SYNTHESIS, GROWTH AND CHARACTERIZATION OF BISTHIOUREA GLYCINE SODIUM NITRATE CRYSTALS

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Abstract: Single crystals of Bisthiourea Glycine Sodium Nitrate (BTGSN) have been synthesized by using slow evaporation method. The title compound has been grown using water as a solvent. Good quality single crystals were harvested in a period of 25 days. The grown crystals were characterized by employing different techniques such as Single crystal XRD, FTIR, UV-Vis-NIR spectrum, Photoluminescence, TGA/DTA analysis and SHG studies. Single crystal X-ray diffraction analysis reveals that the crystal lattice of BTGSN crystal belongs to monoclinic system. FTIR spectral analysis is used to predict the various functional groups present in the crystal. UV-Vis-NIR spectrum and Photoluminescence studies were carried out to investigate the optical features of the grown crystal. TGA/DTA studies were used to explore the thermal behaviour of the crystal. Kurtz-Perry technique was used to find out the NLO behaviour of the crystal which yielded positive results.

Keywords: Crystal growth, Single Crystal XRD, Optical studies, TGA/DTA, NLO behaviour.

1. Introduction

Advancement in device fabrication for practical use has provoked an interest among crystal growers and researchers due to an increase in demand for NLO materials. The reason for growing NLO crystals is due to their applications such as frequency conversion, optical signal processing, frequency doubling, optical computing, photonics and fibre optic communication [1-4]. Thiourea is a centrosymmetric molecule but when associated with metal ions they become non-centrosymmetric [5] being a key factor for the incorporation of NLO behaviour in the crystal. In the recent past, attempts have been made to combine amino acids with the inorganic salts in order to enhance their physical and chemical properties. Complexes of amino acids with inorganic salts are grown widely as such materials show NLO behaviour. In our present work, glycine the smallest non-polar, non-optical amino acid has been chosen as one of the parent compound. Single crystals such as tris thiourea magnesium zinc sulphate (TTMZS), L-alanine mixed Bisthiourea cadmium chloride (LABTCC), L-Cystein doped zinc thiourea chloride (ZTC), thiourea L-alanine acetate (TLAA), urea and thiourea doped L-arginine trifluoroacetate (LATF) crystals which exhibit similar NLO behaviour has already been reported [6-10]. The grown crystals are thus characterized to investigate their spectroscopic, optical, thermal and nonlinear optical behaviour.

2. Experimental details

BTGSN crystals were synthesised at room temperature by adopting slow evaporation method. The powdered AR grade pure thiourea, glycine and sodium nitrate were taken in the molar ratio 2:1:1 and were dissolved using deionized water. The solution was stirred using a magnetic stirrer for about one hour. The completely dissolved solution was then filtered using a filter paper in order to remove any dust or suspended impurities present in it. The solution thus obtained was covered by polythene paper and minute holes were made on it. The saturated solution was then left undisturbed and inspected regularly until good quality crystals of nominal size were obtained. The crystals were harvested after a period of 25 days. Well defined single crystals of good transparency were collected and are shown in Fig.1.

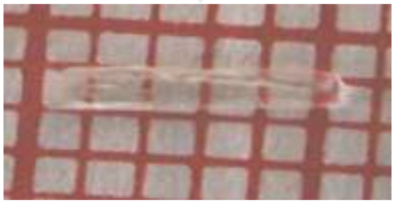

Fig.1. Photograph of the grown crystal

3. Results and Discussion

3.1 Single Crystal X-Ray Diffraction analysis

The grown crystal was subjected to Single Crystal XRD analysis to reveal the crystal system and also to estimate the lattice parameters by employing ENRAF NONIUS CAD 4 X-ray Diffractometer. The Single Crystal XRD data of BTGSN crystal indicates that it crystallizes in monoclinic system. The unit cell parameters are a = 14.33 Å, b = 5.26 Å, c = 9.12 Å, $\alpha = 90^0$, $\beta = 119.10^0$, $\gamma = 90^0$, V = 601 $Å^3$.

3.2 Fourier Transform Infra-Red spectral analysis

The presence of the functional groups has been depicted from the FTIR spectrum. The spectrum was recorded using Perkin Elmer Spectrum-1 Spectrometer between the range 450 – 4000 cm^{-1} and is shown in Fig.2. The peaks at 3251 cm^{-1}, 3008 cm^{-1} and 2898 cm^{-1}

correspond to C-H symmetric stretching vibration. The peaks observed at 3023 cm^{-1} and 2627 cm^{-1} have been assigned to N-H symmetric stretching vibration. The NH_2 symmetric stretching vibration is observed at 2717 cm^{-1}. The characteristic peak at 2012 cm^{-1} occurs due to C-O stretching vibration. Vibrations at 1615 cm^{-1} are attributed to NH_2 bending vibrations. The absorption observed at 1589 cm^{-1} is due to the asymmetric stretching vibration of COO^- molecules. The C-N asymmetric stretching in secondary amines occurs at 1506 cm^{-1}. The presence of C=S asymmetric stretching of thiourea is recorded at 1449 cm^{-1}and 1388 cm^{-1}. The absorption band at 1136 cm^{-1} is attributed to CH_3 bending vibration. A sharp peak at 1116 cm^{-1} corresponds to NH_3 rocking vibrations. A band at 1039 cm^{-1} occurs due to C-N stretching vibrations. Peaks at 937 cm^{-1} and 584 cm^{-1} are due to N-C-N symmetric and asymmetric stretching vibration. Rocking of CH_2 occurs at 891 cm^{-1} and 829 cm^{-1}. A specific sharp peak at 676 cm^{-1} is assigned to COO^- scissoring.

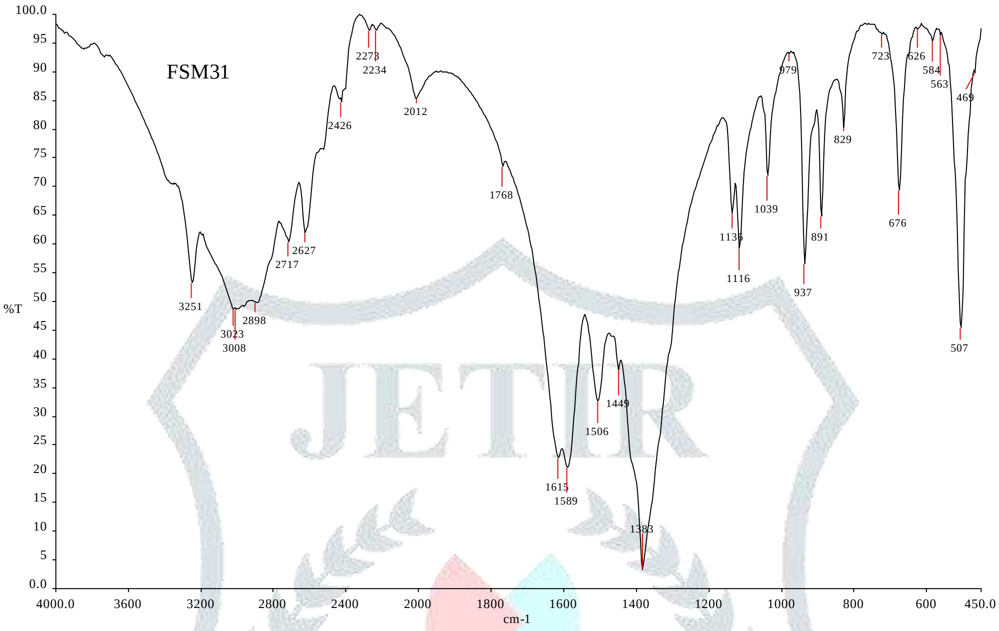

Fig.2. FTIR spectrum of BTGSN crystal

3.3 UV-Visible spectral analysis

The UV-Vis-NIR spectrum for the grown BTGSN crystal was recorded in the wavelength range 200 nm to 1400 nm respectively. Varian Cary 5E UV-Vis-NIR spectrophotometer was used for this study. The UV-Visible transmittance (Fig.3a) and absorbance spectrum (Fig.3b) is given below. From the transmittance spectrum it is observed that the crystal is optically transparent upto 97% and thereby shows uniformity in the entire visible region. The crystal shows no strong absorption in the visible region and therefore its transmittance is close to 100%. The uniform transparency indicates high optical homogeneity and less crystalline defects [11]. The UV cut-off wavelength is found to be 350 nm which is evident from both transmittance and the absorption spectrum.

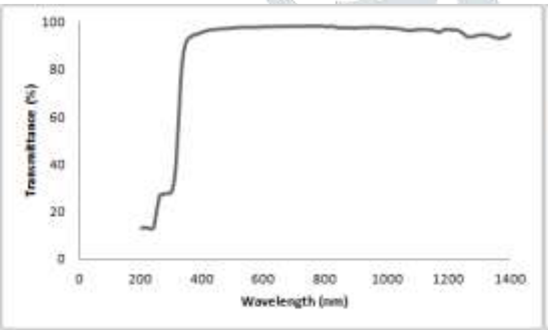

Fig.3a. Transmittance spectrum

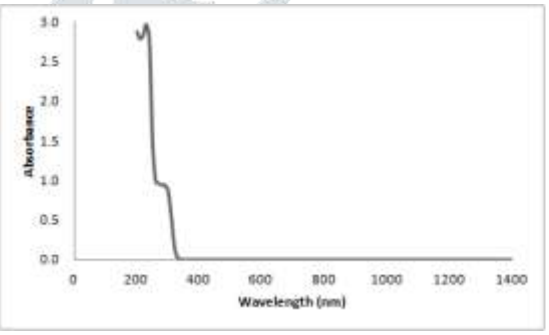

Fig.3b. Absorbance spectrum

3.3.1 Determination of band gap and optical constants

To understand the linear optical properties of the grown crystals, the UV-Vis-NIR spectral study has been employed. The various optical properties such as transmittance, absorbance, refractive index, absorption coefficient, optical conductivity and band gap has been found out and a graph has been plotted for the same. The optical parameters were evaluated using theoretical formula.

The optical absorption coefficient (α) can be obtained from the relation

$$\alpha = \frac{2.303 \times \log\left(\frac{1}{T}\right)}{t}$$

where t is the thickness of the sample and T is the transmittance.

The relation between the optical band gap (E_g), the absorption coefficient and energy (hν) of the incident photon is given by

$$\alpha h\nu = A(h\nu - E_g)^n$$

where E_g is the optical band gap of the crystal, A is a constant, h is the Planck's constant, ν is the frequency of the incident photons. The value of n determines the nature of the electron transition taking place during absorption (n = ½ for allowed direct transition, n = 2 for allowed indirect transition). The band gap value is obtained by the extrapolation of the linear part of the graph drawn between $(\alpha h\nu)^{1/2}$ and hν which is shown in Fig.4. The optical band gap value is found to be 3.56 eV. The high value of band gap and transmittance in the entire visible region makes the crystal suitable for optoelectronics and photonics applications [12-14].

The extinction coefficient (K) can be calculated from the expression

$$K = \frac{\lambda\alpha}{4\pi}$$

The refractive index (n) can be determined from the reflectance (R) data using

$$R = \frac{(n-1)^2}{(n+1)^2}$$

The optical conductivity can be estimated using the following relation

$$\sigma_{op} = \frac{\alpha n C}{4\pi}$$

Fig.5-7 shows the variation of extinction coefficient (K), reflectance (R) and refractive index as a function of wavelength (λ). Fig.8 shows the plot of optical conductivity (σ) verses photon energy (hν). The calculated refractive index (n) is 1.16 at λ = 350 nm for BTGSN crystal.

The electrical susceptibility can be estimated using the expression

$$\chi_c = \frac{n^2 - K^2 - \varepsilon_0}{4\pi}$$

where ε_0 is the permittivity of free space. The electric susceptibility is 0.108 at λ = 350 nm.

The real and imaginary part of the dielectric constant can be calculated using the following relations

$\varepsilon_r = n^2 - K^2$ and $\varepsilon_i = 2nK$

Hence the value of real ε_r and ε_i imaginary dielectric constants at λ = 350 nm are estimated as 1.356 and 2.270×10^{-7} respectively.

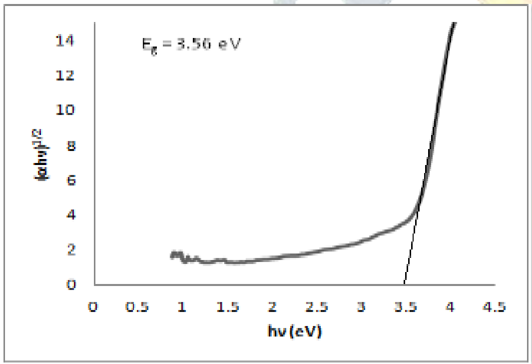

Fig.4. $(\alpha h\nu)^{1/2}$ vs photon energy (hν)

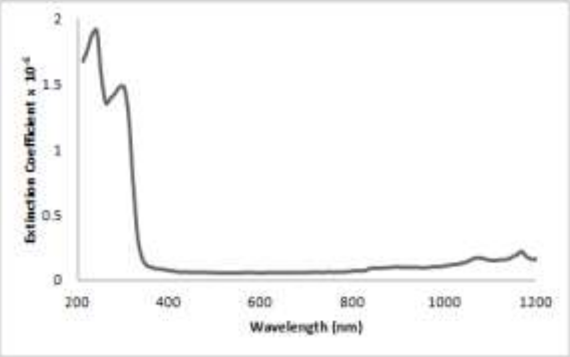

Fig.5. Plot of extinction coefficient (K)

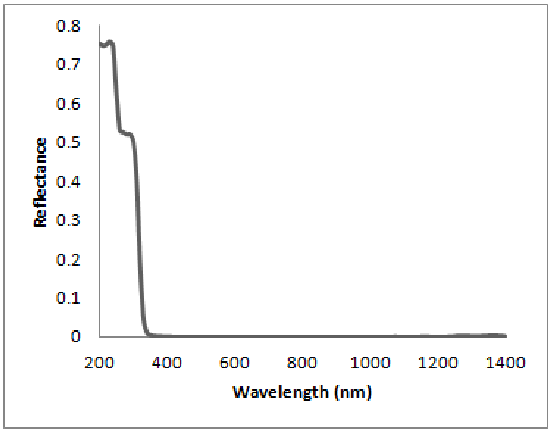

Fig.6. Plot of reflectance (R)

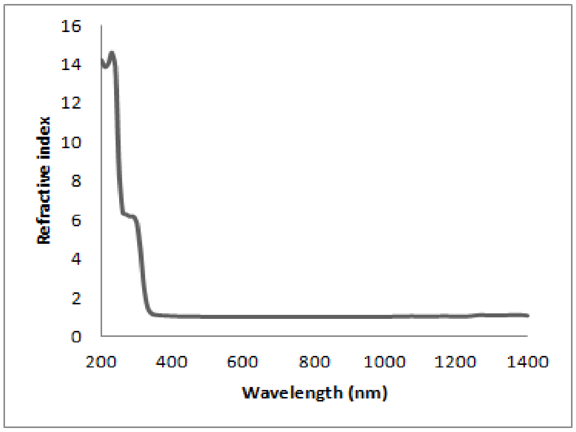

Fig.7. Plot of refractive index (n)

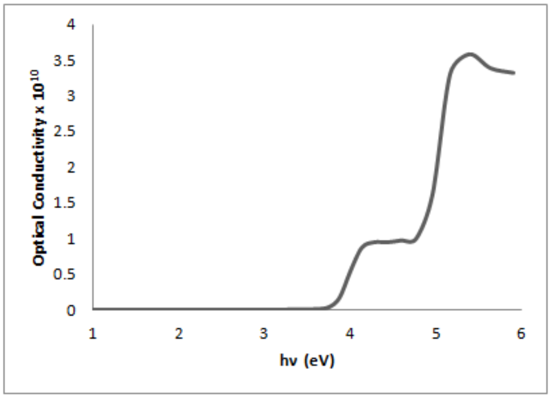

Fig.8. Plot of optical conductivity (σ)

3.4 Photoluminescence Studies

Photoluminescence (PL) is a mechanism which gives the emission of light when photons are excited from ground state. Photoluminescence spectrum was recorded using Jobin Yuon Fluorolog 3 spectrometer in the range 300 – 1000 nm. The beam has been photo-excited and the spectrum with an excitation wavelength of 300 nm is shown in Fig.9. The PL spectrum consists of three emission bands. A prominent violet band was observed at 400 nm and a strong blue band at 469 nm. In addition to that, a weak green band having low intensity was observed at 507 nm. From these wavelengths it is inferred that the BTGSN crystal emits violet and blue fluorescence light when excited at 300 nm.

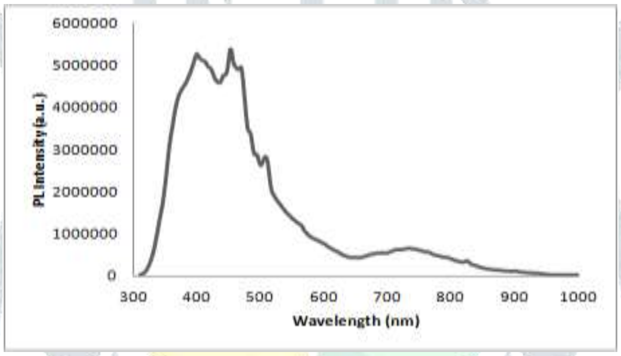

Fig.9. Photoluminescence spectrum

3.5 Thermal analysis

Thermogravimetric analysis (TGA) and Differential thermal analysis (DTA) of BTGSN crystal were carried out using Netzsch STA 409 insturment. An alumina crucible was used for heating the sample and the analysis was carried out in an atmosphere of nitrogen at a heating rate of 20^0C. The initial weight of the sample used was 2.288 mg. From the TGA curve it is inferred that there is a linear behaviour and no significant weight loss takes place upto 110°C. The stable portion of the curve corresponds to a horizontal line. The sample experiences a major weight loss of about 41.5% at around 195°C. From the DTA curve, an endothermic peak is observed at 223.6°C which indicates the melting point of the crystal. The TGA/DTA spectrum is shown in Fig.10.

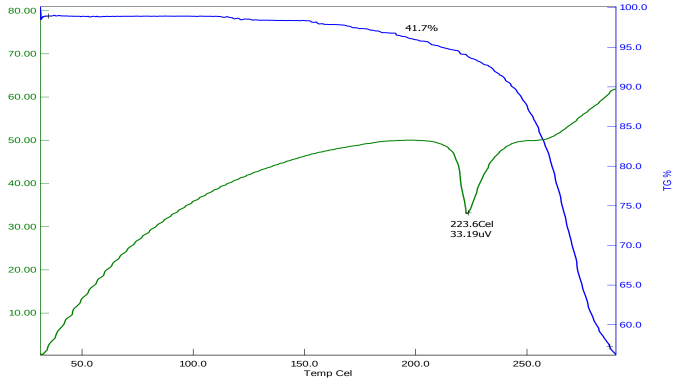

Fig.10. TGA/DTA spectrum

3.6 NLO test

Kurtz Perry powder technique has been employed to carry out the second harmonic generation test [15]. A Q-switched high energy Nd:YAG laser having a wavelength of 1064 nm with a repetition rate of 10 Hz and pulse width of 6 ns has been used for this study. The wavelength of the light emitted from the sample was 532 nm. Thus the emission of sharp green light from the sample confirms the presence of

NLO behaviour. The input energy was measured as 0.70 J and for the same; the sample delivered an output energy of 7.89 mJ whereas the output for the reference KDP material was found to be 8.94 mJ. Hence the relative second harmonic generation efficiency of the BTGSN crystal is 0.88 times more than that of the standard KDP value.

4. Conclusion

A nonlinear optical crystal Bisthiourea glycine sodium nitrate (BTGSN) was synthesized and grown by slow evaporation technique at room temperature. From the single crystal XRD measurements it is seen that the crystal belongs to monoclinic crystal system. The functional groups were identified for the vibrational assignments obtained from the FTIR spectrum analysis. The optical transmittance spectrum was recorded in the range 200 – 1400 nm. From the spectrum, the UV transparency cut off wavelength was found to occur at 350 nm. From the photoluminescence studies it is inferred that the BTGSN crystal emits violet and blue fluorescence light when excited at a wavelength of 300 nm. The melting point of the crystal is assigned as 223.6^0C from the TGA/DTA trace. The NLO property of the BTGSN crystal was inspected using Kurtz Perry second harmonic generation test which showed positive results. Its relative SHG efficiency was found to be 0.88 times that of standard KDP.

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