Growth, Structural, Thermal and Dielectric Studies of Glycine Zinc Sulphate Single Crystals

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Abstract **- The nonlinear optical single crystals of glycine zinc sulphate were grown by slow evaporation method from aqueous solution. The title compound was synthesised and purified by repeated recrystallization process. Optically transparent GZS single crystals with dimensions upto 7 x 3 x 5 mm^3 were obtained in about four weeks. The crystal system has been identified and lattice dimensions are calculated from the powder x-ray diffraction analysis. Its optical behaviour has been analysed by UV-Vis studies. It was found that there is no absorption in the entire visible region and therefore GZS can be used potential material for SHG. Thermal properties of the crystal were investigated by TGA/DTA analysis.**

Keywords **- GZS; TGA/DTA; NLO; dielectric**

I. INTRODUCTION

The growth of new semiorganic single crystals made by researches in recent times increased significantly because of their potential applications in the nonlinear optical field. The material selection for growing semi organic single crystals depends on the physical and properties of crystals and the prospects of their various applications [1]. The main draw back in organic nonlinear optical materials is low mechanical strength and poor physico-chemical stability. To overcome these drawbacks, a combination of organic acids, with inorganic salts and metal organic co-ordination compounds are used to grow semi-organic nonlinear optical crystals which makes the material to be nonlinear and good mechanical strength [2,3] amino acids, specifically are good raw materials to produce semi-organic crystals because of its good optical properties such as optical modulation, optical switching, optical logic, frequency shifting of and optical data storage in telecommunications and signal processing [4,5].

Amino acids are interesting materials for NLO applications. The importance of amino acids for NLO applications lies on the fact that almost all amino acids contain an asymmetric carbon atom and crystallize in non- centro symmetric space group. In solid state amino acids contains a deprotonated carboxylic acid group (COO^-) and protonated amino group (NH^{3+}) [6]. Some amino acids like glycine [7] and L-arginine [8] by itself have higher SHG conversion efficiency. The addition of amino acids of glycine exists as a Zwitterimic nature of favouring crystal hardness with metal complexes may produce modification or changes in the lattices or crystal behaviours. In the formation of semi-organic hybrids the weak forces of organic solids are replaced by stronger ionic forces forming a complex new class of semi organic materials suitable for electronic industries. In this present work the growth of glycine zinc sulphate solution from aqeous solution by slow evaporation method and they characterised by powder X-ray diffraction, infrared spectroscopy, UV-Vis NIR optical absorption transmission spectrum, TGA/DTA analysis and SHG efficiency analysis.

II. EXPERIMENT ANALYSIS

Synthesis and Growth

Commercially available AR grade (Merck) chemicals were used as a starting material. The synthesis was carried out by dissolving glycine and zinc sulphate in this stoichiometric ratio using double distilled water as a solvent.

$$ZnSO_4.H_2O + CH_2NH_2COOH \longrightarrow Zn[CH_2NH_2COOH]SO_4.H_2O$$

The homogenous solution was filtered in a clear beaker covered with a clear filtered paper and kept aside to avoid mechanical disturbance. The filtered solution was allowed to grow at room temperature. Figure 1 shows the solubility curve of GZS. Supersaturated solution of GZS was prepared in accordance with the solubility data. Good optical grade crystals of dimension upto 7 x 3 x 5 mm^3 were conveniently grown in a period of 30 days. Figure 2 shows the photograph of GZS single crystal grown from its aqueous solution by solvent evaporation technique.

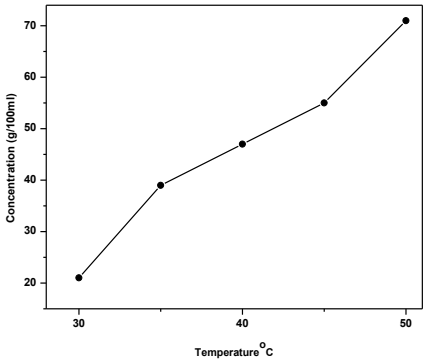

Figure 1 The solubility curve of GZS

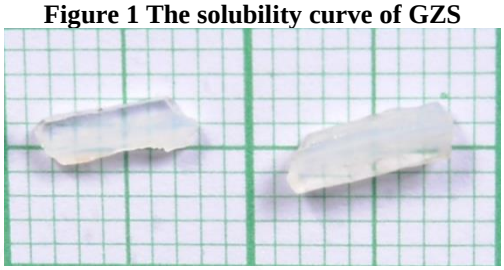

Figure 2 Photograph of as grown GZS single crystal

III. RESULTS AND DISCUSSION

X-ray diffraction analysis

Powder X-ray diffraction studies were used for the identification of crystallinity of the grown crystal. The K_α radiation (λ= 1.5418Å) from a copper target were used the sample was scanned in the range between 10°-40°. Fig.2 represents the powder indexed diffractogram for the grown crystal of GZS. The sharp intensity peaks found in spectra shows good crystalline nature and purity of the grown crystal. It is found that the crystal belongs to the Orthorhombic with $Pca2_1$ space group.

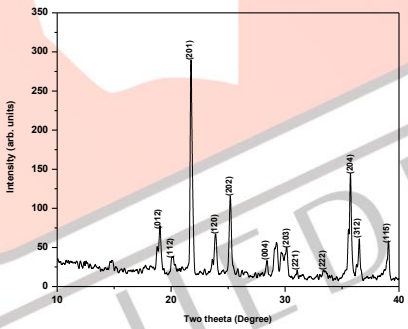

Figure 3 Powder XRD spectrum of GZS crystal

SHG efficiency studies

The nonlinear property of the grown GZS crystal was tested by passing the output of Nd: YAG Quanta ray laser emitting 1064 nm, generating about 6 mJ/pulse. For a laser input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 91.66 mW and 278.32 mW, respectively were obtained for KDP and GZS samples. Thus, the SHG efficiency of GZS is three times higher than KDP.

Optical absorption spectrum

The selective electronic absorption spectrum of GZS crystal was recorded in the range 190-1100 nm. Optical absorption spectrum of grown crystal of GZS is shown in figure 4. From the spectrum, it is evident that the GZS crystal has UV cut off around 240 nm which is sufficient for SHG laser radiation of 1064nm. The crystal has wide transparency window between 240nm to 1100nm which is one of the key requirements for having efficient NLO character. There was no absorption from 240nm-1100nm which clearly shows that the crystal possess good optical transparency for SHG. To estimate the direct band gap value a graph has been plotted between photon energy and ($\alpha h\nu^2$). Where α is the absorption co-efficient and h is the energy of the incident photon from the figure 5, the band gap energy is found to be 4.55.

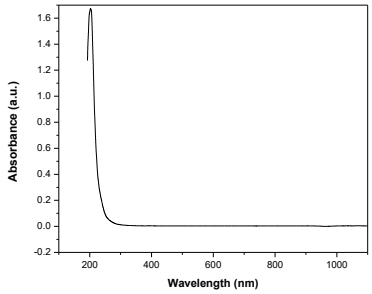

Figure 4 Optical absorption spectrum of GZS crystal

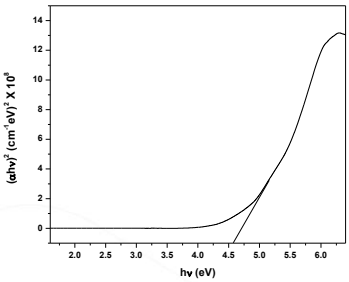

Figure 5 Optical band gap of GZS crystal

Thermogravimetric analysis

Thermo gravimetric (TG) and differential thermal analyses (DTA) for GZS were carried out by NETZSCH STA 409C thermal analyzer. The TGA and DTA traces are shown in Figure 6. TGA curve shows three stages. The first stage occur in the temperature range of 181 – 315 °C with a weight loss of 51.45 % which may be attributed to loss of lattice water and the second stage occurs in the temperature range 315 – 520 °C with a weight loss of 17.4%. The sample then starts the third dissociation at 520 °C. A residue of 16.36 % remains after 910 °C. The TGA trace clearly indicates that the compound is thermal stable upto 181°C. The DTA peaks matches with the weight losses observed in TGA.

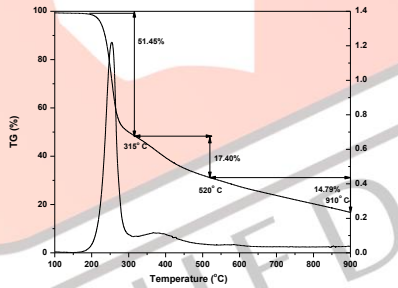

Figure 6 TGA and DTA curve of GZS crystal

Dielectric studies

Dielectric constant and dielectric loss measurements were performed on a crystal of GZS using an LCR meter in the frequency range 50Hz to 5MHz. Capacitance of the sample was measured by varying the frequency from 50Hz to 5MHz. The dielectric constants were calculated based on observed capacitance area and sample thickness. Figure 7 shows a plot of dielectric constant vs log frequency at room temperature. The dielectric constant has high values in the lower frequency region and then decreases with applied frequency. The value of the dielectric constant at low frequencies may be due to the contribution of all four polarizations, namely, dipolar electronic, ionic and space charge polarizations which depend on the frequencies. The variation of dielectric loss with frequency at room temperature is shown in figure 8 at room temperature the dielectric loss decreases with frequency. The low value of dielectric loss at high frequency suggests that the sample possess enhanced optical quality with fewer defects and this parameter is of vital importance for NLO materials in their applications [9].

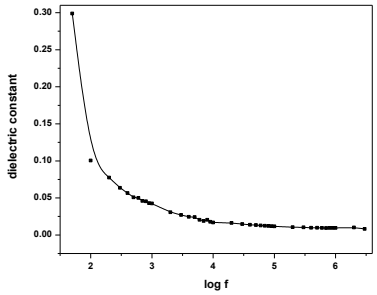

Figure 6 Variation of dielectric constant of GZS single crystal with log frequency

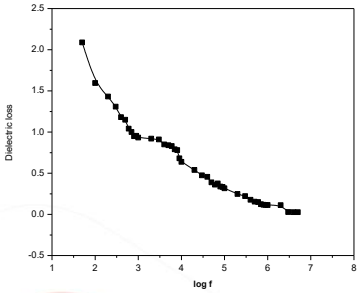

Figure 7 Variation of dielectric loss of GZS single crystal with log frequency

IV. CONCLUSION

Good optical quality GZS single crystals of dimension up to 7 x 3 x 5 mm^3 have been grown successfully by evaporation technique. The solubility curves of GZS in different temperatures have been measured gravimetrically. Molecular formula and the structure of the crystal are confirmed by powder X-ray analysis and it is found that the crystal belongs to the Orthorhombic with $Pca2_1$ space group. Density functional theory (DFT) computations using (B3LYP) level with 6-31G (d, p) basis set gives optimized structure parameters of GZS molecule. The electric dipole moments and the first hyperpolarizabilities of the compound studied have been calculated by B3LYP method. The results of theoretical calculations are substantiated with powder SHG results. The output of green light confirmed its non-centrosymmetric structure and it exhibits powder SHG efficiencies 3 times higher than potassium dihydrogen phosphate (KDP). Molecular energy gap of GZS was found as 0.106 a.u, by HOMO-LUMO analysis. Optical absorption spectrum was recorded for the given crystal. Mechanical strength, Thermal stability and SHG studies were carried out.

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