Investigation on Physical Properties of Semiorganic Nonlinear Optical Glycine Zinc Sulfate Single Crystal

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Nonlinear optical single crystals of Glycine Zinc Sulfate (GZS) were grown by slow evaporation technique. Single crystal X-ray diffraction analysis revealed the crystal system and lattice parameter values. Powder X-ray diffraction analyses have been carried out and the diffraction patterns have been indexed. The optical properties of the crystals were determined using UV-Visible spectroscopy. Optical constants such as band gap, refractive index, extinction coefficient and electric susceptibility were determined from UV-Visible spectroscopy. The refractive index was determined using Brewster's angle method. Hardness of the GZS crystal was estimated by Vicker's hardness studies. Second Harmonic Generation (SHG) of GZS crystal was investigated by Kurtz powder technique. The dielectric constant and dielectric loss measurements were carried out for different temperatures and frequencies. The photoconductivity studies confirm that the grown crystal has negative photoconductivity nature. In order to investigate the growth mechanism and surface features, etching studies are carried out for the crystal.

Keywords: single X-ray diffraction, UV-Vis-NIR spectrophotometer, NLO, SHG, dielectric constant, dielectric loss studies

1. Introduction

The growth of single crystals has been studied for hundreds of years in order to produce materials of aesthetic value such as gemstones. Many also believed that gemstones had medical or mystical virtues, as well, which further added to their value. More recently, crystals of scientific or technological importance such as semiconductors or laser materials have received the greatest attention and have formed the basis of new industries. Today, single crystals and epitaxial layers are the heart of computers, communication systems and medical devices¹. Enormous effort has been put on the growth and perfection of crystals of different materials with regard to the application. Organic crystals have received very little attention for industrial applications, because of the poor mechanical property and chemical instability. Organic NLO materials are attracting a great deal of attention, as they have large optical susceptibilities, inherent ultra fast response times and high optical thresholds for laser power compared with inorganic materials². The rapid development of optical communication systems has led to a demand for nonlinear optical materials of high structural and optical quality. Also, the development of highly efficient nonlinear optical materials for opto-electronic throughput and optical data storage has been the subject of intense research activity the world, over the past two decades^{3,4}. Some organic compounds exhibit high nonlinear optical response and in many cases, orders of magnitude larger than widely known inorganic materials.

In recent years there has been increased need of organic materials for nonlinear optical (NLO) applications because of their usage in devices such as second harmonic generators, electro-optic modulators, frequency conversion, etc.⁵ The development in the growth of highly efficient NLO crystals for visible and ultraviolet regions is important for both Laser spectroscopy and laser processing⁶. They have wide applications in the field of telecommunication and optical information storage devices⁷. In view of this, it is desirable to search for new NLO crystals, which possess shorter cut off wavelength, sufficiently large nonlinear coefficient, transparency in UV region and high damage threshold. Organic crystals have parameters competitive with widely used crystals of KDP type⁷. The present investigation deal with the growth of glycine zinc sulfate single crystal was grown by slow evaporation technique. The grown crystals were characterized by single crystal and powder X-ray diffraction analysis, UV analysis, microhardness, dielectric, SHG, photoconductivity measurements and etching studies. The results of these studies have been discussed in this paper in detail.

2. Growth of Glycine Zinc Sulfate

Glycine zinc sulfate was synthesized by dissolving glycine and zinc sulfate in equimolar ratio (1:1) in double distilled water. The solution was stirred continuously using a magnetic stirrer. The obtained saturated solution was further purified

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and allowed to evaporate at higher temperature. Synthesized material was purified by repeated recrystallization process. Tiny seed crystals with good transparency were obtained due to spontaneous nucleation. Among them, a 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 the collection of monomers at the seed crystal sites from the mother solution, after the nucleation and growth processes were completed. GZS crystal of dimension about $8 \times 5 \times 8 \text{ mm}^3$ was harvested in a growth period of twenty four days by slow evaporation of the solvent. The photograph of the grown GZS crystal is shown in Figure 1.

3. Characterization Techniques

The grown crystal was characterized by the following techniques

3.1. Single crystal X-ray diffraction

Single crystal X-ray diffraction analysis for the grown crystals has been carried out to identify the cell parameters using an ENRAF NONIUS CAD 4 automatic X-ray diffractometer. X-ray powder diffraction is a non-destructive technique widely applied for the characterization of crystalline materials. Since the crystal was transparent, the single crystallinity was studied with Leica polarizing microscope. Single crystal of suitable size was cut and mounted on the X-ray goniometer. The crystal is mounted on a thin glass fiber that is attached to a brass pin and mounted on a goniometer head. Adjustment of the goniometer head in the X, Y and Z orthogonal directions allows centering of the crystal in the X-ray beam. The unit cell dimensions (a , b , c , α , β , γ) can be determined from the accurately measured 2θ values.

3.2. UV - Visible spectroscopy

Ultraviolet-visible spectroscopy (UV/ VIS) is also known as electronic spectroscopy. Ultraviolet (200-400 nm) and visible (400-800 nm) absorption spectroscopy is the measurement of the attenuation of a beam of light after it passes through a sample or after reflection from a sample surface. Sample was typically placed in a transparent cell, known as a cuvette. The crystal holders (cuvettes) are the

rectangular shaped quartz or glass cells of about 10 mm path length. The transmitted light radiation is received at the photomultiplier tube alternately from the reference and the sample beams. A photoelectric signal timing system is synchronized with the alternate pulses which permits the comparison of signals from the two beams. The difference between the two signals is recorded with the help of a motor driven pen or is interfaced with a PC-XT and stored there for easy reference. Samples in solid form, powder, pellets are dissolved in suitable solvents to form the contents of the sample cell and the solvents are taken in the reference cell. In the present work, the UV-Visible transmission spectrum was recorded using PERKIN ELMER LAMDA Instrument.

3.3. Refractive index measurement

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

3.4. NLO Test – Kurtz powder SHG method

In order to confirm the NLO property, the grown specimen was subjected to Kurtz powder test using a Q-switched, mode locked Nd:YAG laser of 106.4 nm and pulse width of 8 ns (spot radius of 1 mm) on the powder of crystal. The input laser beam was directed on the as grown crystal powder to get maximum powder SHG. The emitted light passed through an IR filter was measured by means of a photo multiplier tube and oscilloscope assembly. The green light intensity was registered by a photomultiplier tube and converted into an electrical signal. This signal was displayed on the oscilloscope screen. The crystal was replaced by potassium dihydrogen orthophosphate (KDP) and the signal was displayed in the oscilloscope screen.

3.5. Microhardness test

Microhardness measurement is a general microprobe technique for assessing the bond strength, apart being a measure of bulk strength. The crystal slices are well polished with a thickness variation less than 10 μm to avoid the surface defects, which influence the hardness value strongly. The microhardness characterization is extremely important as far as the fabrication of devices is concerned. Hardness of a material is the measure of resistance when it offers to local deformation. Indentations were made on (1 0 1) plane of GZS crystal using Shimadzu HMV-2000 fitted with Vickers pyramidal indenter. The load P is varied between 20-100 g and the time of indentation is kept constant as 15 seconds for all trials. The diagonal lengths of indentation are measured.

3.6. Dielectric studies

Good quality single crystals of GZS having regular faces were selected for dielectric measurements. The crystal was prepared from large crystals by thinning them to the

Figure 1. Photograph of grown GZS single crystal.

appropriate thickness. Suitably cut and polished GZS crystals (with known dimensions) are subjected to dielectric studies using HIOKI 3532-50 HITESTER LCR meter with a conventional four terminal sample holder. The crystal was prepared and mounted between the copper electrodes. In order to ensure good ohmic contact the sides of the crystal was coated with silver. The experiment was carried out for frequencies varying from 50 Hz to 5 MHz and for different temperatures.

3.7. Photoconductivity studies

The GZS crystal is well-polished and surfaces are cleaned with acetone. This is attached to a microscope slide and two electrodes of thin copper wire (0.14 cm diameter) are fixed onto the specimen at some distance apart using silver paint. A DC power supply, a Keithley 485 picoammeter and the prepared crystal are connected in series. The crystal was covered with a black cloth and the dark current (I_d) of the crystal was recorded with respect to the different applied voltage. Then crystal was illuminated by the radiation from 100 W halogen lamp containing iodine vapour and tungsten filament and the corresponding photocurrent (I_p) is recorded for the same values of the applied voltage.

3.8. Etching studies

Etching studies have been carried out to understand the growth mechanism and to assess the perfection of the grown crystals. Chemical etching is the oldest, easiest and most widely used method to evaluate the quality of the crystal. Etching is selective dissolution of the crystal which is used to reveal the crystal symmetry and lattice defects. The establishment of the relation between etches pits and the dislocation array present in imperfect crystals by employing the etching technique has turned out to be a powerful tool for the preparation and characterization of single crystals for electronic and optical devices. In the present work, the etching studies were carried out using Carl Zeiss optical microscope (Model Imager AIM).

4. Results and Discussion

4.1. Single-crystal X-Ray diffraction

The lattice parameters were calculated by using least-squares refinement and are found to be: $a = 8.52 \text{ \AA}$, $b = 8.64 \text{ \AA}$, $c = 12.50 \text{ \AA}$. The GZS crystal belongs to orthorhombic system with non-centrosymmetric space group $Pca2_1$. These values are in close agreement with the reported values⁸.

4.2. Powder X-Ray diffraction

X-ray powder diffraction was used to confirm single crystal XRD results. The efforts were made to record the powder XRD pattern of the GZS crystal and index them. The indexed powder XRD pattern of the grown GZS crystal is shown in Figure 2. Powder XRD pattern was recorded by scanning the crystal over the range $10-70^\circ$ at a scan speed of $0.02^\circ/\text{min}$. The appearance of sharp and strong peaks confirms good crystallinity of the grown crystal. From the data, the lattice parameters were calculated as $a = 8.52 \text{ \AA}$, $b = 8.64 \text{ \AA}$, $c = 12.50 \text{ \AA}$. The results agree well with single crystal XRD results and also with the available literature values⁸.

4.3. UV-Vis-NIR spectral analysis

The optical transmission spectrum of GZS single crystal was recorded in the wavelength region 200-1000 nm and it is shown in Figure 3. For optical fabrications, the crystal should be highly transparent in the considered region of wavelength^{9,10}. The favorable transmittance of the crystal in the entire visible region suggests its suitability for second harmonic generation¹¹. The UV absorption edge for the grown crystal was observed to be around 230 nm. The lower cut off wavelength is found to be 230 nm for GZS which is in fairly good agreement with reported value¹². The dependence of optical absorption coefficient on photon energy helps to study the band structure and type of transition of electrons¹³. The optical absorption coefficient (α) was calculated from transmittance using the following relation⁹

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

where T is the transmittance and d is the thickness of the crystal. As a direct band gap material¹⁴, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies $(h\nu)^{[10]}$

Figure 2. Powder X-ray diffraction pattern for GZS crystal.

Figure 3. UV-Vis transmission spectrum of GZS.

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

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 $h\nu$ is shown in Figure 4. E_g is evaluated using the extrapolation of the linear part¹⁴. Using Tauc's plot, the energy gap (E_g) was calculated as 5.40 eV and the large band gap clearly indicates the wide transparency of the crystal. These values are found to agree with the reported values of L-Valine Zinc Hydrochloride single crystal¹⁵. This high band gap value indicates that the grown crystal possesses dielectric behaviour to induce polarization when powerful radiation is incident on the material.

4.3.1. Determination of optical constants

Two of the most important optical properties; refractive index and the extinction coefficient are generally called optical constants. The amount of light that transmits through crystal depends on the amount of the reflection and absorption that takes place along the light path. The optical constants such as the refractive index (n), the real dielectric constant (ϵ_r) and the imaginary part of dielectric constant (ϵ_i) were determined. The extinction coefficient (K) can be obtained from the following Equation 11,

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

The extinction coefficient (K) was found to be 4.15×10^{-6} at $\lambda = 1000$ nm. The transmittance (T) is given by¹³

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

Reflectance (R) in terms of absorption coefficient can be obtained from the above equation¹⁵. Hence,

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

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

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 1.587 at $\lambda = 1000$ nm. From the optical constants, electric susceptibility (χ_c) can be calculated according to the following relation¹⁶

$$\epsilon_r = \epsilon_0 + 4\pi\chi_c = n^2 - k^2 \quad (7)$$

Hence,

$$\chi_c = \frac{n^2 - k^2 - \epsilon_0}{4\pi} \quad (8)$$

where ϵ_0 is the permittivity of free space. The value of electric susceptibility (χ_c) is 0.147 at $\lambda = 1000$ nm. The real part dielectric constant (ϵ_r) and imaginary part dielectric constant (ϵ_i) can be calculated from the following relations¹⁵

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

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

The value of real dielectric (ϵ_r) and imaginary constant (ϵ_i) at $\lambda = 1000$ nm were estimated at 1.523 and 7.802×10^{-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.

4.4. Refractive index measurements

Finely polished crystals of the GZS were used for refractive index measurements. This crystal was cleaved and is placed on a rotating mount at an angle varying from 0 to 90 degrees. He-Ne laser of wavelength 632.8 nm was used as the source. Brewster's angle (θ_p) for GZS was measured to be 57.85 degrees. The refractive index has been calculated using the equation $n = \tan \theta_p$, where θ_p is the polarizing angle and it is found to be 1.591^[17].

4.5. NLO Test – Kurtz powder SHG method

The most widely used technique for confirming the SHG efficiency of NLO materials to identify the materials with non-centrosymmetric crystal structures is the Kurtz Powder technique¹⁸. Fine powders of GZS crystals were exposed under 1064 nm laser beam from a pulsed Nd:YAG laser having a repetition rate of 10 Hz and pulse width of 8 ns to test the second harmonic generation (SHG) efficiency. The SHG efficiency of the GZS crystal was evaluated by taking the microcrystalline powder of KDP as the reference material. The output light was passed through a monochromator which detected green light at 532 nm. This confirms the NLO behaviour of the material. The relative conversion efficiency was calculated from the output power of GZS crystals with

reference to KDP crystals. It is observed that the conversion efficiency of GZS is 1.2 times that of KDP crystal.

4.6. Microhardness studies

Hardness is an important mechanical property. The mechanical characterization of the GZS crystals was carried out by Vickers hardness test at room temperature. Crystals free from cracks with flat and smooth faces were chosen for the static indentation tests. The microhardness measurements were carried out with a load range from 20 to 100 g. Indentations were made on (1 0 1) plane of GZS crystal. The Vickers microhardness number was calculated using the relation,

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

where P is the indenter load and d is the diagonal length of the impression. The Figure 5 shows the variation of P with Vickers hardness number (H_v) for GZS single crystal. It is evident from the plot that Vickers microhardness number increases with increasing applied load. 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 ' H_v ' 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 Figure 6. The value of ' n ' for GZS was found to be 2.35. 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 Onitsch¹⁹, n should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials. From the hardness study, the grown GZS crystal is found to be relatively soft material²⁰.

4.7. Dielectric studies

Dielectric properties are related with the electric field distribution within solid materials. Dielectric studies of the grown GZS crystal has been carried out at various frequencies and temperatures. The behaviour of the crystal under electric field has close relationship with the laser light irradiation and hence the power dissipation factor can be studied from the dielectric studies. The plots of dielectric constant and dielectric loss with frequency for various temperatures are shown in Figures 7 and 8. The dielectric constant is high in the lower frequency region and variation of dielectric constant with $\log f$ decreases with an increase in frequency. The very high value of dielectric constant at low frequencies may be due to the presence of all the four components namely, space charge, orientational, electronic and ionic polarizations. The high value of dielectric constant at low frequency may be due to presence of all polarizations and its low value at higher frequencies may be due to the significant loss of all

polarizations gradually²¹. In accordance with Miller rule, the lower value of dielectric constant is a suitable parameter for the enhancement of SHG efficiency. The variation of dielectric constant with temperature is generally attributed to

Figure 5. Variation of H_v with load P .

Figure 6. Plot of $\log d$ Vs $\log p$.

Figure 7. Variation of dielectric constant with log frequency.

the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects.

The dielectric loss was also studied as a function of frequency for different temperatures and is shown in Figure 8. The low dielectric loss at high frequencies for the given crystal indicates very high purity of the material. This parameter is of vital importance for nonlinear optical materials in their applications. These curves suggest that the dielectric loss is strongly dependent on the frequency of the applied field. The higher values of dielectric loss at low frequencies originate from space charge polarization mechanism and the characteristic of low dielectric loss at high frequencies reveals that the grown crystal possesses relatively high optical quality with low defect density. The behaviour of low dielectric loss with high frequency for the crystal suggests that the crystal possess enhanced optical quality with lesser defects and this parameter plays a vital role for the fabrication of nonlinear optical devices^{22,23}.

4.8. Photoconductivity studies

The field dependent photoconductivity of the crystal was shown in Figure 9. From the figure, photocurrent is found to be less than that of the dark current for all ranges of applied field enunciates negative photoconductivity. The negative photoconductivity in this case may be due to the reduction in the number of charge carriers or their lifetime in the presence of radiation. Decrease in lifetime with illumination, could be due to the trapping process and increase in carrier velocity.

In Stockmann's model, a two level scheme is proposed to explain negative photoconductivity²⁴. The upper energy level is situated between the Fermi level and the conduction band, whereas the other one is located in the neighborhood of the valence band. The lower level has high capture cross-section for electrons from the conduction band and holes from the valence band. As a result, sooner the crystal is kept under exposed light, the recombination of electrons and holes take place, resulting in decrease in the number of mobile charge carriers, giving rise to negative photoconductivity. It is seen from the plots that both I_d and I_p of the crystal increase linearly with applied field. It is observed from the plot that the dark current is always higher than the photocurrent, thus confirming the negative photoconductivity nature of the GZS single crystal²⁵.

4.9. Etching studies

Etching is a technique which is used to reveal the defects in crystals like dislocations, growth bands, twin boundaries, point defects etc. Normally when the crystal is dissolved in the solvent, well defined etch pits are formed. The formation of the etch pits is assumed to be the reverse of growth process²³. The surface of the crystals was polished very well before the etching process. The etching studies were carried out on the GZS crystals in order to reveal the dislocations in the crystal. In the present work, water was used as etchant. The photograph was taken with a maximum etching time of 60 s and is presented in Figure 10. It is observed that etch pits are formed to the etching time of 60 seconds. Further increasing the etching time, the pattern remains the same but the numbers of etch pits decrease. While increasing the etching time observed etch patterns are of well defined shape.

Etch patterns were photographed under an optical microscope in the reflected light and the observed well defined parallel etch pits found on the (1 0 0) plane as shown in Figure 10.

Figure 8. Variation of dielectric loss with log frequency.

Figure 9. Field dependent photoconductivity of grown single crystal.

Figure 10. Etch patterns observed on (1 0 1) plane of GZS.

5. Conclusion

Bulk sized good quality crystals of Glycine Zinc Sulfate (GZS) were grown by slow evaporation technique. Orthorhombic structure of the grown crystal was confirmed by single crystal X-ray diffraction analysis. Powder X-ray diffraction studies confirmed the crystallinity and structure of the grown crystals. The UV-Visible transmission spectrum shows excellent transmission in the entire visible region. The band gap, refractive index, extinction coefficient and electrical susceptibility were calculated to analyze the optical

property. Second Harmonic Generation (SHG) efficiency of the GZS is greater than KDP. The microhardness studies indicate that the Vickers hardness number of the crystal increases with the increase in applied load. The dielectric constant and dielectric loss measurements were carried out at different temperatures and frequencies. The photoconductivity studies confirm that this material has negative photoconductivity nature. The etching studies were carried to study the formation of etch pits in water solvent. This material exhibits NLO behaviour remarkably due to its better optical and dielectric properties.

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