MUSLIM ARTS COLLEGE

ISO 9001:2008 CERTIFIED

(Affiliated to Manonmaniam Sundaranar University, Tirunelveli)
Azhagiamandapam, Thiruvithancode - 629 174, Kanyakumari District, Tamilnadu.
Ph: 04651 248842, 248841, 248803 e-mail : muslimartscollege@gmail.com

ISO 9001 : 2008
Reg.No: RQ91/3688

DEPARTMENT OF PHYSICS & RESEARCH CENTRE
NATIONAL SEMINAR ON
FUNCTIONAL MATERIALS AND ITS APPLICATIONS

CERTIFICATE

This is to certify that Mr./Ms./Dr./Prof. ....Dr. D. Shalini..... Asst. prof..... affiliated to .....Muslim Arts College..... has ~~participated~~/ presented paper in National Seminar On Functional Materials And Its Applications (NSFMA –2022), organized by the Department of Physics & Research Centre on 14th October 2022 at Muslim Arts College, Thiruvithancode, Kanyakumari District.

Lion Dr. H. Mohamed Ali
Secretary / Correspondent

Dr. G. Edwin Sheela
Principal

Dr. J.R. Sheeba
Convener

PROCEEDINGS OF NATIONAL SEMINAR ON

FUNCTIONAL MATERIALS AND ITS APPLICATIONS

(NSFMA–2022)

EDITED BY

Dr. J.R.Sheeba
Dr. A. Iren Sobia

14th OCTOBER, 2022

DEPARTMENT OF PHYSICS
&
RESEARCH CENTR

MUSLIM ARTS COLLEGE
Thiruvithancode - 629174
Kanyakumari District
Tamil Nadu, India

The author of the book is fully responsible for the facts and figures presented in this book.

Further it is stated that the publisher is not responsible for the statements or opinions expressed by the author of the book.

ISBN 978-93-84737-37-5

Published by

Raj Pathippakam,
3E, North Street,
Kurusady,
Nagercoil - 4

Synthesis, Growth and Optical Characterization of Organic NIo Single Crystal: 4-Methylpyridinium 5-Sulfosalicylate

D.Shalini

Assistant professor, Department of Physics, Muslim Arts College, Thiruvithancode.

Abstract

A nonlinear optical material 4-methylpyridinium5-sulfosalicylate has been successfully synthesized by slow solvent evaporation method. The single crystal XRD analysis indicated monoclinic system with space group P2₁/m. The presence of various functional groups in the crystal was confirmed by FT-IR spectral analysis. The UV-Visible spectral analysis shows lower cut-off wavelength for the grown crystal was found to be 349 nm. The grown 4MSS crystal possesses an excellent resistance to laser radiation with a high threshold up to 5.09 GW/cm². The third order nonlinear optical properties of the grown crystals were investigated using Z-scan technique.

Key words: Monoclinic; laser radiation; optical; spectral.

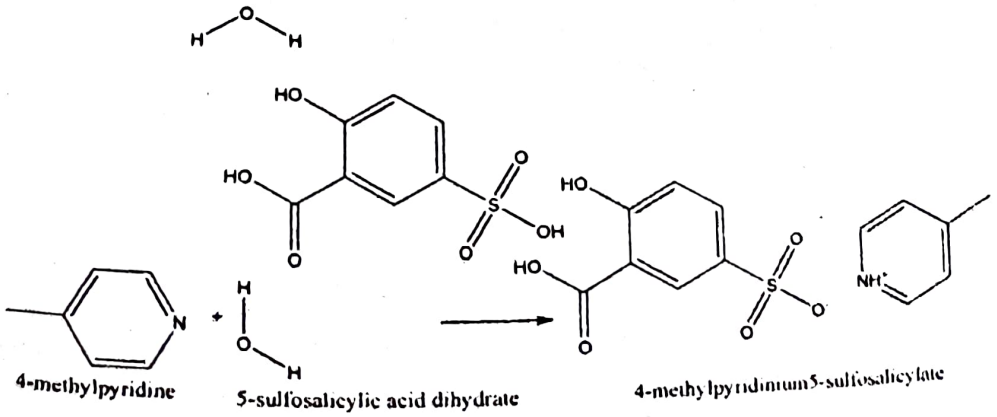
Introduction

The aromatic and hetero aromatic Lewis base salts have an extra potential for structure stabilization through cation-anion interactions. The resultant hydrogen bonding structure is largely dependent on the degree of amine substitution. The proton-transfer compounds of 5-sulfosalicylic acid (3-carboxy-4-hydroxybenzenesulfonic acid) with three interactive functional groups have attracted the specific attention of several researchers for a long time due to their overwhelming practical applications in crystal engineering. In this work, 5-sulfosalicylic acid acts as an electron acceptor and 4-methylpyridine acts as an electron donor.

1.2 Experimental Procedure

1.2.1 Synthesis and Crystal Growth

Commercially available starting materials, 4-Methylpyridine (Sigma-Aldrich, 99%) and 5-Sulfosalicylic acid dihydrate (Loba Chemie, 99%), were dissolved in 100 ml of distilled water. The clear 4MSS solution was obtained after a continuous stirring for about six hours to achieve the homogeneous mixture of the solution. Then, the solution was kept in the constant temperature bath at 39°C with an accuracy of ±0.01°C. The synthesized compound was further purified by successive recrystallization process in water, and it was utilized for the crystal growth. The reaction scheme of the 4MSS compound is shown in Fig 1.1. The well defined 4MSS single crystals with good transparency as shown in Fig 1.2.



$$CH_3C_5H_4N + C_7H_6O_6S \longrightarrow CH_3C_5H_4N^+ . C_7H_6O_3SO_3^-$$

Fig 1.1 Reaction scheme of 4MSS

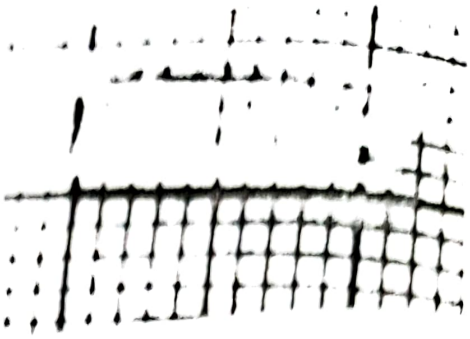


Fig 1.2 As grown crystal of 4MSS

1.3 Single Crystal X-Ray Diffraction Studies

Single crystal X-ray diffraction analysis was carried out to determine the lattice parameters. The single crystal XRD reveals that the crystal belongs to the monoclinic system. The cell parameters are a= 7.07 Å, b= 13.45 Å, c= 15.57 Å, α=90.00°, β=95.11°, γ= 90.00°, with the cell volume of V=1476 Å^3 monoclinic system with space group $P2_1/m$.

1.4 FT-IR analysis

The FT-IR spectrum of 4MSS was recorded in the region 400-4000 cm^{-1} as shown in Fig 1. 4. In 4MSS, there was a formation of strong hydrogen bond between 4-methylpyridine and 5-sulfosalicylic acid. The single crystal structures are reflected in the highly mixed bands of the C-O stretching vibration, N-H$^+$ together with SO_3^- vibrations. The presence of such groups may indicate an existence of great potential to enhance the corresponding optical susceptibilities by application of an external dc-electric field. The N-H$^+$ stretching vibration was observed at 3346 cm^{-1}. The peak was observed at 786 cm^{-1} due to S-O stretching vibration. The bands at 3096 cm^{-1} and 1669 cm^{-1} were assigned to aromatic C-H stretching vibration and C=O stretching vibration of sulfosalicylate compound. The band was observed at 1467 cm^{-1} is due to C=C stretching vibration of an aromatic ring.

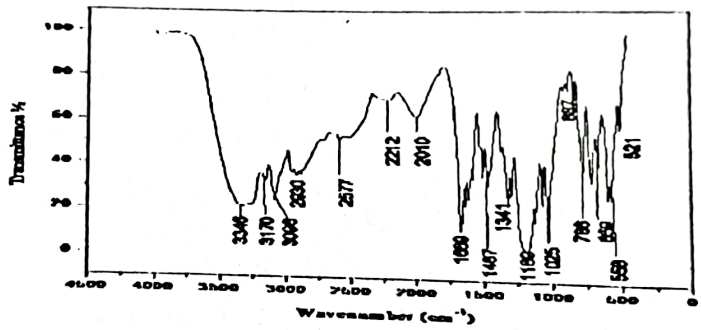


Fig 1.4 FT-IR spectrum of 4MSS compound

1.5 UV-Visible-NIR spectral analysis

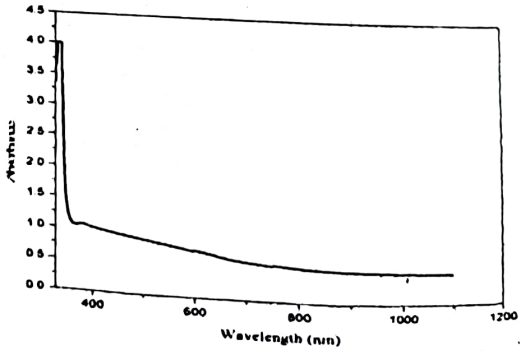


Fig 1.4 UV-Vis-NIR spectrum of 4MSS crystal

The lower cut-off wavelength for the grown crystal was found to be 349 nm, assignable to charge-transfer transition in the [SO_3^-_NH^+] chromophores and intraligand π-π* transition. There is no absorption between 349-900 nm, which indicates that the 4MSS crystal is suitable for nonlinear optical applications.

1.6 Laser Damage Threshold Studies

The laser damage threshold of the grown crystals can be evaluated by the following equation

Power density (d) $= E/\tau\pi r^2$

Where, E is the energy (mJ), τ is the pulse width (ns) and $A = \pi r^2$ is the area of the circular spot size, r is the radius of spot (mm). It was found to be 6.09 GW/cm^2.

1.7 Z-scan technique

Fig 4.13 & 4.14 shows the measurement of open and closed aperture Z-scan curves for 4MSS crystal. The transmittance peak is followed by the transmittance valley, indicating a strong self-defocusing process and negative sign for non-linear refraction. For open aperture Z-scan curve the transmittance will be minimum in case of two-photon absorption and maximum for saturable absorption. The open aperture z-scan curve shows that the 4MSS crystal has two-photon absorption.

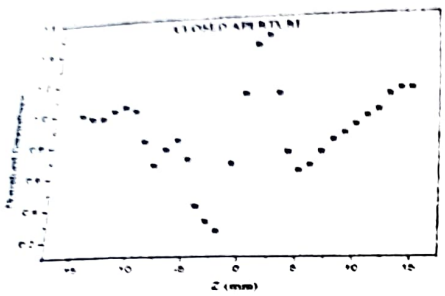


Fig 1.5 Closed aperture of 4MSS crystal

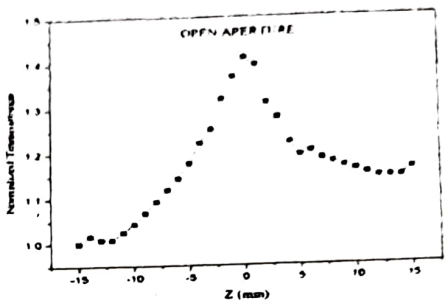


Fig 1.6 Open aperture of 4MSS crystal

The calculated values of the third-order nonlinear optical parameters are listed in Table 1.1

Table.1.1. Measurement and the results of the Z-scan technique

Nonlinear refractive index (n_2)	2.9100×10^{-11} (cm^2/w)
Nonlinear absorption coefficient (β)	3.7028×10^{-17} (cm^2/w)
Third order susceptibility ($\chi^{(3)}$)	$5.0182\times 10^{-9} esu$

Conclusion:

The single crystal XRD analysis indicated monoclinic system with space group $P2_1/m$. The presence of various functional groups in the crystal was confirmed by FT-IR spectral analysis. The UV-Visible spectral analysis shows lower cut-off wavelength for the grown crystal was found to be 349 nm. The grown 4MSS crystal possesses an excellent resistance to laser radiation with a high threshold up to 5.09 GW/cm^2.The third order nonlinear optical properties of the grown crystals were investigated using Z-scan technique.

References:

Sai-Rong Fan, Long-Guan Zhu, (2007), Journal of Molecular Structure 827, 188–194.

Zhen-Huan Li and Kun-Mei Su, (2007). Acta Cryst, E63, o4744.

Wiesbrock F, Schmidbaur H, (2003), Inorg. Chem. 42, 7283–7289.

Marzotto A, Augusto D et al, Polyhedron 20 (2001) 1079–1087.

Bruker APEX2, SAINT, XPREP and SADABS. Bruker AXS, (2004), Inc., Madison, Wisconsin, USA.

Sheldrick G.M, (1997), SHELXS97 and SHELXL97. University of Gottingen Germany.