International Journal of Basic and Applied Science 11 (3) (2022) 124-131

Published by: IOCSCIENCE

International Journal of Basic and Applied Science

Journal homepage: www.ijobas.pelnus.ac.id

Computational molecular structure analysis, electronic properties of sudan dye doped thioureabarium chloride crystals for nlo Applications

[1]S. Panimalar, [2]P.Kumaresan, [3]S. Nithiyanantham, [4]K. Sambath Kumar

[1,2]P.G & Research Department of Physics, Thiru. A. Govindasamy Government Arts College, India.

[3]P.G & Research Department of Physics,,Thiru. Vi. Ka. Govt. Arts College, India.

[4]P.G & Research Department of Physics, Arignar Anna Government Arts College, India.

Article Info

Article history:

Received Aug 25, 2022
Revised Nov 20, 2022
Accepted Dec 11, 2022

Keywords:

DFT Studies;
Methyl Orange;
Nonlinear optical studies;
sudan doped TBC Crystal.

ABSTRACT

Pure thiourea barium chloride (TBC) crystals were grown by slow evaporation from aqueous solution and slow cooling (0.1°C/ day). The growth was carried out for 21 days by keeping the bath at a temperature of 39°C. Optimal molecular structures are explored by DFT / B3LYP method with 6-31G (d, p) based synthesis. Hyper conjugative interactions, charge delocalization and intra molecular hydrogen bonding have been analyzed using natural bond orbital (NBO) analysis. Moreover lower in the HOMO and LUMO energy gap explains the eventual charge transfer interactions taking place within the molecule, which influences the biological activity of the compound and also energy serves as a measure of the excitability of a compound, the smaller the energy gap, the more easily the compound will be excited. Electronic structures were discussed and the displacement of the electron density was determined. Second – order perturbation theory analysis of the intra molecular bonds of Methyl Orange doped TBC were derived.

Corresponding Author:

S. Panimalar,
P.G & Research Department of Physics,
Thiru. A. Govindasamy Government Arts College, India.
Email: panimalar@gmail.com

1. INTRODUCTION

The method of developing crystals varies broadly; it's far specially dictated by way of the traits of the material and its length. In current years there was big progress in the development of coherent UV assets supported non-linear optical techniques. The call for NLO (nonlinear optical) crystals with superior properties is increasing due to quantum bounce within the layout of NLO gadgets with higher overall performance (1)[2][3] .And so, crystal growths of new nonlinear optical substances and investigation into their houses have become most essential and investigations into their residences have become maximum essential and efficacious disciplines within the field of materials technology and engineering. The speedy development of optical verbal exchange machine has brought about a call for NLO substances of excessive performance for use as additives in optical gadgets NLO materials are used in frequency conversion[1] (4-6).

Thus, only a few number of them are currently widely used and commercially available. The opposite, upconversion nonlinear process of frequency doubling is exemplified by lasers. However, both of them exhibit a variety of drawbacks that prevent their practical application, starting with the

polished surface's chemical instability in air. Additionally, the optical damage thresholds and thermal conductivities are among the lowest. For these reasons, better performing crystals have been used in their place whenever possible [2].

In this paper, we review the characteristics of thiourea barium chloride compounds, which are presently regarded as promising and practical nonlinear crystals with effective SHG capabilities for the mid-IR region of the spectrum [3]

2. RESEARCH METHOD

2.1 Experimental Technique

2.1.1 Crystal Growth

The synthesis of Thiourea barium chloride single crystals carried out by taking thiourea and barium chloride with 2:1 molar ratio (3-5). The materials were subjected to dissolve using the double distilled water with continuous stirring by magnetic stirrer for 6 hours. In turn the prepared solution was filtered in order to separate the suspended particles [4](6). The clear mixture was kept for slow evaporation at room temperature (27° C). it was observed that the crystals started to grow from 5th day onwards in undisturbed condition. This process was noted on regular basis. [5]

In order to improve the impurities of material recrystallization was done. Then the grown crystal was kept in Constant Temperature Bath (20°C) for increasing the size of the crystal. Finally, the quality crystals were harvested in four weeks (7). During crystallisation the Sudan dye was added in the concentration of 0.1mM to the solution of TBC [6] (Figure.1.).

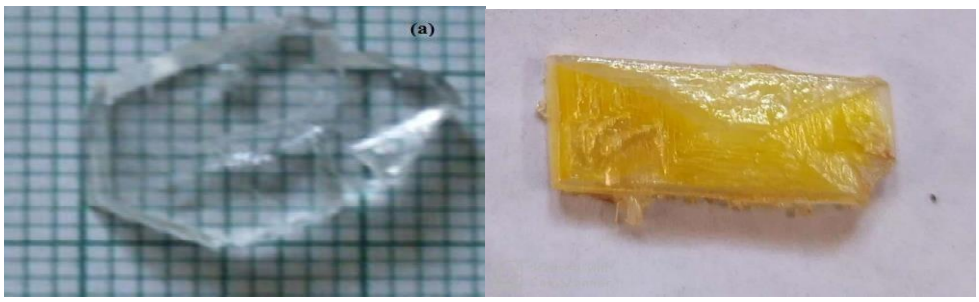


Figure 1. a) Pure TBC b) Sudan doped TBC crystal

3. RESULTS AND DISCUSSIONS

3.1 Characterization

The IR spectra were conjointly recorded on Shimadzu–800, The UV-VIS spectrum of TBC; Sudan doped TBC crystals had been taken inside the wavelength 200nm-1200nm tiers exploitation the Varian CARY5E UV-VIS-NIR photometer. Nd-YAG optical device take a look at became completed to seek out the non- linear optical assets of dye doped TBC crystals. The crystal became lit exploitation spectra – physics Quanta-Ray DHS2Nd-YAG optical tool exploitation the number one harmonics output of 1064 nm with a pulse breadth of eight ns. The Non-linear optical (NLO) efficiency of Sudan doped TBC crystal was compared with that of pure TBC and that the doped crystal has higher efficiency and more applications. [7]

X-RAY Diffraction Studies

The powder XRD studies of synthesized crystals affirm the crystalline nature of the sample. [8]The shift inside the function of peaks justifies the addition of dopant into the host lattice. The transmission spectra were taken using a double beam spectrometer. Which gives a mild shift inside the Bragg angle [8] (9).Powder X-ray diffraction spectra of the grown crystals from pure and Sudan dye doped TBC are proven in Figure 1.2.

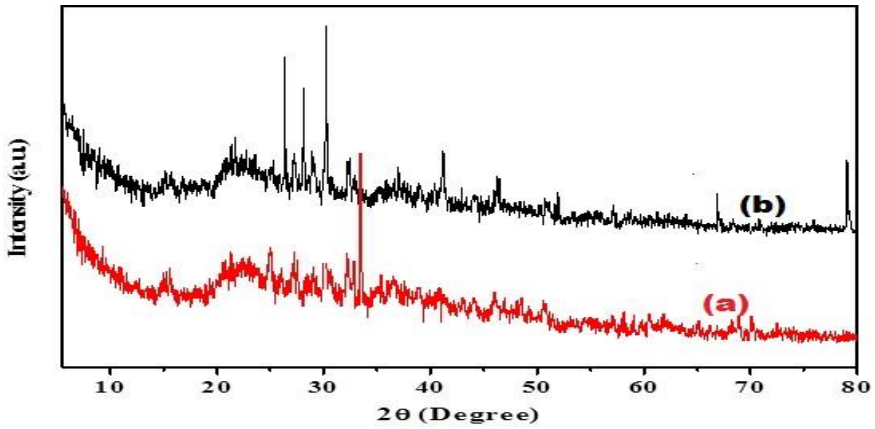


Figure. 2. XRD of (a) Pure (b) Sudan dye doped TBC crystal

FT-IR Studies

The bruker IFS 66V version spectrophotometer with1064 nm, are used to record the FTIR spectra of pure and Sudan dye doped TBC was recorded. The data was recorded with the excitation site of CW diode pumped Nd:YAG laser. The wavenumber is plotted in X axis between 500 to 4000 cm^{-1} and the transmittance is plotted in Y axis. The frequencies for all sharp bands are correct to ± 1 cm^{-1}(9). The observed spectra of Pure and Sudan doped TBC are 1625cm^{-1} and 3812cm^{-1} respectively proven in Figure1.3.

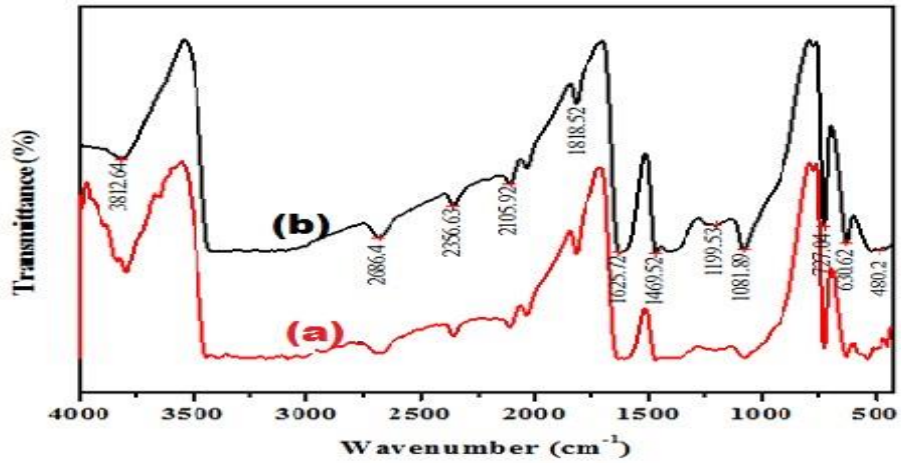


Figure. 3 FT-IR spectra of (a) Pure (b) Sudan dye doped TBC crystal

The bond of thiourea became now not shifted to decrease frequency on formation of TBC. The NH and N-C-N stretching vibrations were additionally seen in those crystals.

UV-visible Studies

The UV-visible spectral studies of grown crystals had been done the use of Shimadzu 1601 UV-spectrophotometer. The UV-visible absorbance spectra of doped TBC crystals are shown in figure 5.4. The absorption spectra reveal that crystals have decrease cut off wavelengths at round 290nm. The huge transmission in the whole seen area enables it be a capability candidate for optoelectronics packages. It indicates that, close to absorption facet the absorption coefficient increases swiftly with power (10-11).

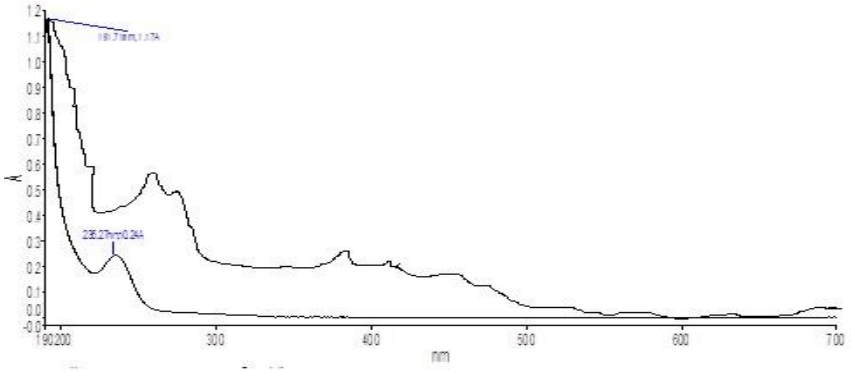
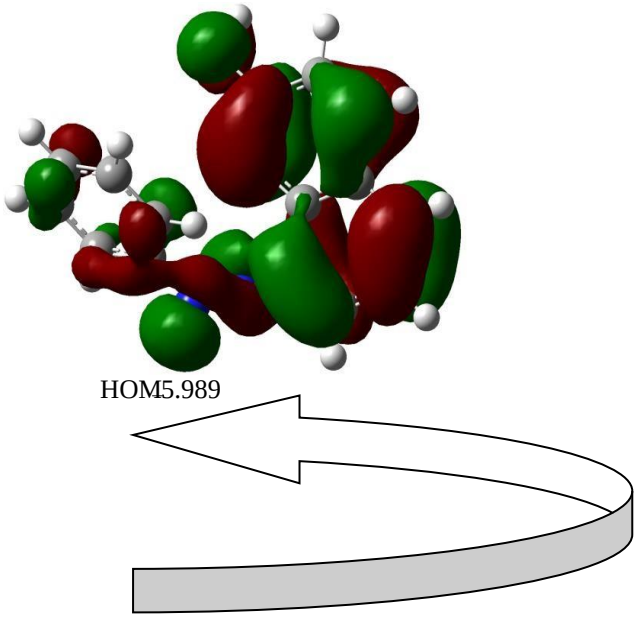


Figure. 4. Absorbance spectra of (a) Pure (b) Sudan doped TBC crystal

Electronic Properties

Electronic shape of the gasoline phase shape has been calculated with DFT exploitation the 6-311++G(d,p) basis set with associate degree trade (12-14) correlation useful (B3LYP). The plots of the HOMO, LUMO, overall lepton density (TED) for sudan1 likewise as that of the static capacity (ESP) mapped on accomplice degree density surface are proven in Figure 1.5 It is seen from the figure that each the HOMO and LUMO have nodes, and, moreover, the nodes inside the orbitals are positioned symmetrically. The HOMO is determined to be centered chiefly over the O internet site and around its encompassing teams, but the LUMO lies chiefly over the benzene [9] (15-18).

The calculated rate of the frontier orbital electricity gap, five.5738 eV, in the case of sudan1 (table 1.1) makes of it a smooth and a variety of polarizable molecule as compared to water. Those are taken as reference molecules, as every ware eminently polar solvents way to their excessive non-conductor regular and feature the lepton donor property and skills to create complexes. Their frontier orbital power gaps are calculated at a similar level of concept exploitation a similar foundation sets. The low frontier orbital hole is additionally associated with a excessive chemical reactivity and low kinetic stability (19).



Movement of Oxidation from HOMO TO LUMO.

LUMO–0.4161

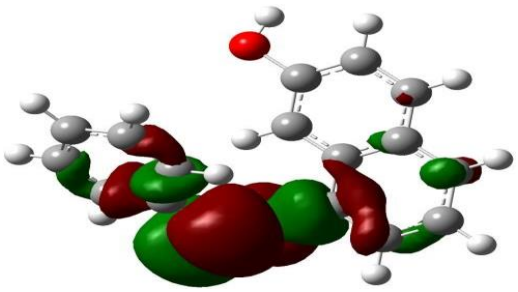


Figure .5 HOMO and LUMO of TBC crystal

Parameters	Ev
HOMO(a.u)	–5.9899
LUMO(a.u)	–0.4161
Energy Gap (Eg) (a.u)	5.5738
Dipole moment (in debye)	2.58
DMF	4.24
Water	2.16

Electrostatic Potential

The ESP is a physical property of a molecule related to how a molecule is first "visible" or "felt" by using another drawing near species (20). A part of a molecule that has a terrible electrostatic capacity is liable to an electrophilic assault the extra poor the higher. The ESP, which is associated with the electro negativity and the partial charges at the distinctive atoms of the molecule, when plotted at the isodensity surface of the molecule is named the MEP. The MEP and the TED are crucial parameters, and their observe ends in a better know-how of complicated biological techniques involving the rate-dipole, dipole-dipole, and quadruple-dipole interactions [10] (21).

As visible from Figure. 6, 7 & 8 the TED surface of rivastigmine depicts a uniform distribution. purple and blue regions in the MEP map discuss with the areas of poor and superb potentials and correspond to the electron-rich and electron-bad areas, respectively, whereas the green colour indicates the impartial electrostatic capability. The MEP surface offers essential data approximately the reactive websites. The MEP of sudan reveals a few thrilling capabilities. The vicinity around the oxygen atom in sudan displays the massive attention of electrons and is liable for

electrophillic interactions/pastime, whereas the alternative regions seem to offer almost impartial capacity as represented by the green vicinity.

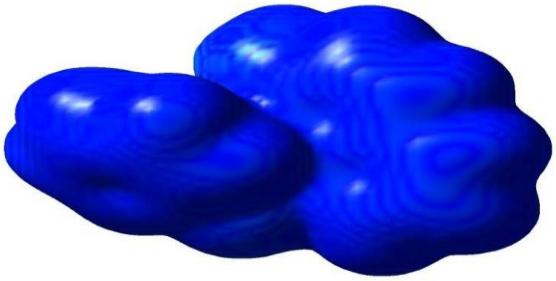


Figure. 6 The molecular electrostatic potential surface of Sudan

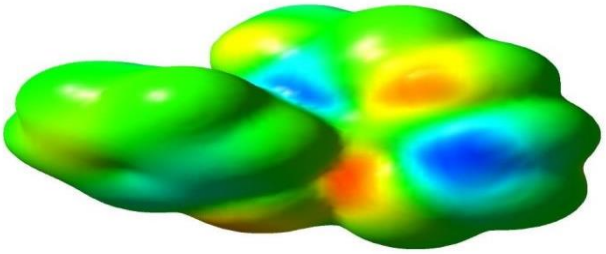


Figure 7. The electrostatic potential contour maps for positive and negative potentials

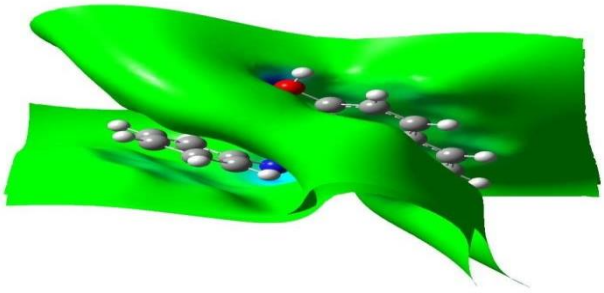


Figure 8. The total electron density surface of Sudan

Sudan is a polar molecule, and its calculated dipole second value is 2.58 Debye. Comparison of the calculated dipole moment of sudan with the ones of water and DMF indicates that it is slightly higher than the previous however distinctly smaller than the latter (22). (Dipole moment values for DMF and water are four.24 and 2.sixteen debye, respectively, at the same stage of calculations i.e., B3LYP/6311G++ (d, p).

NLO dimension. The NLO performance of natural TBC and Sudan yellow doped TBC crystal were offered in Table 2.

Table 2 NLO efficiency pure TBC and doped TBC Crystals

S.No.	Compound		NLO efficiency
1.	TP TBC chrystal	TP	1.79
2.	Sudan TBC	Crystals	1.95

4. CONCLUSION

The quality single crystals of pure and Sudan dye doped TBC were grown within slow evaporation technique. The grown crystal was obtained by 30 days. This grown crystal was subjected to The powder XRD studies ,the crystals affirm the crystalline nature of the sample. The shift inside the function of peaks justifies the addition of dopant into the host lattice. The transmission spectra were taken using a doublebeam spectrometer. The Bruker IFS 66V version spectrophotometer with1064 nm, are used to record the FTIR spectra of pure and Sudan dye doped TBC was recorded.It was observed that the FTIR spectra of Pure and Sudan doped TBC are 1625cm−1 and 3812cm−1 respectively. The UV-visible spectral studies of grown crystals had been done the use of Shimadzu 1601 UV- spectrophotometer. The absorption spectra reveal that all 3 crystals have decrease cut off wavelengths at 290nm.

The essential electronic parameters associated with the orbitals in an exceedingly molecule are the HOMO and LUMO and their electronic energy hole. these orbitals no longer totally verify the approach of molecule interacts with own species; The doped TBC crystal has been tested using the Nd-YAG laser. Small crystals of Sudan dye doped TBC changed into positioned at the sample holder and the red colour laser beam changed into made to pass through the crystal and the incoming beam passing via the crystal transformed into the green mild. The efficiency of doped TBC a crystal was in comparison with pure. It is observed that the NLO efficiency of pure and Sudan doped TBC are 1.79 and 1.95 respectively The distribution of valence electrons of the steel elements is an essential component that strongly influences the linear and nonlinear characters of every kind of constituent chemical bond.

REFERENCES

[1] D. F. Eaton, "Nonlinear optical materials," *Science (80-.).*, vol. 253, no. 5017, pp. 281–287, 1991.https://www.science.org/doi/abs/10.1126/science.253.5017.281

[2] X. Fan, I. M. White, S. I. Shopova, H. Zhu, J. D. Suter, and Y. Sun, "Sensitive optical biosensors for unlabeled targets: A review," *Anal. Chim. Acta*, vol. 620, no. 1–2, pp. 8–26, 2008.https://www.sciencedirect.com/science/article/pii/S0003267008009343

[3] Q. Wu *et al.*, "RbIO3 and RbIO2F2: Two promising nonlinear optical materials in mid-IR region and influence of partially replacing oxygen with fluorine for improving laser damage threshold," *Chem. Mater.*, vol. 28, no. 5, pp. 1413–1418, 2016.https://pubs.acs.org/doi/abs/10.1021/acs.chemmater.5b04511

[4] D. Fairley, "The relationship of daily mortality to suspended particulates in Santa Clara County, 1980-1986.," *Environ. Health Perspect.*, vol. 89, pp. 159–168, 1990.D. Fairley, "The relationship of daily mortality to suspended particulates in Santa Clara County, 1980-1986.," Environ. Health Perspect., vol. 89, pp. 159–168, 1990.

[5] R. Bartussek, P. Hänggi, and J. G. Kissner, "Periodically rocked thermal ratchets," *EPL (Europhysics Lett.*, vol. 28, no. 7, p. 459, 1994.https://iopscience.iop.org/article/10.1209/0295-5075/28/7/001/meta

[6] J. Wilschut, N. Duzgunes, R. Fraley, and D. Papahadjopoulos, "Studies on the mechanism of membrane fusion: kinetics of calcium ion induced fusion of phosphatidylserine vesicles followed by a new assay for mixing of aqueous vesicle contents," *Biochemistry*, vol. 19, no. 26,

pp. 6011–6021, 1980.https://pubs.acs.org/doi/pdf/10.1021/bi00567a011

[7] X. Gu, X. Yu, K. Guo, L. Chen, D. Wang, and D. Yang, "Seed-assisted cast quasi-single crystalline silicon for photovoltaic application: Towards high efficiency and low cost silicon solar cells," *Sol. Energy Mater. Sol. Cells*, vol. 101, pp. 95–101, 2012.https://www.sciencedirect.com/science/article/pii/S0927024812000980

[8] U. Gottlieb, A. Sulpice, B. Lambert-Andron, and O. Laborde, "Magnetic properties of single crystalline Mn4Si7," *J. Alloys Compd.*, vol. 361, no. 1–2, pp. 13–18, 2003.https://www.hindawi.com/journals/jnm/2018/7547295/

[9] Y. Xue and M. A. Ratner, "Microscopic study of electrical transport through individual molecules with metallic contacts. I. Band lineup, voltage drop, and high-field transport," *Phys. Rev. B*, vol. 68, no. 11, p. 115406, 2003.https://journals.aps.org/prb/abstract/10.1103/PhysRevB.68.115406

[10] C. Andraud *et al.*, "Biscyanine dye with Shiff base as new chirooptical materials," *Mater. Lett.*, vol. 57, no. 9–10, pp. 1489–1495, 2003.https://www.sciencedirect.com/science/article/pii/S0167577X02010121