studies were made on the synthesis and crystal growth of nonlinear optical materials over the past decade because of their potential applications in the field of telecommunications, optical signal processing and optical switching [1, 2]. Among the organic crystals for NLO applications, amino acids display special features of interest, such as molecular chirality which secures acentric crystallographic structure, wide transparency in the visible and UV range, zwitterionic nature of the molecule which favors the hardness of the crystal etc [3, 4]. In solid state, amino acid contains the donor and acceptor groups, which give the ground state charge asymmetry of the molecule, essential for second order nonlinearity. These better properties of amino acids are due to the being there of a proton donor carboxylic acid (COOH) group and the proton acceptor amino (NH_2) group. Due to this dipolar nature, amino acids contain physical properties which create them ideal candidates for applications [5]. Hydrogen bonds have also been used in the probable generation of noncentrosymmetric structures, which is a requirement for a useful NLO crystal. The amino acid family crystals were subjected to broad analysis by several researchers because of the excellent characteristics of these materials. Glycine is the simplest amino acid and it can exist in zwitterionic form. Different other amino acids, it has no centre of chirality and is optically inactive. While glycine can be present as a neutral molecule in the gas phase, it exists as a zwitterion in solution and in the solid state. The present investigation deals with the growth of dichloro-diglycine zinc II single crystal that was grown by slow evaporation technique. The grown crystals were characterized by single crystal X-ray analysis, FTIR, thermal, UV spectral analysis, microhardness, dielectric, SHG and photoconductivity measurements.

2. EXPERIMENTAL PROCEDURE

The dichloro-diglycine zinc II single crystal was synthesized from glycine and zinc chloride were taken in the molar ratio 2:1. Calculated amount of reactants were thoroughly dissolved in double distilled water and stirred well by using magnetic stirrer to ensure homogeneous solution. The solution was then filtered using filter paper and transferred to a Petri dish. The prepared solution was allowed to evaporate at room temperature. Tiny seed crystals with good transparency were obtained due to spontaneous nucleation. Among them, defect free seed crystal was selected and suspended in the mother solution, which was allowed to evaporate at room temperature. Large size single crystals were obtained due to collection of monomers at the seed crystal sites from the mother solution after the nucleation and growth processes were completed. The quality of the crystal was improved by recrystallization process. After a period of 30 days, good quality of the crystal was harvested with more transparency.

3. RESULTS AND DISCUSSION

3. 1. Single-Crystal X-Ray Diffraction

Single crystal XRD studies were carried out using ENRAF NONIUS CAD4 automatic X-ray diffractometer to determine the lattice parameters and the crystal system of the grown dichloro-diglycine zinc II crystal. Single crystal XRD analysis reveals that the grown crystal belongs to monoclinic structure. The lattice parameters were calculated by using least-squares refinement and are found to be a = 11.653 Å, b =15.583 Å, c = 15.325 Å, These results are found to be in good agreement with the earlier reported values [6].

3. 2. FTIR Spectrum Analysis

In order to analyze qualitatively the presence of functional groups in the dichloro-diglycine zinc II single crystal, Fourier transform infrared spectra has been taken for the powder form of dichloro-diglycine zinc II crystal using BRUKER IFS 66V spectrometer with KBr pellet technique. The spectrum was recorded in the wavelength range 400-4000 cm^{-1}. The recorded spectrum of dichloro-diglycine zinc II crystal is shown in Fig. 1. From the observed spectrum, the peak at 3092 cm^{-1} is attributed to NH_3^+ stretching. The peaks observed at 2325 cm^{-1} is attributed to CH_2 group. The absorption peaks observed at 1033 cm^{-1} respond to C-C-N group. The peaks observed at 1585 cm^{-1} is attributed to COO- group. The asymmetric and symmetric stretching modes of carboxylate group are observed at 1576 cm^{-1} and 1412 cm^{-1}. The strong peak at 1637 cm^{-1} is due to the C=O stretching modes of vibration. The strong peak at 1333 cm^{-1} is attributed to C-C stretching vibrations. The analysis of the spectrum shows amino acid characteristics and the results agree very well with the already reported prediction [6]. The IR peak assignments are found to be in good agreement with the literature [6]. The FTIR spectrum obtained thus shows the presence of functional groups of dichloro-diglycine zinc II single crystal.

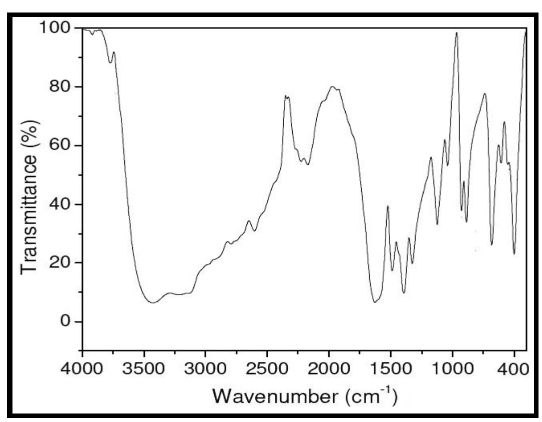

Fig. 1. FTIR spectrum of the grown crystal dichloro-diglycine zinc II

3. 3. Thermal Analyses

The TGA and DTA of the dichloro-diglycine zinc II single crystal were studied using the instrument NETZSCH STA instrument in the temperature range of 100 to 900 ºC under nitrogen atmosphere to understand the thermal behaviour. Thermogravimetry analysis (TGA) and differential thermal analysis (DTA) were made to investigate the thermal properties of the grown crystal. The recorded plots are shown in Fig. 2. There is a minute weight loss starting at 95.8 ºC, due to loss of physically adsorbed water on the crystal surface. This is followed by another sharp weight loss starting close to 110.3 ºC, which is assigned to loss of water of crystallization. There is major weight loss starting close to 205 ºC, due to decomposition. The DTA trace illustrates three endosperms at 110 ºC, 125.6 ºC and 202.5 ºC. In the DTA curve, a sharp endothermic peak was observed at 110 ºC, indicating the melting point of dichloro-diglycine zinc II. It shows that there is no decomposition before the melting of the material. Hence, for NLO applications of the crystal the maximum temperature is limited to 110 ºC.

3. 4. UV-Vis-NIR Spectral Analysis

The absorption spectrum of the dichloro-diglycine zinc II crystal was recorded in the wavelength range of 200-1200 nm covering the entire near ultraviolet, visible and near infrared regions using the Perkin Elmer Lamda 35 UV-VISNIR spectrophotometer. Fig.3 shows the spectrum recorded for single crystal of dichloro-diglycine zinc II. In the UV-Vis-NIR spectrum, a strong absorption found at 255 nm is due to π-π* transition and then there is no remarkable absorption peak obtained in the entire region of the spectrum, which clearly indicates that the synthesized compound is transparent in the UV, visible and infrared region. The UV-VIS-NIR spectrum clearly reveals the transparency of the material in the region 255-1200 nm. Therefore the material is found to be accessible for initiating the induced polarization when the incident radiation is in this region. The UV absorption edge for the grown crystal was observed to be around 255 nm, makes it suitable for SHG laser radiation of 1064 nm or other applications. 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 absence of absorption of light in the visible range of the electromagnetic spectrum is an intrinsic property of all the amino acids. The dependence of optical absorption coefficient on photon energy helps to study the band structure and type of transition of electrons [7].

The optical absorption coefficient (α) was

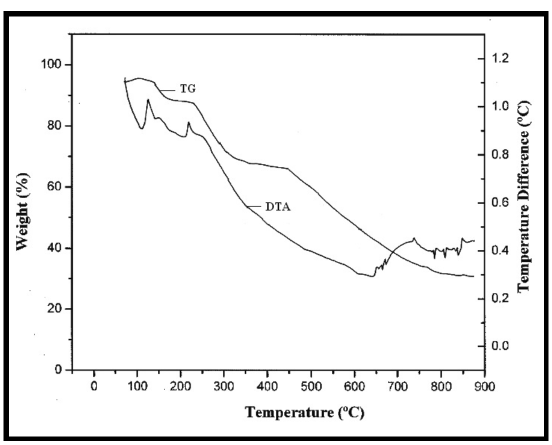

Fig. 2. TGA and DTA thermograms of dichloro-diglycine zinc II crystal

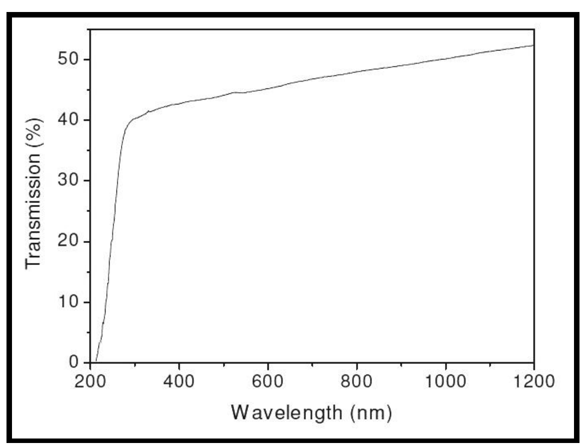

Fig. 3. UV-Vis absorbance spectrum of dichloro-diglycine zinc II

calculated from transmittance using the following relation

$$\alpha = \frac{1}{d}\log\left(\frac{1}{T}\right) \quad (1)$$

where T is the transmittance and d is the thickness of the crystal. As a direct band gap material, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies (hν)

$$\alpha = \frac{A(h\nu - E_g)^{1/2}}{h\nu} \quad (2)$$

where E_g is the optical band gap of the crystal and A is a constant. A plot of variation of $(\alpha h\nu)^2$ versus hν is shown in Fig. 4. E_g is evaluated using the extrapolation of the linear part [8]. Using Tauc's plot, the energy gap (E_g) was calculated as 4.60 eV and the large band gap clearly indicates the wide transparency of the crystal. This high band gap value indicates that the grown crystal possesses dielectric behaviour to induce polarization when powerful radiation is incident on the material.

3. 4. 1. Determination of Optical Constants

The extinction coefficient (K) can be obtained from the following equation,

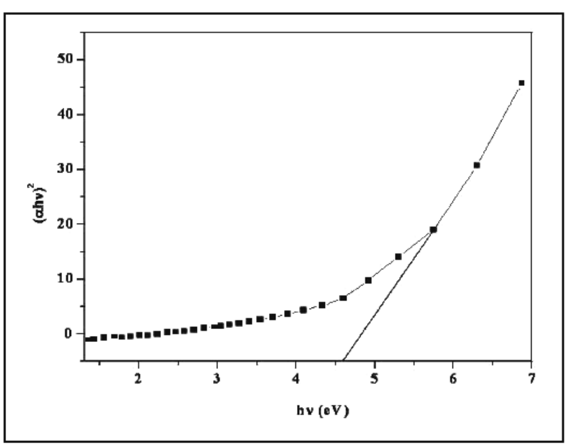

Fig. 4. Plot of $(\alpha h\nu)^2$ Vs photon energy

$$K = \frac{\lambda\alpha}{4\pi} \quad (3)$$

The transmittance (T) is given by

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1 - R^2 \exp(-2\alpha t)} \quad (4)$$

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation. Hence,

$$R = \frac{1 \pm \sqrt{1 - \exp(-\alpha t + \exp(\alpha t)}}{1 + \exp(-\alpha t)} \quad (5)$$

Refractive index (n) can be determined from reflectance data using the following equation,

$$n = -\frac{(R+1) \pm \sqrt{3R^2 + 10R - 3}}{2(R-1)} \quad (6)$$

The refractive index (n) was found to be 1.763 at λ =1200 nm. The high value of refractive index and low value of reflectance reveal that the grown crystal is more transparent to transmit the light from 255 to 1200 nm. From the optical constants, electric susceptibility (χc) can be calculated according to the following relation [9]

$$\varepsilon_r = \varepsilon_0 + 4\pi\chi_C = n^2 - k^2 \quad (7)$$

Hence,

$$\chi_C = \frac{n^2 - k^2 - \varepsilon_0}{4\pi} \quad (8)$$

where ε_0 is the permittivity of free space. The value of electric susceptibility χc is 0.132 at λ=1200 nm. The real part dielectric constant ε_r and imaginary part dielectric constant ε_i can be calculated from the following relations [10]

$$\varepsilon_r = n^2 - k^2 \quad (9)$$

$$\varepsilon_i = 2nk \quad (10)$$

The value of real ε_r and ε_i imaginary dielectric constants at λ=1200 nm were estimated as 1.453 and 8.712x10^{-5}, respectively. The moderate values of refractive index and optical band gap suggest that the material has the required transmission range for NLO application. The lower value of dielectric constant and the positive value of the material are capable of producing induced polarization due to intense incident light radiation.

3. 5. NLO Test – Kurtz Powder SHG Method

Nonlinear optical property of dichloro-diglycine zinc II crystals was confirmed by the Kurtz and Perry powder technique using Q-switched high energy Nd:YAG laser (QUANTA RAY model LAB-170-10). The emission of green radiation of wavelength 532 nm from the sample confirms that the material exhibits nonlinear optical property. The output radiation from the crystal was allowed to fall on a photomultiplier tube which converts the light signal into electrical signal. A potassium dihydrogen phosphate (KDP) crystal was used as a reference material in the SHG measurement. The relative conversion efficiency was calculated from the output power of dichloro-diglycine zinc II crystal with reference to KDP crystal. For a laser input of 4.2 mJ, the second harmonic signal (532 nm), 23 mW, and 21 mW was obtained for KDP and dichloro-diglycine zinc II. It is observed that the conversion efficiency of dichloro-diglycine zinc II is 0.9 times that of KDP crystal.

3. 6. Microhardness Studies

Hardness is an important mechanical property required for the fabrication of electronic and optical devices. Microhardness measurements of the grown crystal were carried out using REICHERT MD 4000E ULTRA microhardness tester with diamond pyramid indenter attached to an optical microscope. Microhardness studies have been carried out on a (001) face of a selected well transparent single crystal using microhardness tester, fitted with a Vickers diamond pyramidal indenter. To get accurate results of hardness of the grown crystal, several indentations were made on the sample for different applied loads from 20g to 100g and mean diagonal length was measured. The hardness was calculated for different loads. The time of indentation was kept constant for 10s. The Vickers microhardness number was calculated using the relation,

$$H_v = 1.8544\left(\frac{P}{d^2}\right) kg/mm^2 \quad (11)$$

where P is the indenter load and d is the diagonal length of the impression. The Fig. 5 shows the variation of P with Vickers hardness number (H_v) for grown single crystal. It is evident from the plot that Vickers microhardness number increases with increasing applied load. The microhardness measurements at different loads show that as dichloro-diglycine zinc II crystal exhibits the reverse indentation size effect in which the hardness value increases with the increasing load. At low loads, the indenter pierces only top surface layers generating dislocations results in the increase of hardness. When load increases, the indenter penetrates through surface and inner layer. So mutual interaction between dislocations is created and they restrict the motion of dislocations and high resistance is offered by crystal lattice to the motion of dislocations. Crystals exhibit the formation of cracks above 100 g due to the release of internal stress generated locally by indentation. According to Meyer's law, the relation connecting the applied load is given by

$$P=k_1 d^n \quad (12)$$

$$\log P = \log k + n \log d \quad (13)$$

where n is the Meyer index or work hardening exponent and k_1, is the constant for a given material. The above relation indicates that 'Hv' should increase with load P if n>2 and decrease with load P when n<2. We have determined 'n' from slope of the plot that is shown in Fig. 6. The value of 'n' for dichloro-diglycine zinc II was found to be 3.35. Low value of work hardening coefficient 'n' illustrates fewer defects in the as grown crystal. The large value of n indicates large effect of dislocations. According to Onitisch [11] if n is greater than 2, the microhardness will increase with the increase of load. Hence, the material shows increasing trend for the hardness of the material up to a particular load 100g. Since dichloro-diglycine zinc II is having moderately higher value of hardness number, the material is found to be suitable for device fabrications.

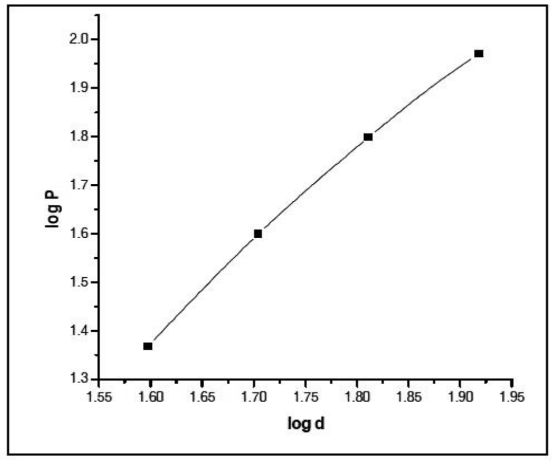

Fig. 6. Plot of log d Vs log p

3. 7. Dielectric Studies

The dielectric study of dichloro-diglycine zinc II was carried out using the instrument, HIOKI 3532-50 LCR HITESTER. The face of single crystal was cut in to rectangular shape and well-polished, so that it behaves as a parallel plate capacitor. Silver paste was used for making the electrode plates on these surfaces of the crystal. The sample holder was heated at a slow rate from room temperature to 120ºC below the decomposition or melting temperature. The temperature of the sample was allowed to stabilize for a few minutes and subsequently capacitance and dielectric loss values were recorded for different frequencies from 50 Hz to 5MHz. The plots of dielectric constant and dielectric loss with frequency for various temperatures are shown in Figs 7 and 8. At low frequencies, the dielectric constant is found to be maximum and then it decreases with increasing frequency. The high dielectric constant at low frequency is due to the presence of all types of polarizations viz., electronic, ionic, orientation and space polarizations. The space polarization will depend on the purity and perfection of the crystal. The low value of dielectric loss at high frequency implies that the crystal possesses good optical quality with lesser defects and this parameter is of vital importance for NLO materials in their applications [12, 13].

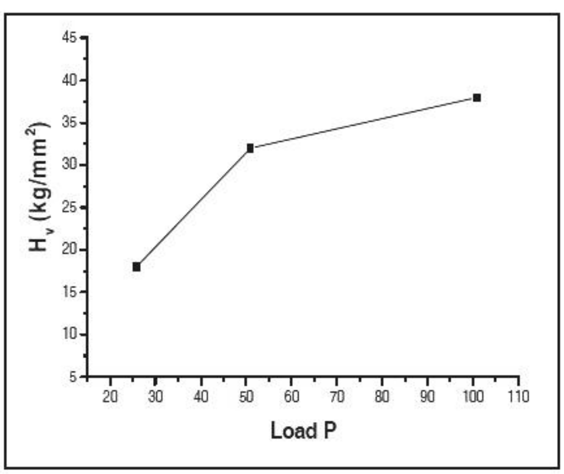

Fig. 5. Variation of Hv with load P

3. 8. Photoconductivity Studies

The photoconductivity measurements were carried out by using Keithley 485 picoammeter. The dark current was recorded by keeping the

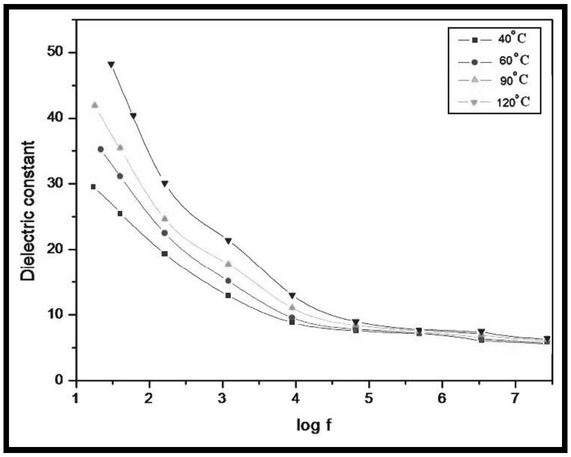

Fig. 7. Variation of dielectric constant with log frequency

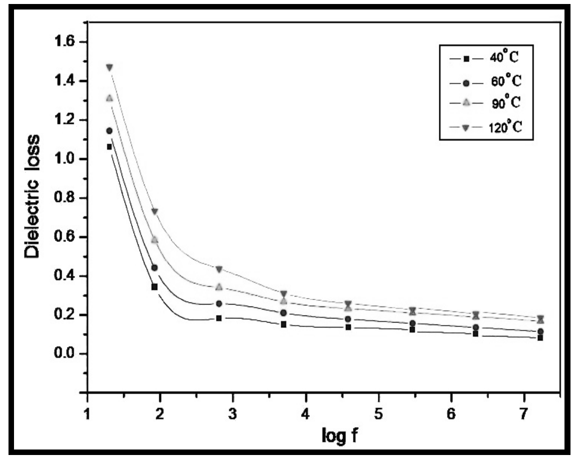

Fig. 8. Variation of dielectric loss with log frequency

sample unexposed to any radiation. The Fig. 9 shows the variation of both dark current (I_d) and photocurrent (I_p) with the applied electrical field. It is seen noted from the plots that both Id and I_p of the sample increase linearly with the applied electrical field. It is observed from the plot that the dark current is always greater than the photo current, thus confirming the negative photoconductivity [14].

4. CONCLUSION

Dichloro-diglycine zinc II single crystal was successfully grown by slow evaporation technique. From single crystal XRD data, it is observed that the grown crystal belongs to monoclinic structure. The presence of functional groups was established by FTIR studies. From the thermal studies, the thermal stability was analyzed. Optical absorption was found to be absent in the UV, visible and near IR regions indicating that the crystal is completely transparent in the entire range of 255 nm to 1200 nm. The band gap, refractive index, reflectance, extinction coefficient and electrical susceptibility were calculated to analyze the optical property. Kurtz and Perry powder technique confirms that dichloro-diglycine Mechanical behaviour has been studied by Vickers microhardness test. Dielectric studies establish the dielectric behaviour of the grown crystal. The dielectric constant and dielectric loss have been studied as a function of frequency at different temperatures. The photoconductivity studies confirm that this material has negative photoconductivity nature.

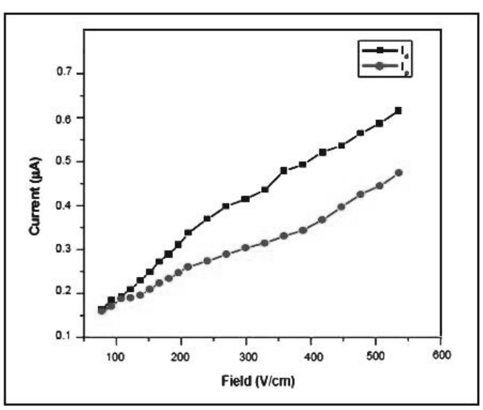

Fig. 9. Field dependent photoconductivity of grown single crystal

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