



GROWTH AND CHARACTERIZATION OF SOLUTION-GROWN TRIS-GLYCINE ZINC CHLORIDE (TGZC) SINGLE CRYSTALS

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ABSTRACT

Good optical quality single crystals (size 30.05 x 18.66 x 7.41 mm³) of Tris-glycine Zinc Chloride (TGZC) were grown by slow evaporation technique from its aqueous solution at room temperature. Single crystal X-ray diffraction (XRD) studies revealed the presence of orthorhombic structure with space group Pbn2₁ and Fourier transform infrared transmission (FTIR) have confirmed the presence of the functional groups present in the single crystal system. UV spectrum showed no significant absorption in the region 200-800nm suggesting the optical transparency of the grown crystals. The refractive index was measured by the Brewster's angle method. The density measurements were carried out by both theoretical and experimental methods. The Non Linear Optical (NLO) behaviour of TGZC crystals was tested by Kurtz- Perry technique. The dielectric studied was carried out by room temperature.

Keywords: Growth from solution; Single-crystal growth; X-ray diffraction.

INTRODUCTION

Amino acids and their complexes belong to a family of organic materials that have been considered for photonic applications¹. Photonic crystals, which prohibit the propagation of light for frequencies within a band gap, have enabled exciting new ways to control light and construct integrated optical devices. In recent years the amino acid group materials were mixed with organic² or inorganic salts³ in order to improve their chemical stability, laser damage threshold, thermal, physical properties and linear and non-linear optical properties. Glycine (NH₂-CH₂-COOH) is the simplest amino acid. Unlike other amino acids, it has no asymmetric carbon atom and is optically inactive. It has three polymeric crystalline forms α , β and γ . α -glycine is commonly available. Glycine and its methylated analogs form complexes with mineral acids exhibiting interesting physical properties like ferroelastic, ferroelectric or antiferroelectric behavior often associated with transitions to commensurate or incommensurate phases⁴. The complete understanding of the optical properties of amino acid crystals, as well as other organic crystals, still requires more information. Some complexes of glycine with HCl^{5,6}, lithium sulfate⁷, H₃PO₃⁸, H₂SO₄⁹, Ca(NO₃)₂¹⁰, CoBr₂¹¹, LiNO₃¹², H₂SO₄^{13,14}, sodium nitrate¹⁵, benzoyl glycine¹⁶ form single crystals, but some of these are reported to have NLO property and some are reported not to have NLO property. Effects of hydrogen bonds on optical non-linearities of complex crystals have also been studied^{17,18}. Hariharan et al.¹⁹ and Fleck et al.²⁰ have studied the crystal structure and phase matching studies on Tris-glycine zinc chloride (TGZC). The present paper deals with characterization by single-crystal X-ray diffraction (XRD), Fourier Transform Infrared (FTIR) spectrum, UV analysis, NLO test and dielectric studies.

EXPERIMENTAL

A supersaturated solution of glycine and zinc chloride prepared in 3:1 proportion (20) was stirred continuously using magnetic stirrer for 3 days. The prepared solution was filtered and kept undisturbed in room temperature. Tiny seed crystals with good transparency were obtained due to the spontaneous

nucleation. Among them, defect free seed crystal was suspended in the mother solution, which was allowed to evaporate at a room temperature. The chemical reaction may be represented as



The identity of grown crystal was confirmed from the lattice parameter. The grown crystal to dimension of $(30.05 \times 18.66 \times 7.41 \text{ mm}^3)$ obtained over a period of 45 days is shown Figure 1.

Characterization Studies:

The grown crystals were subjected to single-crystal XRD studies using ENRAF NONIUS CAD4-F single X-ray diffractometer with $\text{MoK}\alpha$ radiation ($\lambda = 0.71069 \text{ \AA}$) to estimate the lattice parameter values. The absorption spectrum for the grown crystal was recorded using a PERKIN-ELMER LAMBDA 25 UV spectrometer in the region 200-800 nm. The FTIR spectrum was recorded using BRUKER IFS 66 V by KBr pellet technique to confirm the presence of functional groups. The NLO study was carried out using Nd: YAG laser. LAB-170-10 (A DCR) Quanta ray of spectra physics Nd:YAG laser producing a pulse width of 8 ns and repetition rate of 10 Hz was used. The dielectric studies for the grown crystals were carried out by using HIOKI 3532-50 LCR HITESTER.

RESULTS AND DISCUSSION

Single-crystal X-ray diffraction

The grown crystal was subjected to single-crystal XRD analysis and the data were collected at room temperature. Calculated lattice parameter values are $a = 11.26 \text{ \AA}$, $b = 15.26 \text{ \AA}$, $c = 15.65 \text{ \AA}$, $\alpha = \beta = \gamma = 90$ and volume of the unit cell is 2688 \AA^3 . The XRD data prove that the crystal is orthorhombic in structure with the space group $\text{pbn}2_1$.

FTIR spectral analysis

The FTIR spectra of the grown TGZC crystals were recorded in the KBr phase in the frequency region $400-4000 \text{ cm}^{-1}$ using Perkin Elmer spectrometer. The recorded FTIR spectrum as shown in Figure 2 was compared with the standard spectra of the functional groups^{19,20}. The characteristic peaks at 1610 cm^{-1} and 1580 cm^{-1} due to NH_2 deformation and COO^- stretching confirmed the existence of amino group. The broad peak at 1638 cm^{-1} established the presence of $\text{C}=\text{O}$ group. The very broad peak at 3186 cm^{-1} is due to O-H stretching. The peak at 2694 cm^{-1} established the presence of CH_2 symmetric and antisymmetric stretching. The strong band at 1125 cm^{-1} established the presence of C - N stretching.

UV- Visible analysis

The optical absorption spectrum of the grown crystals was recorded in the range 200-800 nm and the absorption spectrum is shown in Fig.3. From the UV absorption spectrum, it was found there is very low absorbance in the entire visible region. Excellent optical absorbance with the lower cut-off wavelength at 220 nm makes it as a potential material for device fabrication.

Refractive index (n) measurement

The refractive index of the TGZC crystal was determined by Brewster's angle method using He-Ne laser of wavelength 632.8 nm. A polished flattened single crystal of TGZC was mounted on a rotating mount at an angle varied from 0 to 90 degrees. The angular reading on the rotary stage was observed, when the crystal is perfectly perpendicular to the intra-cavity beam. The crystal was rotated until the laser oscillates and the angle has been set for maximum power output. Brewster's angle (θ_p) for TGZC is measured to be 56.30 ± 0.5 degree. The refractive index has been calculated using the equation $n = \tan\theta_p$, where θ_p is the polarizing angle and n is found to be 1.500.

Density measurements

The density of TGZC crystal was calculated by using the equation (2)²¹

$$\rho = MZ / N_A abc \quad (2)$$

Where M is molecular weight of TGZC; Z = 8; N_A is Avogadro's number and a, b and c are the cell parameters of TGZC crystal. The theoretical density is found to be 1.801 g/cm³. The density of TGZC crystal was measured experimentally by the floatation method at room temperature (32°C), and the measured density can be obtained by the following equation²¹

$$\rho = M \rho_{\text{solvent}} / m - m' \quad (3)$$

where m is the mass of ABGZC crystal sample in the air, m' is the mass when the TGZC crystal sample was immersed in CCl₄ and ρ_{solvent} is the density of solvent (CCl₄) used at measured temperature. The density was measured by floatation technique. From this measurement, the density of the crystal is found to be 1.792 g/cm³. The experimentally measured density is in good agreement with the theoretically found values

NLO test

The NLO property of the crystal was confirmed by Kurtz Perry technique. The determination of Second Harmonic Generation (SHG) intensity of the crystals using powder technique by Kurtz and Perry²². The crystals are ground to powder and packed between two transparent glass slides. The first harmonic output 1064 nm from an Nd: YAG laser was made to fall normally on the prepared sample with a pulse width of 8 ns. The second harmonic signal generated in the crystal was confirmed from the emission of green radiation by the sample.

Dielectric studies

Single crystals of Tris-glycine Zinc Chloride (TGZC) of thickness 1mm were subjected to dielectric studies at room temperature for various frequencies ranging from 50Hz to 5MHz using HIOKI 3532-50 LCR HITESTER. The dielectric constant is evaluated using the relation

$$\epsilon' = Cd/\epsilon_0 A \quad (4)$$

where d is the thickness and A is the area of the cross section of the grown crystal. The variation of dielectric constant as a function of frequency at room temperature is shown in Figure 4. From the graph, the dielectric constant is found to decrease with increase in frequency. The very low value of dielectric constant at higher frequencies is important for the fabrication of ferroelectric, photonic and electro-optic devices. The dielectric loss was studied as a function of frequency at room temperature is shown in Figure 5. These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field, similar to that of dielectric constant.

CONCLUSIONS

Good optical quality TGZC crystals (30.05 x 18.66 x 7.41 mm³) were grown by slow evaporation technique. Single-crystal XRD analysis confirmed that the crystals belong to orthorhombic system with the space group Pbn2₁. The functional groups present in the grown crystal have been confirmed by FTIR spectral analysis. Both UV absorption spectrum and refractive measurements confirm the quality optical transparency of the crystals. The density of TGZC crystals is found to be 1.836 g/cm³ which are in accordance with theoretical calculations. The NLO behaviour of the TGZC crystals was observed by Kurtz-Perry powder technique. The variations of dielectric constant / dielectric loss of TGZC were studied with varying frequency at room temperature.

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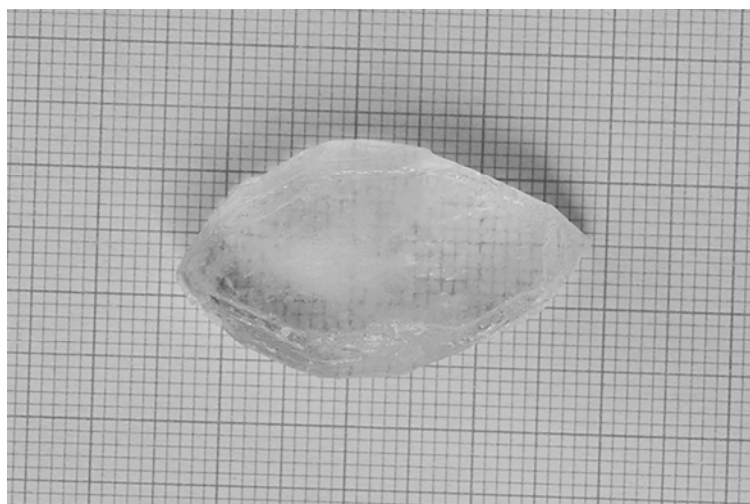


Fig.-1: The grown single crystal of TGZC

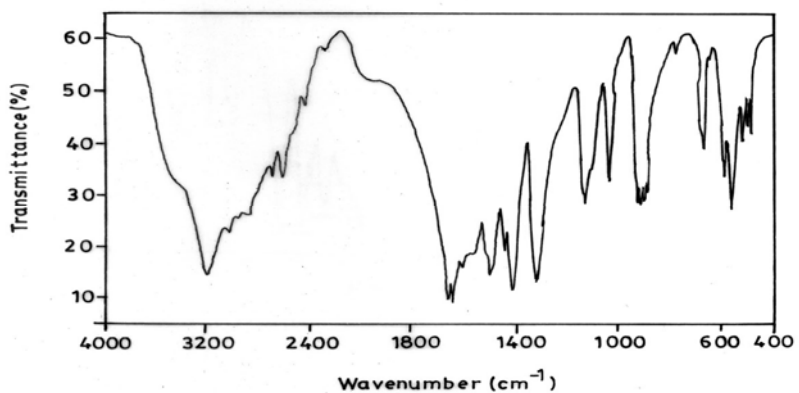


Fig.-2: FTIR spectrum of TGZC crystal

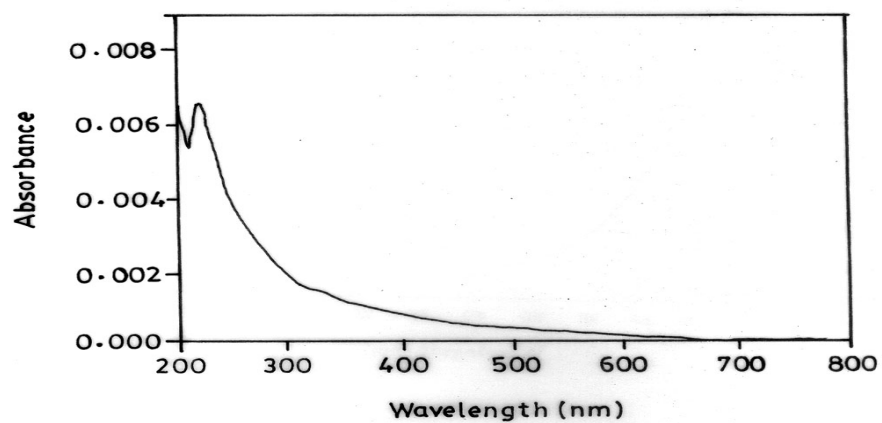


Fig.-3: Optical absorption spectrum of TGZC

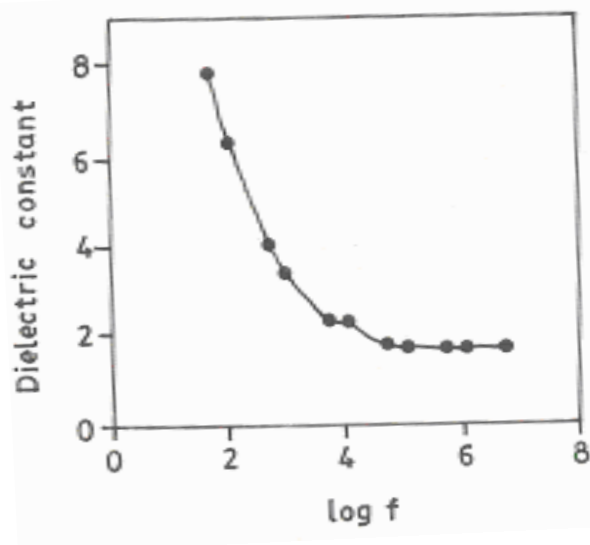


Fig.-4: Frequency Vs dielectric constant

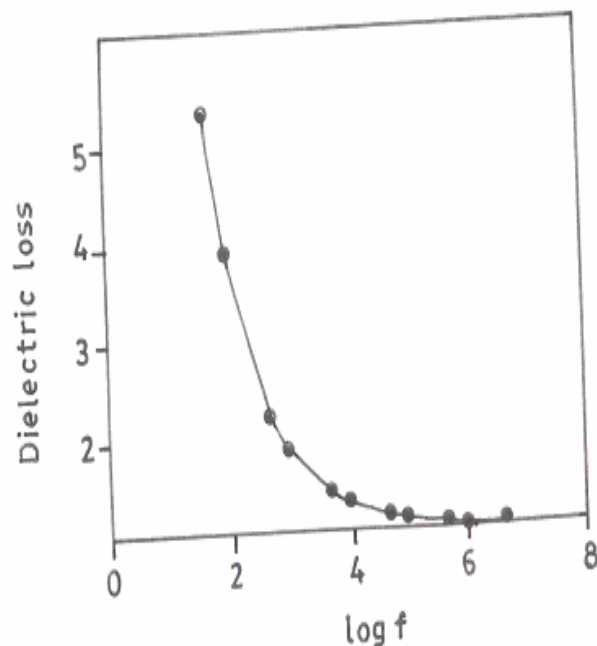


Fig.-5: Frequency Vs dielectric loss

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