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# Crystal Growth and Spectroscopic Studies of Marine Dye Nlo Material: 4-Amino-3, 6-Bis[[4-[[4-Chloro-6-[(3-Sulfophenyl)Amino]-1, 3, 5-Triazin-2-Yl]Amino]-2-Sulfophenyl]Azo]-5-Hydroxy-2, 7-Naphthalenedisulfonic Acid Hexasodium Salt (Reactive Green -19) Crystals

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**Abstract**

The marine compound 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt as a marine dye was synthesized by taking and 4-amino-3, 6-bis((4-((4-chloro-6-((3-sulfophenyl)amino)-1, 3, 5-triazin-2-yl)amino)-2-sulfophenyl)azo)-5-hydroxy-, and hexasodium salt reacted with -2, 7-Naphthalenedisulfonic acid, are used to synthesized marine dye like hexasodium salt reactive green-19 Dyes ($C_{40}H_{23}Cl_2N_{15}O_{19}S_6 \cdot {}_6Na$ ). It is soluble in water. The crystals of 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonicacid hexasodium salt have been grown by diluting the substances with slow evaporation technique. The grown crystals were characterized by powder crystal X-ray diffraction (XRD) analysis, FTIR studies and UV-visible transmittance studies and the NLO activity of the grown crystal have been identified by Second Harmonic Generation (SHG) test.

**Keywords:** Green HE4BD Or Reactive Green-19; solubility; solution growth; FTIR; UV; XRD; SEM; SHG.

## Introduction

Nonlinear optical (NLO) materials have gained considerable attention due to their practical applications in the field of optoelectronics (1, 2). The development of NLO materials led to compounds potentially suitable for application in frequency conversion, optical telecommunication, image processing, optical computing, and data storage devices(3-6) disulfonic acid family-type crystals have over the years have been subjected to extensive investigation by the researchers for their non-linear optical properties(7, 8). Among the disulfonic acid, phenyl is the simplest molecule with second harmonic generation efficiency of about one-third of that of the well known KDP (9, 10), it is expected to get improved NLO properties. Keeping this in mind, the phenyl mixtures have been mixed to form a novel NLO material. 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt reported the details of crystal structure of Reactive Green-19 Dyes and it is observed from the various properties of crystals report. Hence the aim of this paper is to report the growth, spectroscopic studies and NLO activity of Reactive Green -19 crystals for the first time.

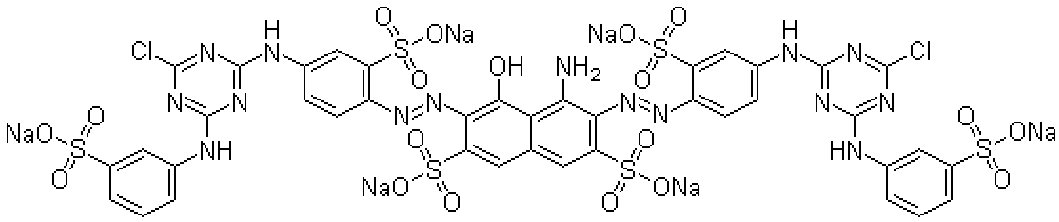

**Figure 1:** Structure of 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt (Green HE4BD or Reactive Green-19)

## Experimental Methods

### Growth of Reactive Green -19 Dyes Powder Crystals

The purity of the synthesized salt of 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt (Reactive Green -19) has been improved by re-crystallization. Using the solubility data, the saturated solution of 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt in deionized water was prepared and it was stirred using a magnetic stirrer for about one hour to get homogeneous solution.

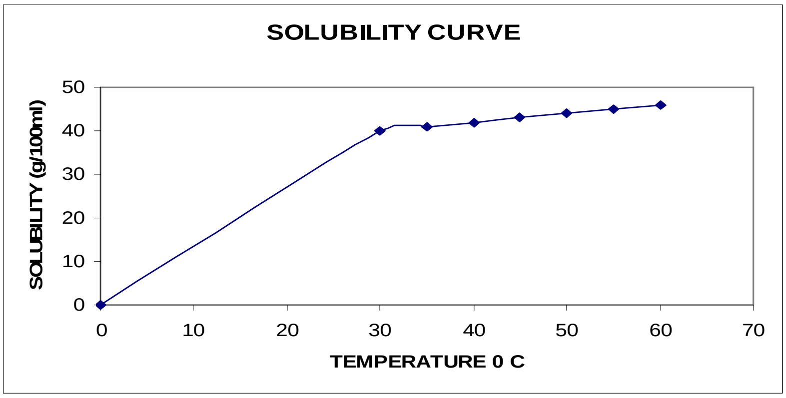


**Figure 2:** Solubility curve for GREEN HE4BD crystal

The saturated solution was filtered using 4 micro Whatmann filter paper. Then the filtered solution was taken in a beaker and covered by a perforated cover for controlled evaporation. A typical single crystal with size 13 x 12 x 6 $mm^3$ was obtained within a period of 20-25 days. The grown crystal is shown in the Figure 3.

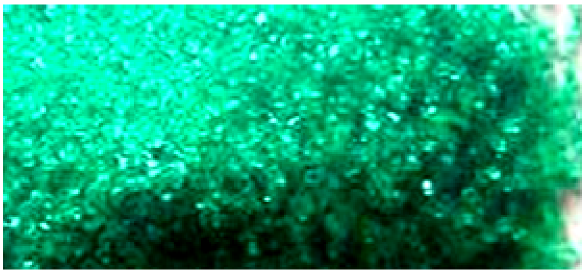

**Figure 3:** Photograph of as-grown crystal of GREEN HE4BD

**Characterization Powder crystal XRD studies**

The grown crystals were subjected to Powder crystal XRD to confirm the crystallinity and also to estimate the lattice parameters by employing Bruker-Nonious MACH3/CAD4 powder X-ray diffractometer. From crystal X-ray diffraction data, it is observed that the 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium (Reactive Green-19) crystal is green monoclinic crystal in structure with space group P212121. The lattice parameters are observed to be a=8.258(2) Å, b=9.931(1) Å, c=6.614(3) Å, α=β=γ=90° and V =112(2) Å3. The obtained lattice parameters for 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt (Reactive Green-19) crystal in this work are found to be in good structure. The peaks in the fig show the crystalline nature of Reactive Green-19. Further the peaks are indexed. This is shown in Figure 4.

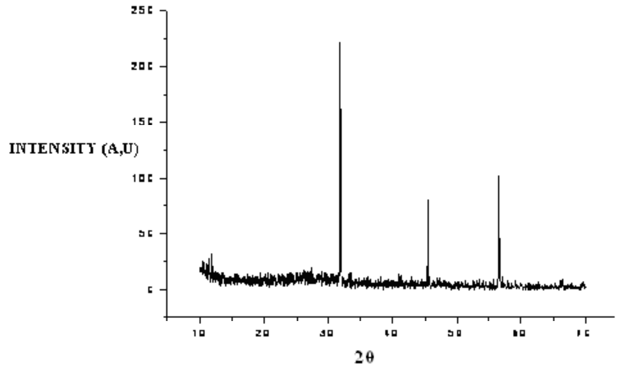


**Figure 4:** XRD patterns recorded from Reactive Green -19 crystal

## FTIR analysis

The Fourier Transform Infrared (FTIR) spectrum of GREEN HE4BD crystal was recorded in the region 400 - 4000 cm-1 using FTIR SHIMADZU 8400S. Amide functional group appeared at 3417.84 $cm^{-1}$ with sharp absorption and also giving C=O stretching absorption at 1576 $cm^{-1}$. It was further confirmed by observing C=O overtone absorption appeared at 3944.03 $cm^{-1}$ and 3825.35 $cm^{-1}$. The strong absorption at 1135 $cm^{-1}$ was assigned to C-O group due to its stretching vibrations. The strong absorption at 1047.47 $cm^{-1}$ confirms the presence of $SO_3$-Na substitution groups along with the group. Also, strong absorption at 1485.15 $cm^{-1}$ was due to bending absorption of alkyl group. And also C-Cl stretching vibrations was confirms at 633.38 $cm^{-1.}$ The sample was prepared by mixing 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt (Reactive Green-19) with KBr into pellet form. The observed spectrum is shown in the Figure 5.And the absorptions were summarized in table-1.

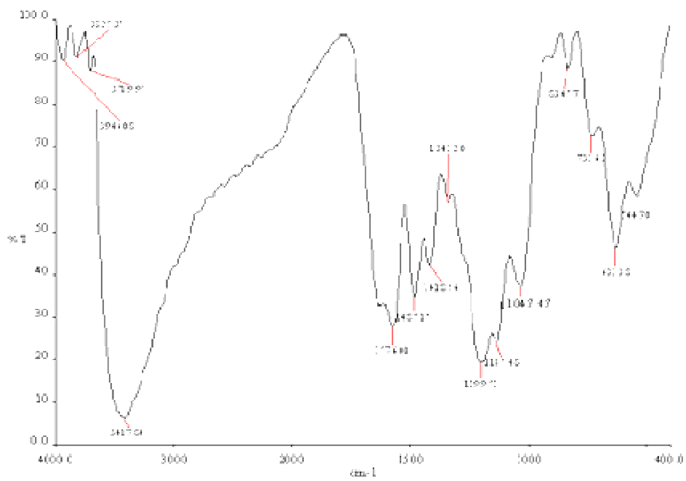


**Figure 5:** FTIR spectrum of Reactive Green -19

**Table 1:** Frequencies of the fundamental vibrations of GPC

| S.No. | Frequency in wavelength (in $cm^{-1}$) | Assignment of vibration |
|---|---|---|
| 1 | 3944.03 and 3825.35 | C=O Overtone absorption |
| 2 | 3417.84 | -NH stretching vibration |
| 3 | 1576 | COO asym. Stretching |
| 4 | 1485.15 | $sp^3$ alkyl bending |
| 5 | 1418.26 | $Sp^3$ sym. Strectching |
| 6 | 1135.48 | C-O stretching |
| 7 | 1047.47 | $C\text{-}SO^3$ |
| 8 | 633.38 | C-Cl stretching |

**Optical transmission spectral analysis**

The UV-Visible transmittance spectrum (Fig.6) of Reactive Green-19 crystal was recorded in the wavelength range 200-1200 nm, using Lambda 35 spectrometer. Optically polished powder crystal of thickness 1.3 mm was used for this study. This spectral study may be assisted in understanding electronic structure of the optical band gap of the crystal. The study of the absorption edge is essential in connection with the theory of electronic structure, which leads to the prediction of whether the band structure is affected near the band extreme. The peak appeared at 380 nm and 600 nm corresponding to the phenyl moiety. The UV-Visible transmittance spectrum shown in Figure.6.

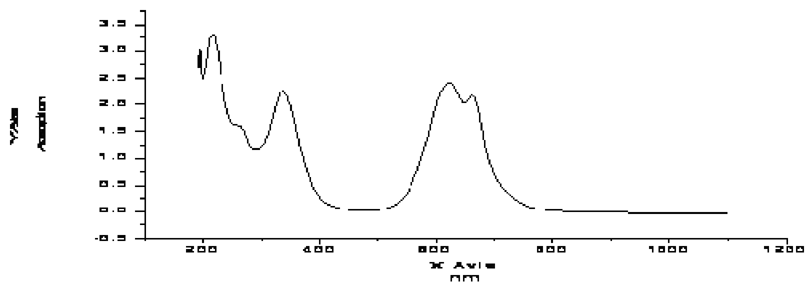

**Figure 6:** UV-Visible transmittance spectrum for Reactive Green-19 crystal

**Crystal Surface Analysis by SEM**

Surface analysis of 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt is carried out through Scanning Electron Microscopy. The magnification 500 times has been studied for this crystal. The maximum magnification studied in the equipment is 3, 00, 000 times with a resolution of 3 nm. The surface of the crystal was coated with gold to make the sample conducting. From the Figure.7, it is clear that the size of the crystals is 100 microns thick. Further the surface is very smooth without any defects.

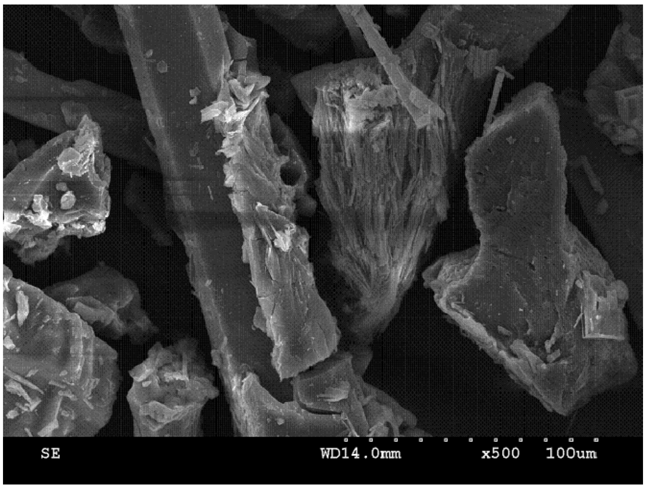


**Figure 7:** SEM Analysis 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt

## Second Harmonic Generation (SHG) test

The Nonlinear Optical (NLO) property of the grown crystal was confirmed by Kurtz-Perry powder technique14. The 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt (Reactive Green-19) crystal was powdered with uniform particle size using a ball mill and it was packed densely between two transparent glass slides. An Nd:YAG laser was used as a light source. This laser device can be operated in two different modes. In the single-shot mode, the laser emits an 8 ns pulse. While in the multi-shot mode, the laser produces a continuous train of 8 ns pulse at a repetition rate of 10 Hz. In the present study, a multishot mode of 8 ns laser pulse with a spot radius of 1mm was used. The experimental setup for measuring SHG efficiency is shown in the Figure 8.A fundamental laser beam of 1064 nm wavelength, 8 ns pulse with 10 Hz pulse rate was made to fall normally on the sample cell(S). The power of the incident beam was measured using a power meter. The filter F1 removes the 1064 nm light and the filter F2 is a BG-38 filter, which also removes the residual 1064 nm light. F3 is an interference filter with bandwidth of 4 nm and central wavelength 532 nm.The green light was detected by a photomultiplier tube (PMT) and displayed on a Cathode Ray Oscilloscope(CRO). KDP crystal was powdered into identical size as 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt (Reactive Green-19) crystal and it was used as reference material in the SHG measurement. In the NLO process that taking place in the sample, it converts the 1064 nm radiation into green light ($\lambda$=532 nm) when Nd:YAG laser light is passed into the sample and this confirms the SHG . It was found that the efficiency of SHG is 0.76 times that of the standard KDP.

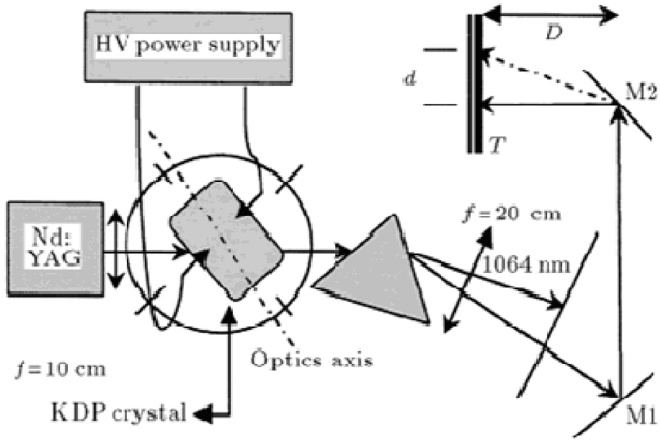


**Figure 8:** Experimental setup for SHG measurement

## Conclusion

4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt (Reactive Green-19) salt was synthesized and solubility was determined at various temperatures. Bulk powder crystals of 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium (Reactive Green-19) salt was grown by solution method. It is observed that the grown crystal is transparent, coloured and has good morphological edges. Powder crystal X-ray analysis reveals that the crystal belongs to orthorhombic system with space group P212121. The grown crystals were subjected to SEM analysis. The functional groups present in 4-amino-3, 6-bis[[4-[[4-chloro-6-[(3-sulfophenyl)amino]-1, 3, 5-triazin-2-yl]amino]-2-sulfophenyl]azo]-5-hydroxy-2, 7-naphthalenedisulfonic acid hexasodium salt (Reactive Green-19) crystal are confirmed by the FTIR spectral analysis. The optical absorption study reveals high transparency of the crystal with a UV cut off wavelength of 380 nm and 600 nm. The NLO efficiency of the crystal is found to be 1.02 times that of KDP.

## Acknowledgement

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