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Structural, Growth and Optical Characterization of Guanidinium Sulphanilate (GSA) Single Crystal

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Guanidine Sulphanilate (GSA) single crystal was grown by slow evaporation growth method. Single crystal X-ray diffraction studies show that the crystal grows in a centro symmetric monoclinic system and its space group is P21/c. Optical studies were carried out using UV visible spectroscopy and the grown crystal shows the the lower cutoff wavelength of 220 nm. Photoluminescence studies show that GSA crystals have good luminescence properties. Laser damage threshold was found to be 0.24GW/cm^2. Nonlinear optical studies show green light emission.

Keywords: Crystal Growth, Hydrogen bond, GSA, Optical, Structure.

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Introduction

Now a days organic nonlinear optical (NLO) materials have emerged as a potential candidate due to their optical applications in communication, computing, laser remote sensing, colour display, optical switching etc. [1-4]. The amazing properties of organic materials are valued for their versatility and synthetic flexibility [5]. Guanidine is one such important material which is a strong base and has six potential giver destinations for hydrogen holding intelligent [6]. In this way, guanidine cations are promptly protonated by most natural and inorganic acids. Sulfamic acid has many applications in the production of organic dyes [7]. It has a zwitterionic structure and contains NH_{3+} and SO_3- groups [8]. Additionally, sulfonamides and their complexes are widely used as diuretic, antiglaucoma or antiepileptic drugs. [9-10]. In the context of NLO many organic molecules can increase the molecular hyper polarizability and are able to manipulate photonic signal efficiency [11]. Owing to the applicability of sulphanilic acids and the existence of zwitter ionic groups it can be a potential material to manipulate optical signal efficiency through structural modifications. Therefore, an attempt has been made to grow single crystals by combining sulphanilic with guanidinium groups. Many potential guanidine based organic materials with high NLO efficiency have been reported [12-15]. Here we report the synthesis, structural, linear, nonlinear optical property and laser damage threshold behaviour of guanidinium sulphanilate single crystal.

I. Experimental Details

1.1. Material Synthesis and Growth

Guanidinesulphanilate is made from AR grade guanidine carbonate and sulphanilic acid dissolved in deionized water in a 1:1 molar ratio. The synthesized salts were utilized to look at the solvency of the compounds at distinctive temperatures by gravimetric method. Dissolve an amount of synthezised salt in 100 mL of solvent and stirred well with a magnetic stirrer for 2 hours until obtaining a saturated solution. Saturated solution was filtered using No.1 grade whatmann filter paper and kept the filtered solution at room temperature. After 30 days, needle-shaped crystals of 17x9x3 mm^3 were collected. A photograph of the grown crystal is shown in Figure 1.

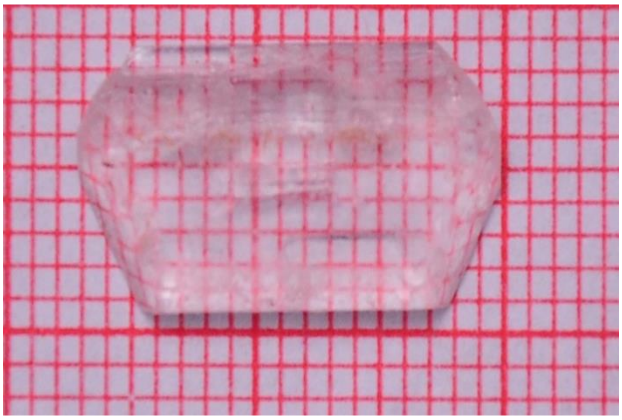

Fig. 1. Photograph of GSA crystal.

II. Result and Discussion

2.1. Crystal Structure

Grown GSA crystal was characterized by single crystal X-ray diffraction study using Brucker Kappa Apex III diffractometer with MoKα radiation (λ = 0.71073 Å) to determine crystal structure. The dimension of the crystal used for structure analysis was $0.550 \times 0.200 \times 0.150\ mm^3$. The crystal structure was solved by direct method and refined by full matrix least squares technique on F^2[16]. The GSA crystal crystallizes in centro symmetric monoclinic system is with a space group P21/c. The obtained unit cell parameters are a = 7.7559(9) Å, b= 7.7559(9) Å, c = 15.523(3) Å and α = 90º, β = 90º, γ = 90º.The crystallographic data of the grown compound are given in Table 1.The ORTEP picture is shown in Fig. 2.

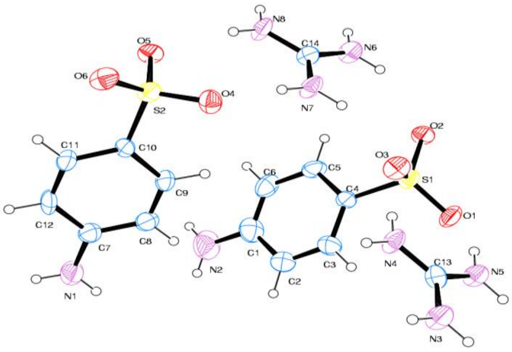

Fig. 2. ORTEP Plot of GSA compound

The sharp peak distance and bond angles are listed in Table 2. The bond distance C_5-C_6(1.391(15)Å), C_1-C_2(1.409(17)Å), C_7-C_{12}(1.404(14)Å) and

Table 1.

Crystal data and structure refinement for GSA

Identification code	**Shelx**	
Empiricalformula	C7 H12 N4 O3 S	
Formula weight	232.27	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.167(3) Å b = 7.4427(16) Å c = 25.057(6) Å	α= 90°. β= 97.413(6)°. γ = 90°.
Volume	2250.1(9) $Å^3$	
Z	8	
Density (calculated)	1.371 Mg/m^3	
Absorption coefficient	0.283 mm^{-1}	
F(000)	976	
Crystalsize	0.550 x 0.200 x 0.150 mm^3	
Theta range for data collection	3.191 to 25.000°.	
Index ranges	-14<=h<=13, -8<=k<=8, -29<=l<=29	
Reflections collected	19347	
Independent reflections	3930 [R(int) = 0.1679]	
Completeness to theta = 25.000°	99.5 %	
Refinement method	Full-matrixleast-squareson F^2	
Data / restraints / parameters	3930 / 0 / 272	
Goodness-of-fit on F^2	1.094	
Final R indices [I>2sigma(I)]	R1 = 0.1146, wR2 = 0.2475	
R indices (alldata)	R1 = 0.2207, wR2 = 0.2917	
Extinction coefficient	0.0029(6)	
Largestdiff. Peak and hole	0.457 and -0.467 e.$Å^{-3}$	

C_9-C_{10}(1.411(13)Å) shows the same dimension and is higher than the other C-C bond lengths (Table 2) which shows the single bond nature of the C-C bond in the aromatic ring. All the C-N bond lengths of guanidine molecule are found to be much lowered than the aromatic C-N bond lengths indicate the double bond nature. In the aromatic ring all C-C-C bond angle found to be deviated from the regular hexagon symmetry and it may be due to substituent effect.

In the crystal structure all potential hydrogen atom of guanidinium cation participate in the interaction to all sulphanilic oxygen atom. The N-H...O hydrogen bonding geometry is listed in Table 3. Totally 16 interactions are there including the intra molecular interaction made by N_1 atom with sulphanilic oxygen atom.

2.2. Optical Transmittance Analysis

A 2 mm thick defect-free crystal grown was used for UV–visible spectroscopy analysis. Analysis was performed using a Perkin Elmer Lamda model 35 spectrometer in the 190 to 1100 nm ranges. Figure 3 shows the recorded spectra. The spectra shows that, the GSA single crystal is transparent throughout the visible region, and has high absorption at 220 nm. Low absorption throughout the visible region is one of the most important factors for high-frequency processing using diodes and solid-state lasers [17]. Optical research was performed on the crystal to determine the nature of the optical transition. The dependence of optical absorption coefficient on

Table 2.

Selected bond distance (Å) andbond angles (°) for GSA crystal

Bonddistance	**BondAngle**	**Bonddistance**	**BondAngle**
C(5)-C(6)	1.391(15)	C(6)-C(1)-C(2)	118.8(12)
C(1)-C(2)	1.409(17)	C(3)-C(2)-C(1)	118.6(12)
C(7)-C(12)	1.404(14)	C(4)-C(3)-C(2)	122.7(11)
C(9)-C(10)	1.411(13)	C(3)-C(4)-C(5)	118.7(10)
C(1)-C(6)	1.340(17)	C(4)-C(5)-C(6)	118.9(11)
C(2)-C(3)	1.369(15)	C(1)-C(6)-C(5)	122.3(12)
C(3)-C(4)	1.358(14)	C(8)-C(7)-C(12)	117.9(11)
C(4)-C(5)	1.385(13)	C(9)-C(8)-C(7)	121.2(11)
C(7)-C(8)	1.368(15)	C(8)-C(9)-C(10)	121.4(10)
C(8)-C(9)	1.360914)	C(11)-C(10)-C(9)	116.9(12)
C(10)-C(12)	1.369(15)	C(12)-C(11)-C(12)	122.3(10)
C(13)-N(4)	1.296(12)	N(4)-C(13)-N(5)	122.2(11)
C(13)-N(5)	1.303(12)	N(4)-C(13)-N(3)	119.4(10)
C(14)-N(8)	1.314(12)	N(5)-C(13)-N(3)	118.4(9)
C(14)-N(6)	1.314(12)	N(8)-C(14)-N(6)	121.2(10)
C(14)-N(7)	1.326(13)	N(8)-C(14)-N(7)	118.5(10)
C(13)-N(3)	1.342(13)	N(6)-C(14)-N(7)	120.3(9)
C(1)-N(2)	1.378(15)		
C(7)-N(1)	1.373(13)		

Table 3.

Hydrogen bonds for GSA

D-H...A	**d(D-H) Å**	**d(H...A) Å**	**d(D...A) Å**	**<(DHA)(°)**
N(1)-H(1A)...O(1)#1	0.86	2.48	3.285(12)	155.6
N(1)-H(1B)...O(5)#2	0.86	2.27	3.130(12)	174.9
N(3)-H(3A)...O(1)#3	0.86	2.19	2.977(12)	151.3
N(3)-H(3B)...O(6)#4	0.86	2.04	2.883(12)	166.9
N(4)-H(4A)...O(3)	0.86	1.99	2.842(12)	171.8
N(4)-H(4B)...O(2)#3	0.86	1.98	2.826(11)	168.3
N(5)-H(5A)...O(1)	0.86	2.29	3.095(12)	155.9
N(5)-H(5B)...O(5)#4	0.86	2.13	2.951(11)	158.9
N(6)-H(6A)...O(4)#5	0.86	2.09	2.927(11)	164.5
N(6)-H(6A)...S(2)#5	0.86	2.94	3.711(9)	150.8
N(6)-H(6B)...O(2)	0.86	2.16	2.931(11)	149.2
N(7)-H(7A)...O(4)	0.86	2.01	2.870(11)	175.4
N(7)-H(7B)...O(3)	0.86	2.11	2.928(11)	159.2
N(7)-H(7B)...S(1)	0.86	3.00	3.697(9)	139.9
N(8)-H(8A)...O(6)#5	0.86	2.11	2.946(12)	163.0
N(8)-H(8B)...O(5)	0.86	2.14	2.969(11)	161.7

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,y+1/2,-z+3/2 #2 -x,y+1/2,-z+3/2 #3 x,y+1,z#4 x+1,y,z #5 x,y-1,z.

photon energy helps to study the band structure and type of transition of electron [18].

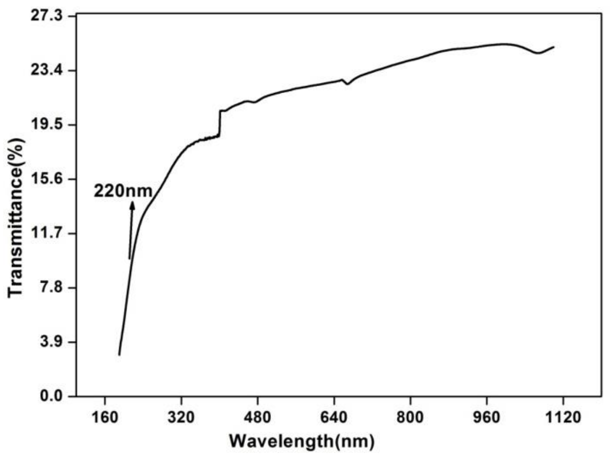

Fig. 3. UV-Vis spectrum of GSA.

The Absorption coefficient (α) is calculated from the transmittance using the following relationship:

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

where T is the transmittance and t is the thickness of the grown crystal. Owing to the direct band gap, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies (hυ)

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

Where E_g is the optical band gap of the crystal and A is a constant. The variation of $(\alpha h\upsilon)^2$ with hυ gives the Tauc's plot. The Tauc curve for as-grown guanidine crystals is shown in Figure 4. From the graph, the energy band gap (Eg) is found by by extrapolating the linear part [19]. The Eg of the GSA crystal is calculated as 5.6 eV.

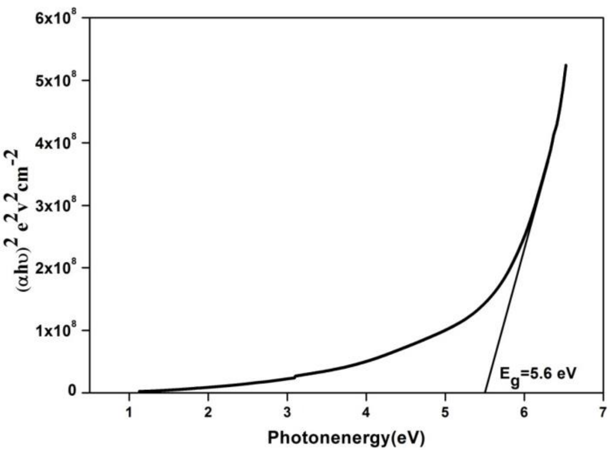

Fig. 4. Tauc's Plot of GSA crystal.

2.3. Photoluminescence

The photoluminescence studies were found by the grown good quality crystal. The variation of emission intensity was observed for various wavelengths for excitation wavelength at 220 nm. The recorded spectra is shown in Figure 5. GSA shows the peaks at 3.4 eV and 3.8 eV which implies the emission of light in blue region. Hence the grown crystal shows the good luminescence property with the emission of blue light, and it may be applicable in optical LED devices [20].

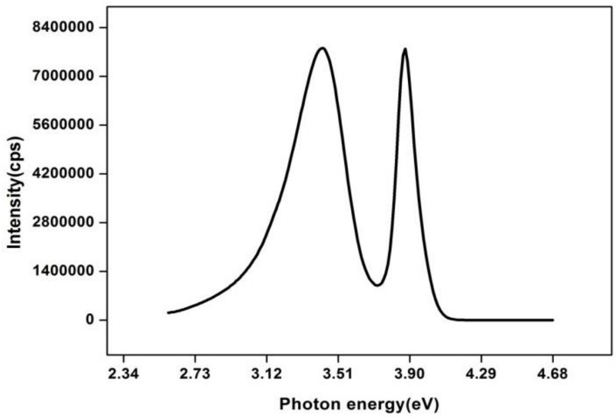

Fig. 5. Photoluminescence Plot of GSA crystal.

2.4. Laser Damage Threshold (LDT)

One of the important criteria for device fabrication of nonlinear optical devices is their resistance to laser damage, because the nonlinear process involves high optical intensities. Hence an NLO crystal used for application should sustain the high intensity laser light apart from its NLO efficiency [21]. This LDT study uses a pulse width of 10 ns, a repetition rate of 10 Hz, and a critical wavelength of 1064 nm. The laser damage threshold value is found as 0.24 GW/cm^2.It is higher than the standard KDP value [22].

2.5. Second Harmonic Generation Study (SHG)

A Q-switched Nd-YAG laser beam with an input power of 0.68 mJ, pulse width of 8 ns, with repetition rate of 10 Hz and a wavelength of 1064 nm was utilized. The crystalline powder is firmly stuffed into a microcapillary tube and exposed to laser radiation. The output from the sample was monochromated to collect the intensity of the 532 nm component and eliminate with the fundamental wave. Second harmonic radiation delivered by arbitrarily arranged microcrystals is focoused by a lens and recorded by a photomultiplier tube. The generation of the second harmonic was confirmed by the emission of green light. The efficiency is found to be 0.06 times of KDP. The value is compared with other organic single crystal in Table 4.

Table 4.
Comparisonof SHG efficiency with other organic crystal

Compound	**SHG efficiency in comparison with KDP**
R,S-Serine[23]	0.02
Guanidinium trifluoro acetate(GIFA)[24]	0.87
GSA(present work)	0.06

Conclusion

The single crystal GSA were grown using the slow evaporation method. XRD data show that the GSA has a monoclinic structure, and the space group is P21/c. The structure parameters show intermolecular interactions and intra molecular hydrogen bond relationships. UV-visible spectroscopy studies show that it has a wide band gap of 5.6 eV and no absorptions in the visible region. Photoluminescence spectra show that the GSA has fluorescent properties, with the emission of light in the blue region and can therefore be used in the design of optical devices. It was found that the laser damage of the centro symmetric GSA was 0.24 GW/cm^2 and the SHG efficiency was 0.06 times that of the KDP crystal.

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Структура, ріст та оптичні характеристики монокристалу сульфанілату гуанідинію(GSA)

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Монокристали гуанідинсульфанілату (GSA) вирощено методом повільного випаровування. Дослідження рентгенівської дифракції монокристалів показують, що кристал росте в центросиметричній моноклінній системі, а його просторова група P21/c. Оптичні дослідження проводили за допомогою УФ-спектроскопії, а ріст кристалу спостерігали на низьких довжинах хвилі ~220 нм. Дослідження фотолюмінесценції показали, що кристали GSA володіють чудовими люмінесцентними властивостями. Лазерне пошкодження визначено як 0,24 ГВт/см^2. Нелінійно-оптичні дослідження вказують на випромінювання зеленого світла.

Ключові слова: ріст кристалів, водневий зв'язок, GSA, оптика, структура.