

HUMO-LUMO Studies on Methyl Orange Doped ZTS Crystals for Laser Applications

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Abstract:

Zinc Thiourea Sulphate (ZTS), crystal is a magnificent metal natural compound, which consolidates the upsides of both natural and inorganic materials when contrasted and other customary non-linear optical materials and in this way can be utilized as a part of a more extensive scope of uses. Late endeavors at delivering new recurrence transformation materials have concentrated essentially on expanding the extent of the NLO properties that can recurrence twofold low pinnacle control sources, for example, diode lasers. The thermo gravimetric examination (TGA) and differential warm investigation (DTA) were completed utilizing Seiko warm analyzer at warming rate 20°C/min in air to decide the warm dependability of the compound. ZTS crystals were developed by moderate cooling procedure. This empowers the development of mass gems along all the three bearings at an ideal pH. FTIR examines demonstrate that in the spectra of ZTS there is a move in the recurrence band in the low-recurrence district which uncovers that thiourea shapes sulfur-to-zinc securities in the ZTS crystals. The stability and charge delocalization of the molecule were also studied by natural bond orbital (NBO) analysis. The HUMO-LUMO energies describe the charge transfer takes place within the molecule. Molecular electrostatic potential has been analyzed. The developments try in extensive scale with this enhanced pH qualities is required to yield mass crystal appropriate for laser combination tests and SHG device applications.

Key words: ZTS crystal, FT-IR studies, Thermal studies, HUMO-LUMO studies, SHG measurements

I. INTRODUCTION

Non-linear optical (NLO) materials significantly affect laser innovation, optical correspondence, optical capacity innovation and electro optic adjustment. The hunt down new recurrence change materials over the previous decade has prompted to the disclosure of numerous semiorganic materials [1-3]. These materials groups vast nonlinearity, high resistance laser prompted harm and low precise affectability. The semi natural NLO materials pick up significance over natural and inorganic NLO materials due to their huge polarizability and wide transmission window.

To understand the kinetics and mechanisms involved in the process of crystal growth, many theories such as surface energy theory, diffusion theory, surface adsorption theory, etc. have been proposed. The first theory of crystal growth was proposed as early as the late 19th century [4]. The development of the theories of crystal growth has thrown more light on the understanding of crystal growth phenomena. Compared with inorganic NLO materials, organic materials may fulfill many of these requirements, but there are also some drawbacks with organic NLO materials such as environmental stability, poor chemical and mechanical stability, red-shift of the cut-off wavelength, low laser damage thresholds and poor phase matching properties [5-12]. In order to overcome these drawbacks and improve the properties, the growth of semi-organic crystals has nowadays come into prominence. In order to meet this increasing demand of new material with good optical properties, identifying and growth of new optical crystals with good crystalline nature has become an interesting branch in crystal growth[8]. Broad examination in this course brought about the disclosure of another stage coordinate inorganic material like ZTS crystals

II. EXPERIMENTAL PROCEDURE

2.1 Crystal Growth

Pure ZTS crystals were grown from aqueous solution by slow evaporation and also by slow cooling method (0.5^o C/Day). The same method is followed for doped ZTS crystals (0.1 mole % of Methyl Orange). The solubility of doped ZTS in the solvent was measured for each dopant, it was found to be 31.5-gms/100 ml at 42°C for Methyl Orange. The seed crystals are prepared at low temperature by spontaneous nucleation. The seed crystals (Fig. 1 a,b) with perfect shape and free from macro defects were used for growth experiments. Large single crystals of ZTS and doped ZTS were grown using constant temperature bath (CTB) controlled with an accuracy of 0.01^oC. The mother solution was saturated with the initial pH value, 4.2 for Methyl Orange. The growth was carried out for more than 22 days by keeping the bath at a temperature of 39^oC.

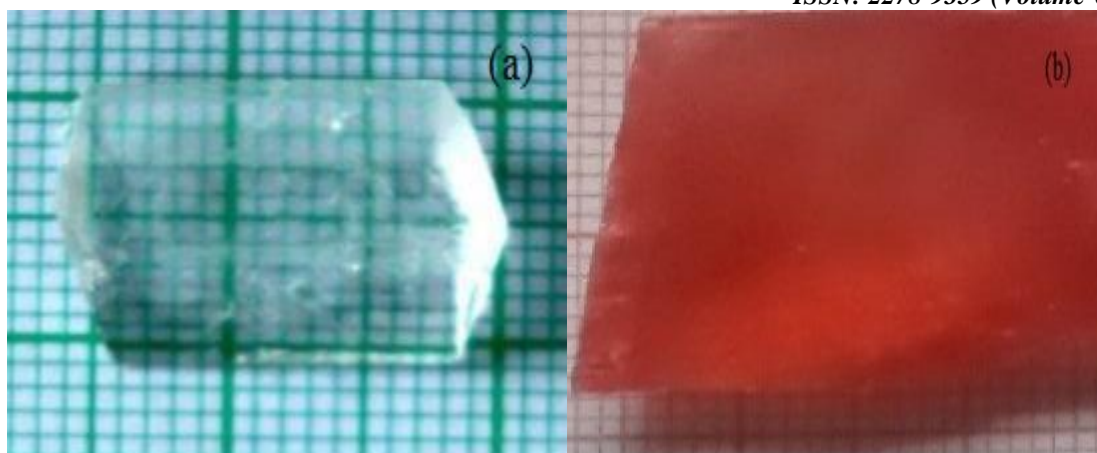


Figure 1. (a) Pure and (b) Methyl Orange doped ZTS Crystal

2.2 FT-IR Analysis

The FT-IR range was recorded between 1000 cm^{-1} and 4000 cm^{-1} , utilizing BRUKER IFS 66V FT-IR spectrometer. The FT-IR Spectra of both the unadulterated and doped ZTS precious stones are appeared in Figure 2. The FT-IR spectra of immaculate and doped ZTS show up practically like each other. N-H extending frequencies of amino gathering are found between 3026 cm^{-1} and 2923 cm^{-1} for both unadulterated and doped precious stones. Both the immaculate and doped mixes demonstrate ingestion at 1620 cm^{-1} showing the nearness of essential amino gathering. The trademark ingestion for the -NH gather in the fragrant ring is seen at 2421 cm^{-1} for ZTS. The expansive ingestion around 3000 cm^{-1} demonstrates the co nearness of C=O extending and O-H extending.

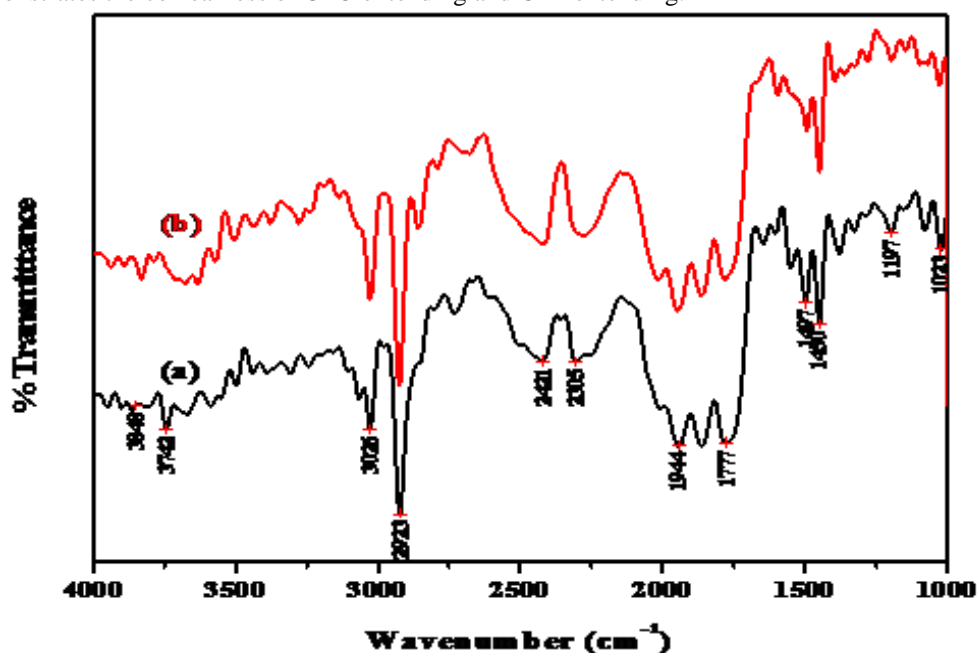


Figure 2. FT-IR spectra of (a) pure and (b) Methyl Orange doped ZTS crystal

The FT-IR spectra of both the pure and doped ZTS affirm the auxiliary viewpoints. Doping of metal particle into the crystal lattices does not demonstrate any centrality change in assimilation design. A portion of the assimilations demonstrate a stamped contrast in rate transmittance. The rate change of transmittance particularly, at 950 cm^{-1} and 690 cm^{-1} are important. It is induced that the metal particle, shape powerless linkages in the interstices of the relating crystals.

2.3 Microhardness Studies

Microhardness is one of the essential mechanical properties of the ZTS precious stones. It can be appropriately used to quantify the plastic properties and quality of a material. Microhardness estimations were completed utilizing Leitz Weitzler hardness analyzer fitted with a precious stone indenter (Fig.3). The all around cleaned Methyl Orange doped ZTS precious stone was set on the stage of the Vickers small scale hardness analyzer and the heaps of various sizes were connected over an analyzer at a settled interim of time [13]. The space time was kept as 8 sec for every one of the heaps. The microhardness esteem was computed utilizing the connection $H_v = 1.8544 \times P/d^2\text{ kg/mm}^2$, where P is the connected load in kg and d is the corner to corner length of the space impression in mm. Color doping enhances the mechanical quality of ZTS.

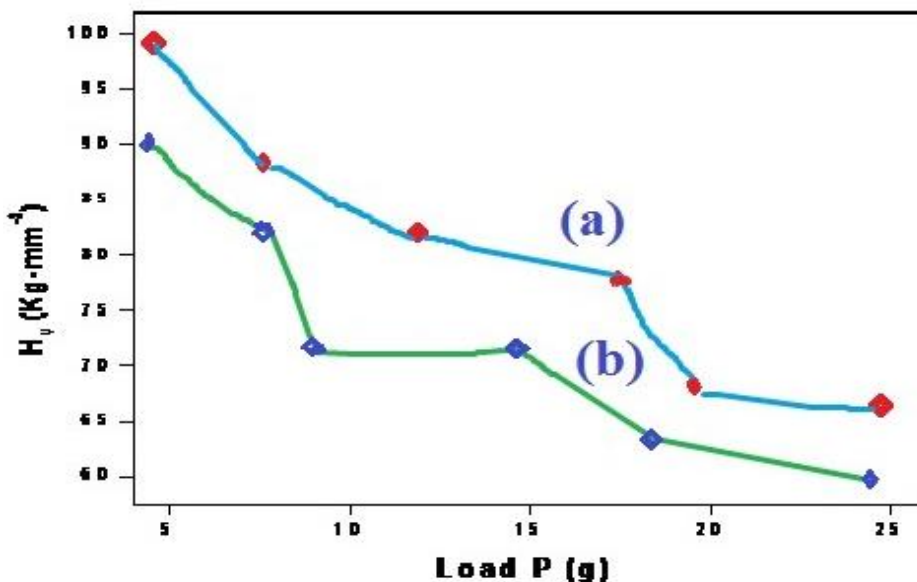


Figure3. Microhardness studies of (a) Methyl Orange doped ZTS and (b) Pure ZTS crystals

2.4 THERMAL STUDIES

Figure 4. shows the Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA) bends for the developed) Methyl Orange doped ZTS precious stone. The DTA bend infers that the material experiences an irreversible endothermic move at 200°C where the liquefying starts. This pinnacle was endothermic pinnacle, speaks to the temperature at which the dissolving ends which relates to its liquefying point at 210°C. In a perfect world, the liquefying purpose of the follow relates to a vertical line. The sharpness of the endothermic pinnacle indicates great level of crystallinity of the developed ingot[10]. The exothermic crest at 290°C demonstrates a stage change from fluid to vapor state as obvious from the loss of weight of around 87% in TG curve.

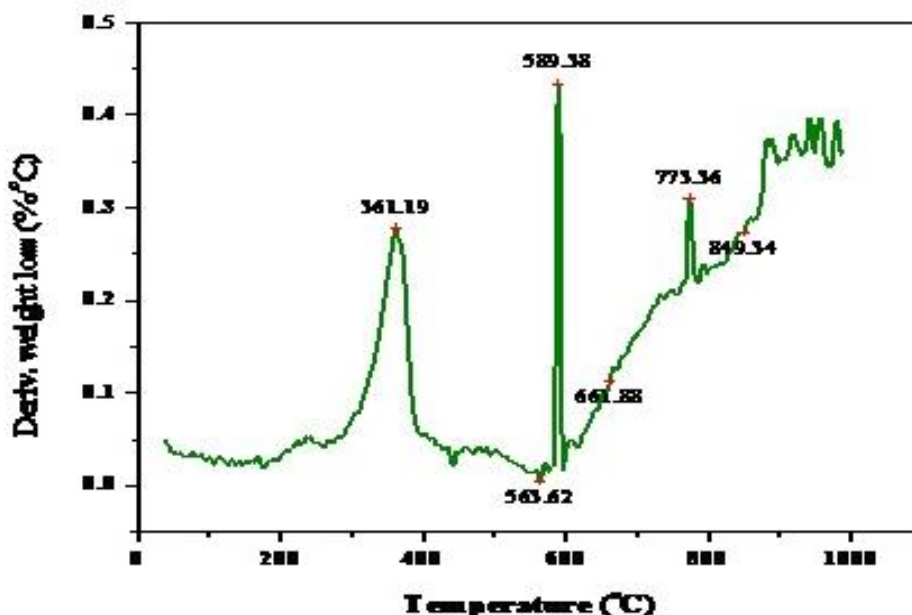


Figure 4. TGA-DTA curves of Methyl Orange doped ZTS Crystal

2.5 Frontier Molecular Orbitals

Many organic molecules that contain conjugated π electrons are characterized hyperpolarizabilities and are analyzed by means of vibrational spectroscopy [14]. In most cases, even in the absence of inversion symmetry, the strongest bands in the Raman spectrum are weak in the IR spectrum and vice versa. But the intramolecular charge transfer from the donor to acceptor group through a single-double bond conjugated path can induce large variations of both the molecular dipole moment and the molecular polarizability, making IR and Raman activity strong at the same time. It is also observed in Methyl orange doped ZTS orange the bands in FTIR spectrum have their counterparts in Raman shows that the relative intensities in IR and Raman spectra are comparable resulting from the electron cloud movement through pi conjugated frame work from electron donor to electron acceptor groups.

Numerous natural particles that contain conjugated π electrons are portrayed hyperpolarizabilities and are dissected by method for vibrational spectroscopy [15-17]. Much of the time, even without reversal symmetry, the most

grounded groups in the Raman range are feeble in the IR range and the other way around. Be that as it may, the intramolecular charge exchange from the contributor to acceptor gather through a solitary twofold bond conjugated way can actuate substantial varieties of both the sub-atomic dipole minute and the sub-atomic polarizability, making IR and Raman movement solid in the meantime. It is additionally seen in Methyl orange doped ZTS orange the groups in FTIR range have their partners in Raman demonstrates that the relative powers in IR and Raman spectra are practically identical coming about because of the electron cloud development through pi conjugated edge work from electron benefactor to electron acceptor bunches.

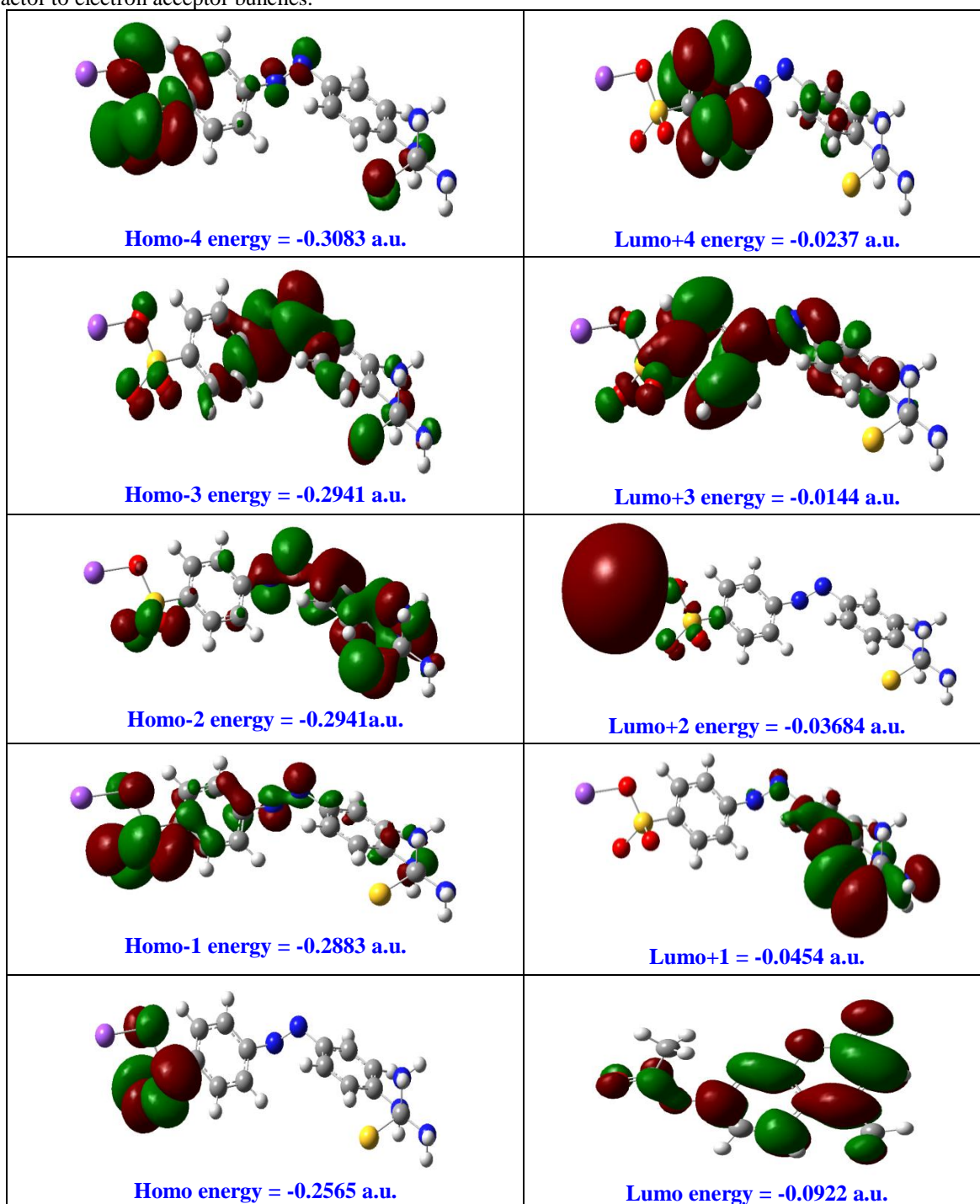


Figure 5. HOMO-LUMO plot of Methyl Orange doped ZTS

Highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are very important parameters for quantum chemistry. We can determine the way the molecule interacts with other species; hence, they are called the frontier orbitals. HOMO, which can be thought the outermost orbital containing electrons, tends to give these electrons such as an electron donor. On the other hand; LUMO can be thought the innermost orbital containing free places to accept electrons [18]. Owing to the interaction between HOMO and LUMO orbital of a structure, transition, state transition of π^* type is observed with regard to the molecular orbital theory [19].

Therefore, while the energy of the HOMO is directly related to the ionization potential, LUMO energy is directly related to the electron affinity. Energy difference between HOMO and LUMO orbitals is called as energy gap

that is an important stability for structures [20]. In addition, the pictorial scheme of few MOs of Methyl orange doped ZTS is shown in Fig. 5. HOMO is localized on the central ring and has no contribution from the substitution groups such as methyl and oxygen. LUMO is quite localized on the central ring and has contribution from the substituted electronegative oxygen atom. The energy gap between HOMO and LUMO is 0.1643 a.u., which shows that charge transfer may be taking place from the ring to oxygen atom. As seen from the Fig. 5, HOMO-1 is very similar to HOMO, rotated by 90°. HOMO-3 is mainly localized on oxygen atom whereas LUMO+3 is localized on ring carbon atoms and oxygen atom.

2.6 Global and local reactivity descriptors

Based on density functional descriptors global chemical reactivity descriptors of compounds such as hardness, chemical potential, softness, electronegativity and electrophilicity index as well as local reactivity have been defined. Pauling introduced the concept of electronegativity as the power of an atom in a compound to attract electrons to it. Hardness (η), chemical potential (μ) electronegativity (χ) and softness are defined follows.

$$\eta = \frac{1}{2}(\partial^2 E / \partial N^2)_{V(r)} = \frac{1}{2}(\partial \mu / \partial N)_{V(r)}$$

$$\mu = (\partial E / \partial N)_{V(r)}$$

$$\chi = -\mu = -(\partial E / \partial N)_{V(r)}$$

where E and V(r) are electronic energy and external potential of an N-electron system respectively. Softness is a property of compound that measures the extent of chemical reactivity. It is the reciprocal of hardness.

$$S = 1 / \eta$$

Using Koopman's theorem for closed-shell compounds, η , μ and χ can be defined as

$$\eta = (I - A) / 2$$

$$\mu = -(I + A) / 2$$

where A and I are the ionization potential and electron affinity of the compounds respectively. Electron affinity refers to the capability of a ligand to accept precisely one electron from a donor. However in many kinds of bonding viz. covalent hydrogen bonding, partial charge transfer takes places. Recently Parr *et al.* have defined a new descriptor to quantify, the global electrophilic power of the compound as electrophilicity index (ω), which defines a quantitative classification of the global electrophilic nature of a compound have proposed electrophilicity index (ω) as a measure of energy lowering due to maximal electron flow between donor and acceptor. They defined electrophilicity index (ω) as

$$\omega = \mu^2 / 2 \eta$$

The usefulness of this new reactivity quantity has been recently demonstrated in understanding the toxicity of various pollutants in terms of their reactivity and site selectivity [16]. The calculated value of electrophilicity index describes the biological activity for Thiourea Methyl orange respectively. All the calculated values of HOMO-LUMO, energy gap, ionization potential, electron affinity, hardness, potential, softness and electrophilicity index are shown in Table 1 respectively.

Table 1: HOMO - LUMO energy gap and related molecular properties of Methyl orange doped ZTS

Molecular Properties	B3LYP/6-311+G(d,p)
HUMO	-0.2565
LUMO	-0.0922
Energy gap	0.1643
Ionisation Potential (I)	0.2565
Electron affinity (A)	0.0922
Global softness (s)	12.1728
Global Hardness (η)	0.08215
Chemical potential (μ)	-0.17435
Global Electrophilicity (ω)	-0.2063

2.7 ¹³C AND ¹H NMR Spectral Analysis

The molecular structure of Thiourea Methyl orange is optimized by using B3LYP method with 6-311+G basis set. Then, GIAO ¹³C calculations of Thiourea Methyl orange are calculated and compared with experimental values [17] and that are shown in Table 1. Relative chemical shifts are then estimated by using the corresponding TMS shielding calculated in advance at the theoretical level as reference. Changes in energy needed to flip protons are called chemical shifts. The location of chemical shifts (peaks) on a NMR spectrum are measured from a reference point that the hydrogen's in a standard reference compound – (CH₃)₄Si or tetramethylsilane (TMS) – produce. The amount of energy necessary to flip protons in TMS is assigned the arbitrary value of zero δ . Chemical shifts are measured in parts per million magnetic field strength difference (δ -scale), relative to TMS. The experimental values for ¹H and ¹³C isotropic chemical shielding for TMS are 22.41 ppm and 154.54 ppm, respectively. All the calculations are performed using Gauss view molecular visualization program and GAUSSIAN 09W program package. The result shows that the range ¹³C NMR chemical shift of the typical organic compound usually is > 100 ppm [18], the accuracy ensures reliable interpretation of

spectroscopic parameters. It is true from the above literature value in our present study, that the title compound also shows the same. In practice, it is easier to fix the radio wave frequency and vary the applied magnetic field than it is to vary the radio wave frequency [19].

The magnetic field "felt" by a hydrogen atom is composed of both applied and induced fields. The induced field is a field created by the electrons in the bond to the hydrogen and the electrons in nearby π bonds. When the two fields reinforce each other, a smaller applied field is required to flip the proton. In this situation, a proton is said to be deshielded[20]. When the applied and induced fields oppose each other, a stronger field must be applied to flip the proton. In this state, the proton is shielded. Electronegative atoms such as S O, N, Na and halogens deshield hydrogens. The extent of deshielding is proportional to the electronegativity of the heteroatom and its proximity to the hydrogen. Electrons on a heterocyclic ring, double bonded atoms, and triple bonded atoms deshield attached hydrogens. These sulphur, amino and oxygen atoms show electronegative property, so the theoretical the chemical shift of C2, C3, C4, C5, C6, C15, C16, C17 and C18 seems to be 156.28, 112.63, 155.06, 126.65, 119.69, 150.80, 102.31, 123.01 and 116.5 ppm for Thiourea Methyl orange[21-23]. The chemical shift of C2 is greater than the other carbon values. This increase in chemical shift is due to the substitution of more electronegative oxygen and methyl atoms in the heterocyclic ring.

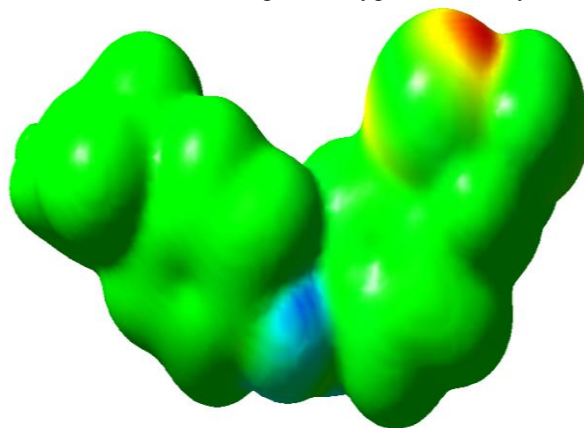


Figure 6. The molecular electrostatic potential surface of Methyl orange doped ZTS

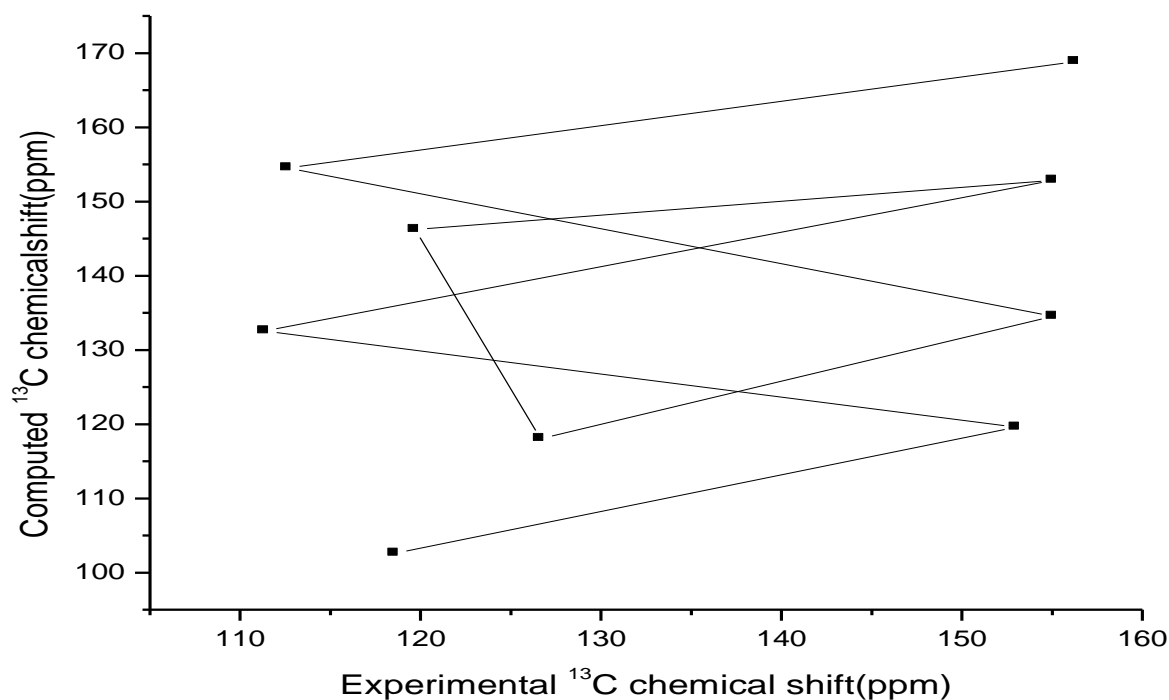


Figure 7. Comparative graph of computed and experimental of Methyl Orange doped ZTS

The presence of electronegative atom attracts all electron clouds of carbon atoms towards the oxygen and methyl atoms, which leads to deshielding of carbon atom and net result in increase in chemical shift value. The NMR shielding surfaces of C4 is shown in this work (Table.2) the chemical shift (δ) for carbon atoms presented in the Thiourea Methyl orange has been studied and theoretical ^{13}C , ^1H -NMR isotropic shielding of carbon and Hydrogen atom are shown. In the NMR shielding surfaces, the blue region represents shielding and red region represents de-shielding are shown in Fig. 6. The relationship between the experimental chemical shift and computed GIAO/B3LYP/6-311+G(d,p) levels for ^{13}C are shown in Fig. 7 for Thiourea Methyl orange.

Table 2. The calculated shifts of carbon and hydrogen atoms of Thiourea Methyl orange using B3LYP/6-311+G(d,p) GIAO method

Atom position	Isotropic chemical shielding tensor (σ) (ppm)	Chemical shifts (δ) (ppm)		
		Theoretical	Expt ^a	Δ
C1	51.2597	51.259		
C2	-19.327	156.28	168.86	12.58
C3	62.2180	112.63	154.54,	41.91
C4	34.6855	155.06	134.54	-20.52
C5	57.4111	126.65	118.07	-8.58
C6	57.3342	119.69	146.23	26.54
H7	18.5263	155.06	152.86	-2.2
H8	67.9329	111.35	132.57	21.22
H9	34.7143	153.01	119.57	-33.44
H10	65.3596	118.57	102.58	-15.99
N11	-359.58	-359.58	559.58	
H12	25.5446	25.544	22.41	-3.13
N13	172.2939	13.15		
N14	30.7272	30.727	18.41	-12.31
C15	31.0491	150.80		

^a Taken from Ref [6] and $\Delta(\delta_{\text{exp}}-\delta_{\text{the}})$; difference between respective chemical shifts.

III. CONCLUSION

The dye doped GLS crystals are used for the generation of second harmonics of Nd-based near-infrared solid-state lasers. The fundamental of an Nd:YAG laser (1064 nm) can be converted to 532 nm of second harmonic or its 355 nm of third harmonic or its 266 nm of fourth harmonic by using ZTS crystals. The performance of these frequency conversion devices can be seriously degraded if there are defect-associated absorption bands in the crystal which overlap the fundamental pump wavelength or one of the output wave lengths. Thus, it is important to identify and characterize all potentially harmful absorption bands in non-linear optical crystals. In order to confirm the suitability of the doped ZTS crystal, the non-linear application, harmonic generation was tested using the Nd-YAG laser. The HOMO– LUMO energy gap calculated at the B3LYP/6-311++G(d,p) level reveals the chemical activity and kinetic stability of the molecule. The large negative ESP is observed at oxygen atom in the compounds and this starts to spreads near hydrogen atom under the increase of field. The NBO analysis indicates the intramolecular charge transfer between the bonding and antibonding orbitals. The NBO analysis indicates the intramolecular charge transfer between the bonding and antibonding orbitals. This implies that the electrophilic attack is also taking place at hydrogen atom as field increases. The corresponding maps from the theoretical analysis explain similar features. Single crystals grown by the various methods need to be characterized to assess the suitability of the crystal for various applications including NLO device application. A sample of ZTS, also powdered was used for the same experiment as a reference material in the SHG measurement. It was found that the frequency doubling efficiency of the doped ZTS was better than KDP.

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