

Structural, Optical, Mechanical Studies of Guanidine Tartarate Single Crystals

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ABSTRACT

Good quality novel organic Guanidine tartarate has been grown from the aqueous solution by low temperature solution growth method. X-ray diffraction reveals that the crystal crystallises into orthorhombic system with noncentrosymmetric space group $P2_12_12_1$. The functional groups present in the grown crystal were confirmed by Fourier transform infrared spectral analysis. Ultraviolet- visible-near infra-red absorption studies on this crystal reveal that the cutoff region is around 235 nm. The optical band gap of the crystal was found to be 4.07 eV. Photoluminescence studies show that the material emits violet fluorescence. The mechanical behavior of the title compound was analyzed by Vickers's microhardness test.

Keywords: X-ray Diffraction, Band Gap, Guanidine, Photoluminescence.

I. INTRODUCTION

Nonlinear optics is the one of the most active area of interdisciplinary research from the past decades [1-3]. Nonlinear optical crystals very useful in the field of telecommunications, optical storage devices, optoelectronics and photonic applications, etc.,[4]. In order to provide constructive NLO material for optical device applications- material chosen is necessary. Such understanding would help to design better NLO materials, improve device performance and invent novel materials. However this task is very challenging because of the complexity and enormous variety of the compounds like organic and inorganic as well as π - π interactions, hydrogen bond, charge transfer, electron transfer that define their structure of solids[5].

In general, organic materials have a conjugated system caused by nonlinear polarization that occurs because of the interaction of laser light with strong electromagnetic waves. An important aspect of

organic materials is that, increasing the nonlinear polarization of this molecule requires introducing an electron donor or electron acceptor group into the organic molecules [6]. Organic single crystals are chosen for both slow evaporation processes and molecular structures specifically tailored for achieving enhanced solubilities [7]. Attempts have been made to forming acentric crystal structures by hydrogen bonding interactions for second order nonlinear applications [5]. Among the various organic compounds, guanidinium ion can form a wide family of hydrogen-bonded crystals and this cation is relatively simple [8]. Guanidine is a strong base that readily protonated by most organic acids with the resulting guanidinium species being useful for molecular assembly purposes, forming hydrogen bonding associations through its six donor protons[9]. In continuation of our research in Guanidine family single crystals [10-13] we are reporting here about Guanidine tartarate single crystals. The aromatic carboxylic acids used in the present work, Guanidine tartarate crystals have orthorhombic structure with

the space group $P2_12_12_1$. Structural, mechanical and optical properties of Guanidine tartarate of the organic single crystals were reported [14-16]. But there are no systematic studies available on the growth of guanidine tartarate single crystals. Therefore, growth and properties of the Guanidine tartarate single crystals is reported in this article. The crystal system of the grown crystals was confirmed by powder X-ray diffraction (XRD) studies. Fourier Transform Infrared (FT-IR), UV-Visible-NIR, photoluminescence and hardness studies were carried out to analyse the functional groups, optical and mechanical properties of the grown crystals.

II. EXPERIMENTAL PROCEDURE

2.1 Synthesis and crystal growth

Guanidine carbonate 99% pure% and Tartaric acid 99% pure% were taken in equimolar 1:1 ratio in excess of deionized water for the growth. The calculated amount of Guanidine carbonate was dissolved in deionized water for one and half hours to get complete dissolution. Then the appropriate amount of Tartaric acid was added to the solution. The resultant solution was continuously stirred for 3 hours. The homogeneous solution was filtered to keep away from impurities if any and transferred to the beaker. This solution was kept in room temperature and allowed to evaporate slowly. After 15 days, a well-developed and optically transparent single crystal with the maximum dimension of $15 \times 7 \times 7 \text{ mm}^3$ was harvested. The grown crystals were tested by various techniques and found that they are Guanidine tartarate single crystals and the photograph of as grown single crystals is shown in the inset of Figure 1



Figure 1. As grown Guanidine Tartarate single crystals

2.2 Characterization

The powder X-ray diffraction pattern was recorded by using X- pert pro diffractometer with a monochromatic $\text{Cu K}\alpha$ radiation ($\lambda=1.54060 \text{ \AA}$). The FTIR spectrum was recorded in the range 400 cm^{-1} - 4000 cm^{-1} using a Bruker IFS-66 v spectrometer. The optical transmission spectrum of the grown crystal was recorded in the range of 190-1000 nm using Shimadzu 1601UV-Vis spectrophotometer. The Varian Cary Eclipse Photo Luminescence Spectrophotometer, 450W high pressure xenon lamp was used to measure the PL spectrum. The microhardness was determined using Shimadzu HMV-2T Vicker's Tester.

III. RESULTS AND DISCUSSION

3.1 PXRD analysis

The well ground powder of the grown samples of grown crystals was subjected to powder X-ray diffraction (PXRD) analysis. The data have been collected at 298 K between 10° and 80° of diffraction angles with the source wavelength of 1.54 \AA . The step size of 2θ and the scan step time were fixed as 0.017° and 10.325 seconds respectively. The sharp diffraction peaks have been observed in the XRD pattern which ensures the good crystalline nature of the grown samples. The d-spacing of the diffraction peaks were calculated using the 2θ value. The diffraction peaks corresponding to different crystal planes were indexed by using the 2θ and d-spacing for the obtained crystal system in the single crystal x-ray diffraction study. The indexed powder X-ray diffraction (PXRD) pattern of the grown crystal is shown in Figure 2. It is observed that the powder diffraction pattern is reasonably coinciding with the previously reported crystal [16].

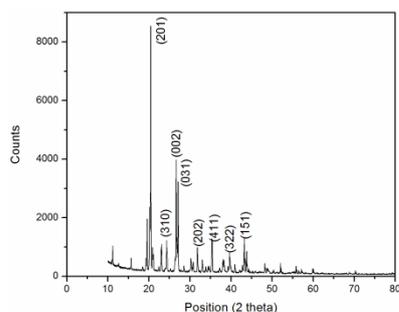


Figure 2. PXRD graph of Guanidine tartarate single crystals

3.2 FTIR analysis

Fourier transform infrared analysis was carried out for the grown Guanidine tartarate crystal to find the functional groups of the crystal. A fine powdered sample of Guanidine tartarate was used in the FT-IR spectral analysis. The absorption due to various functional groups is shown in Fig. 3. The recorded IR spectrum was compared with the standard spectra of the functional groups [17]. The presence of Guanidine is evident from the FTIR spectrum that the asymmetric and symmetric stretching vibrations of N H groupings are present at 3363 cm^{-1} . The band at 1570 cm^{-1} is associated with C N vibration. The N H wagging frequency is assigned to the peaks at 700 cm^{-1} . The very strong peak observed at 1667 cm^{-1} indicates the presence of C O. The weak peak at 1385 cm^{-1} is due to the combination of C-O stretching and O—H deformation. C-H stretching observed at 1123 cm^{-1} . This confirms the presence of free carboxylate anion where in the negative charge is localized on the oxygen atoms in carboxylate anion. The FTIR spectrum confirms the presence of Guanidine Tartarate compounds by the above vibration modes.

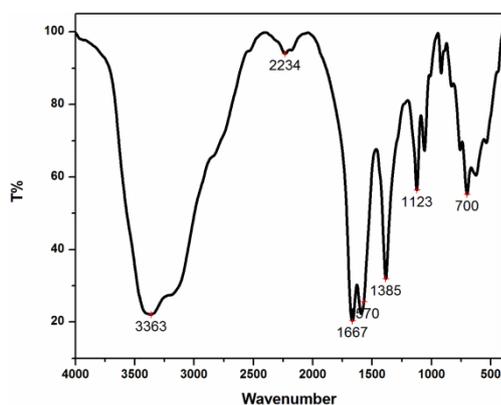


Figure 3. FTIR spectrum of Guanidine Tartarate single crystals

3.3 Optical characterization

3.3.1 Optical absorption studies

UV-visible spectral study is a valuable tool to determine the transparency, which is an important condition for a material to be optically active. Fig.4 shows the UV-vis absorption spectrum of Guanidine tartarate crystal. Here, clearly no absorbance due to electronic transitions is indicated. UV- cut off wavelength is 235 nm. It may be noted that less absorbance in the entire visible region is an essential condition for non-linear optical (NLO) applications [16].

3.3.2 Determination of optical band gap and optical conductivity

To study the band structure and the electrons transition of the material Guanidine tartarate crystal has been taken for determination of optical absorption co-efficient (α) with the photon energy (E).

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

T- transmittance of the crystal, t- thickness of the crystal. The optical band gap (E_g) of Guanidine Tartarate crystal has been calculated using the formula [18]. $\alpha h\nu = A(h\nu - E_g)^n$

A-Constant, E_g - optical band gap, h- Planck's constant, ν - frequency of the incident photons.

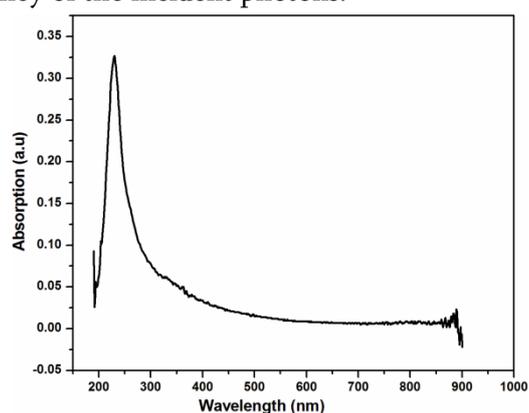


Figure 4. Uv Absorption spectrum of Guanidine tartarate single crystals

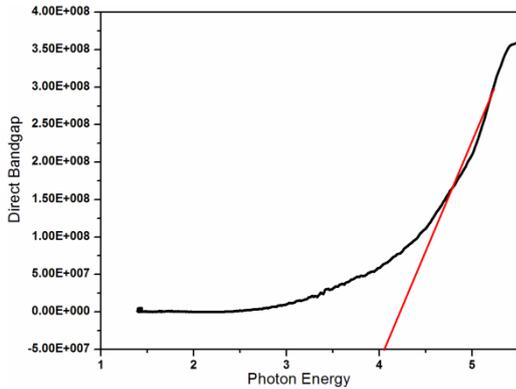


Figure 5. Band gap Vs Energy spectrum of Guanidine tartarate single crystals

$n=1/2$ for direct allowed transition. The value of energy band gap is calculated from the graph drawn between $(\alpha h\nu)^2$ versus energy axis $(h\nu)$ as shown in Fig. 5. The energy band gap is figured out by extrapolating the linear part from the maximum absorption end to the photon energy axis. The intersecting point on energy axis is band gap energy of Guanidine tartarate crystal. The energy band gap of Guanidine tartarate crystal has been found to be 4.07eV. The colourless nature of the title compound shows its high transmission in the entire UV-VIS—NIR region and the obtained values are in well agreed with the reported values [22]. The band gap value of Guanidine tartarate crystal could be used in optical devices like optical switching and electro optic modulations. Extinction coefficient is a measure of the rate of loss of electromagnetic radiation through scattering and absorption for Guanidine tartarate crystal per unit thickness. Extinction value (K) has been calculated using the following equation $K=\lambda\alpha/4\pi$, The extinction value of Guanidine tartarate crystal is decreasing with respect to wavelength as shown in Fig. 6. Optical conductivity of the title compound is measured using the equation $\alpha nc/4\pi$, where α is absorption coefficient, n is linear refractive index and c is speed of light in vacuum [19]. The optical conductivity of the Guanidine tartarate crystal is varying with respect to increasing wavelength (nm) as shown in Fig. 7. It's found that extinction coefficient almost remains constant for incident photon energy of 2 eV to 7 eV and Variation of optical conductivity of the material with incident photon energy is analysed from Figure

8. The high optical conductivity confirms the high photo response nature of the material.

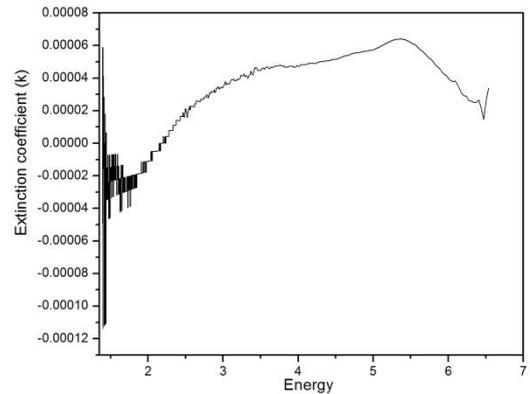


Figure 6: Energy Vs extinction coefficient spectrum of Guanidine tartarate single crystals

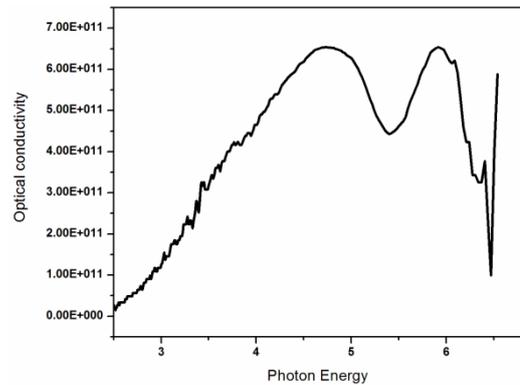


Figure 7. Energy Vs Optical conductivity of Guanidine tartarate single crystals

3.3.3Photoluminescence (PL) studies

The PL intensity is most probably dependent on the crystallinity and structural perfection of the title compound. Radiative recombination of the grown crystal is achieved using PL spectrum by the different energy states available between the valence band and conduction band [20]. The Photoluminescence (PL) spectrum of Guanidine tartarate crystal at room temperature is shown in Fig.8. PL spectrum was recorded in the range of 400-750nm and 390 nm input excitation wavelength was given. The sharp green fluorescence spectrum excitation peak of high intensity was observed at 502.04nm.

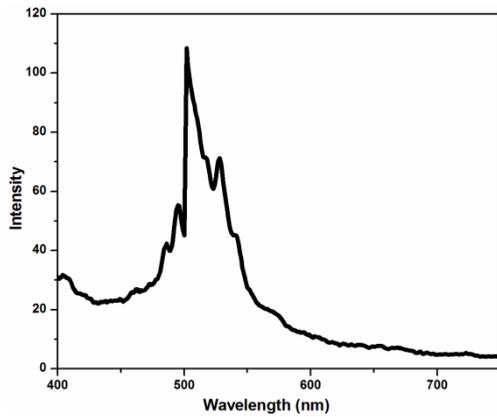


Figure 8: Photoluminescence spectrum of Guanidine tartarate single crystals

3.4 Microhardness studies

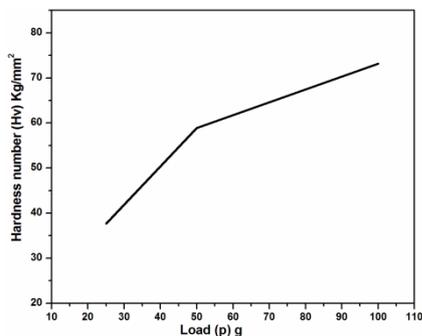


Figure 9. Load Vs Hardness graph of Guanidine tartarate single crystals

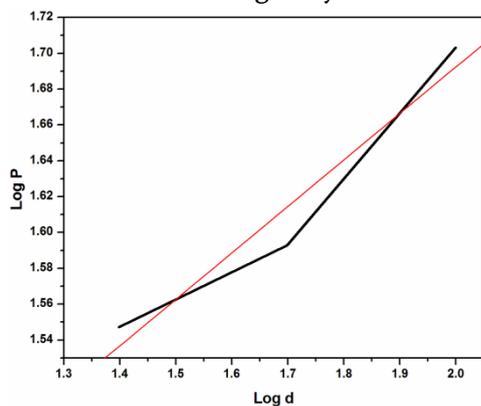


Figure 10. Log d Vs Log P graph of Guanidine tartarate single crystals

The polished Guanidine tartarate crystal has been chosen for Vickers micro hardness. For the static indentation test, loads varying from 25 to 100 g were applied on the grown crystal using Vickers diamond pyramid indenter connected to an incident ray microscope. For each load P , an average of two impressions were recorded and the average of diagonal lengths (d) of the indentation mark after

unloading was measured using a calibrated micrometer attached to the eyepiece of the microscope. The Vickers micro hardness was calculated using the general formula,

$$H_v = 1.8544 P/d^2 \text{ kg/mm}^2$$

Where, P – applied load in kg, d – diagonal length of the indentation in mm. The estimation of error in hardness value H_v can be calculated using Figure 9 shows the graph of Load Vs H_v . The hardness test could not be carried out above 100 g because crack initiation and materials chipping become significant beyond this load. The hardness of the material is found to be increases with increase in the applied indentation load. The observed increase in hardness with increase in load is usually termed as reverse indentation size effect [21]. Figure 10 shows the Log d Vs Log P used to determine the work hardening coefficient (n). The work hardening coefficient $n=3$ (n should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials) was calculated from the Mayer's relation $P=Kd^n$. Where k is the material constant, d is indentation diagonal length and ' n ' is Meyer's index. It implies that Guanidine tartarate crystal belongs to the soft material category [22]. The toughness of the material can be determined by using fracture toughness (K_c). It determines how much fracture stress is applied under uniform loading and is given by a relation [23]

$$K_c = P/\beta_0 c^{3/2} \text{ for } c \geq d/2$$

Where, β_0 is a constant that depends upon the indentation geometry. For Vickers indenter β_0 is equal to 7. For the title compound the cracks are varying from 8.42-1.5(MNm^{3/2}) in the load range 0.245-0.98N. Brittleness is an important property that affects the mechanical behavior of a material and gives an idea about the fracture induced in a material without any appreciable deformation. The value of brittleness index B_i is computed using relation, $B_i = H_v / K_c$. It varies from 2.89 to 0.98x10² m^{-1/2}.

IV. CONCLUSION

The guanidine tartarate crystal has been grown by slow evaporation method at room temperature. The crystalline nature of the grown crystals was confirmed by the powder XRD studies. FTIR spectral analysis confirmed the presence of functional groups in the crystals. From the UV-Visible spectrum of the Guanidine tartarate crystal shows low absorbance with cutoff 235 nm in the visible region and shows low absorbance in the entire near IR region. The optimum band gap (E_g) of the grown crystal is determined from optical absorption studies is found to be 4.07 eV. The PL spectrum shows the Green emission in the crystal. The microhardness studies confirmed that the Guanidine tartarate crystal exhibit improved mechanical behavior than and belongs to a soft material category and suggests the suitability of material in device fabrication. Thus, the characterizations support the basic and complete suitability of the title compound for NLO applications.

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