STRUCTURAL, OPTICAL, MECHANICAL AND ELECTRICAL PROPERTIES OF ORGANIC SINGLE CRYSTAL: 4-N, N-DIETHYLAMINO-4-N-METHYL-STILBAZOLIUM IODIDE (DESI)

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Abstract: ***Organic stilbazolium family single crystal 4-N, N-diethylamino-4-N-methyl-stilbazolium Iodide (DESI) has been successfully grown from aqueous methanol solution by adopting slow solvent evaporation technique. Single crystal X-ray diffraction analysis was carried out and it shows that DESI crystal belongs to triclinic structure with P-1 space group. Its absorption spectrum was found by UV-Vis spectrum. Hardness study was also carried out for applying different loads. Dielectric studies were also carried out for different temperature by varying the frequency.***

Keywords: Organic compound; X-ray diffraction; Hardness study; Optical absorption; dielectric study

INTRODUCTION

The design and synthesis of organic materials for high second order nonlinear optical effect has become an important research area due to their potential and wide applications in the fields of optical signal processing, integrated photonics, optical switching, optical data storage, bioimaging, electro-optic modulation, spectroscopy and THz wave generation and detection. Further, the presence of styryl pyridinium compounds is being mainly used as antibacterial drugs, herbicides, environmental disinfection, disinfection in hospital environments and food industry due to their low toxicity to humans and animals. Hence, the efforts have been made to engineer the novel π-conjugated organic molecules because of their second and third-order nonlinear optical activities. Ionic organic crystals with high chromophore density are of special interest for large NLO effect [1-3]. The stable packing of chromophores in these crystals results in high thermal, mechanical and photochemical stability. The design of NLO chromophore crystals has an electron withdrawing group that bear an electron donating group interacting through the π-conjugated system with parallel alignment in the crystal structure. The formation of the carbon-carbon bridge (C=C) with π-conjugation chromospheres of an organic molecule can be obtained by Knoevenagel condensation reaction. This method is most favorable and easy method for to form a carbon–carbon double bond. By engineering the organic chromophore many crystals has been grown, among that one such material is 4-N, N-diethylamino-4-N-methyl-stilbazolium iodide (DESI). This single crystal has been grown by adopting slow evaporation solution growth technique. In this article, we report the Structural, optical and mechanical properties of the title compound.

SYNTHESIS AND CRYSTAL GROWTH

DESI was synthesized by employing, the condensation of 1,4 dimethylpyridinium iodide and 4-N-N-diethylamino-benzaldehyde in the presence of piperidine. The resultant material was kept in an oven, and the temperature was maintained around 100 °C for 1 h. Afterwards, the DESI was purified by successive recrystallization from methanol. In a 250 ml beaker 2g of the DESI was dissolved in methanol. After getting the homogeneous solution it is sealed with appropriated cover and kept in the temperature bath. The growth temperature was maintained at 35 °C after a period of 10-15 days the crystals were harvested shown in Fig 1.

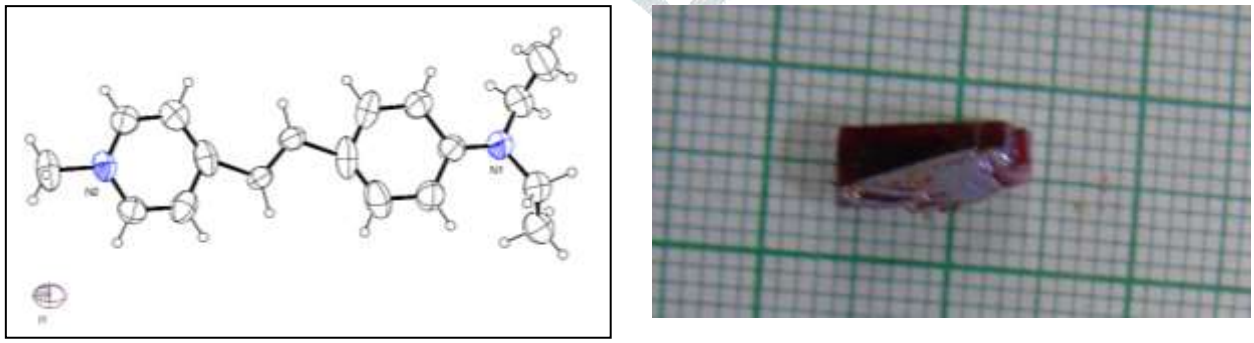

Figure 1 Ortep diagram and Photograph of DESI crystal

RESULTS AND DISCUSSION

SINGLE CRYSTAL X-RAY DIFFRACTION ANALYSIS

The grown crystal was subjected to single crystal X-ray diffraction studies using Bruker Kappa APEXII single crystal X-ray diffractometer with MoK_α radiation (λ = 0.7170 Å) to solve the structure. The XRD data indicates that the crystal is t*riclinic* structure and it belongs to centrosymmetric space group P-1. The calculated lattice parameters of grown DESI crystals are Unit cell dimensions a = 7.8203(7) Å, b = 15.3176(15) Å, c = 17.1742(17) Å, α= 75.323(3)°., β= 87.401(3)°. γ = 89.396(3)°. Volume 1988.1(3) $Å^3$

OPTICAL ABSORPTION SPECTRAL ANALYSIS

The absorption spectra of the DESI crystal recorded in the solid phase as well as in solution phase (methanol) are shown in Figure 2. It is observed that absorption spectrum of bulk crystalline DESI has a single strong absorbance band below 552 nm; which is due to J-type organization of chromophores within the crystalline structure of DESI. The absorption spectrum of DESI in methanol is different from that of crystalline form which shows two distinct absorption peaks. The minor peak at 271 nm corresponds to the n-π* transition and the major peak with maximum absorption at around 487 nm represents the π-π*. The major absorption peak of the title compound in the visible region is good agreement with the stilbazolium chromophore with the unsaturated bond. Absence of absorption in the region between 487 and 800 nm for this crystal suggests it is an essential requirement for optoelectronics applications.

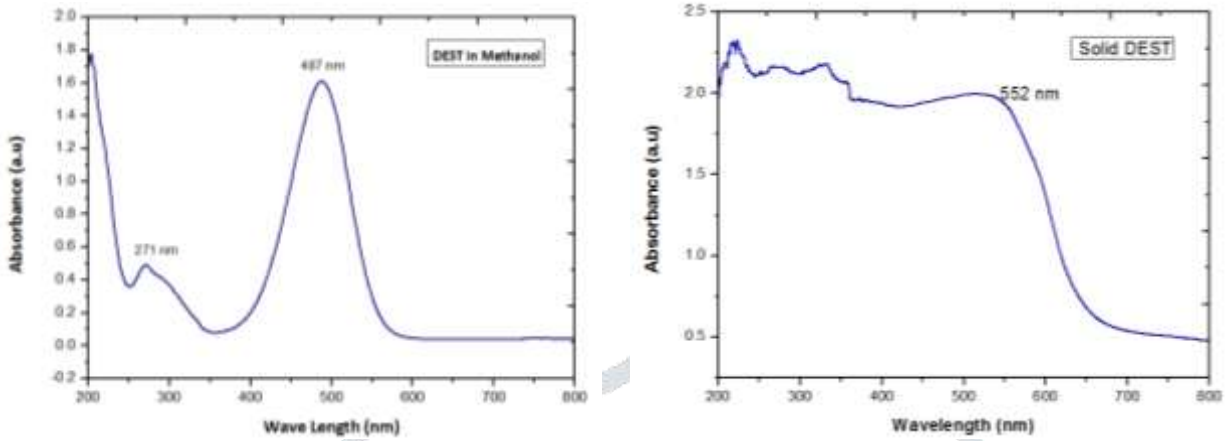

Fig 2 Absorption spectrum of DESI single crystal

MICROHARDNESS STUDY

Mechanical strength of the materials plays a key role in device fabrication. During an indentation process, the external work applied by the indentor is converted to a strain energy component which is proportional to the volume of the resultant impression. The hardness of a material is influenced by various parameters such as the lattice energy, Debye temperature, heat formation and inter atomic spacing. The Vickers hardness indentations were made on the as grown crystal of DESI. At room temperature, the load was varied as 10, 25, 50 and 100 grams for the slow evaporation grown DESI crystal. The Vickers hardness number (H_v) was calculated using the relation,

$$H_v = 1.8544\ (p/d^2)\ \ kg/mm^2$$

Where, p is applied load and d is diagonal length of the indentations. The variations of H_v with the applied load p are shown in Figure 3a for grown crystal of DESI. The plot between log p vs log d for the crystals are shown in Figure 3b and it yields a straight line. The slope gives the work hardening index 'n', which is found to be 10 for grown sample. The microhardness study indicates that the crystal belongs to the class of soft materials. If n <2, H_v decreases with increasing load (reverse indentation type), whereas for n>2, H_v increases with load [5].

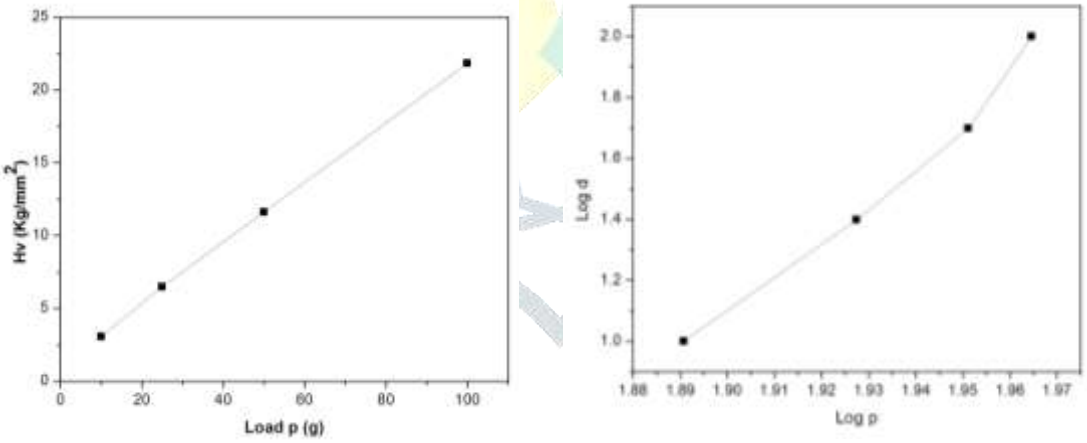

Fig. 3a. Variation of Hv (Vickers hardness) with load (P) and 3b. Graph between log p vs log d

DIELECTRIC STUDIES

Dielectric permittivity measurements were carried out for DESI crystals. The sample was silver coated and then placed inside a dielectric cell and the capacitance measurements were done for temperature at 40, 50, 75, 100, 125 and 150 ^oC in the frequency range 50 Hz to 7 MHz. Figure 4 of log dielectric constant ε′ as a function of log frequency and the plot of dielectric loss (D) as a function of log frequency for grown DEST crystals. It is observed that both dielectric constant and dielectric loss exhibits similar variation with frequency. The graphs show that the dielectric constant and the dielectric loss are both inversely proportional to frequency. This is a normal dielectric behaviour that both ε′ and D decrease with increasing frequency. This can be understood on the basis that the mechanism of polarization is similar to that of conduction process. Further, the dielectric constant value of DESI sample is found to increase with increasing temperature. In DESI, as temperature increases it normally becomes more ionic in nature.

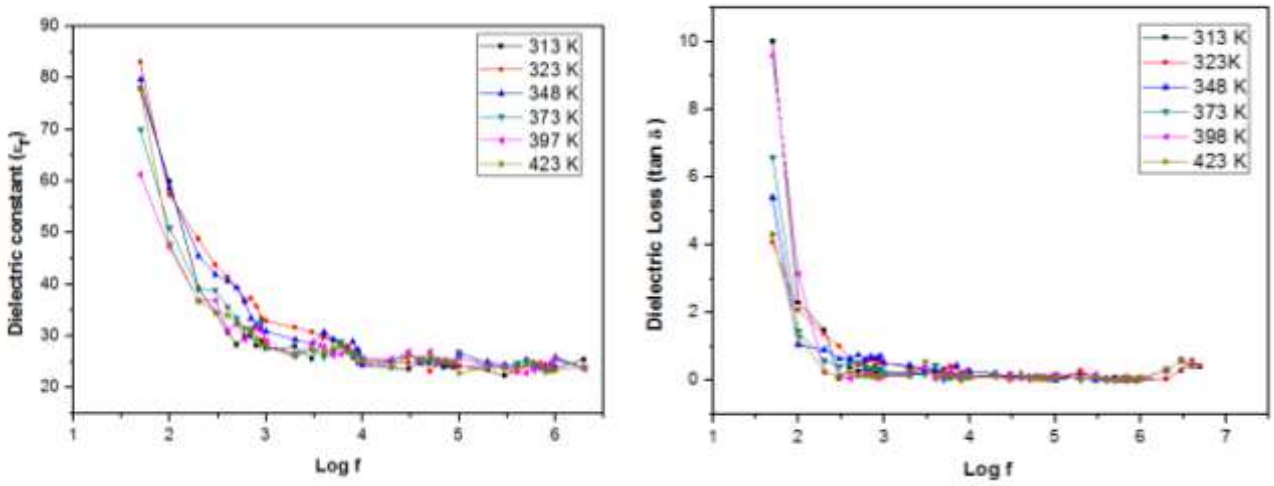

Figure 4 Dielectric constant and Dielectric loss measurement as the function of frequency

CONCLUSION

Organic stilbazolium family single DESI has been successfully grown from aqueous methanol solution by adopting slow solvent evaporation technique. Single crystal X-ray diffraction analysis was carried out and it shows that DESI crystal belongs to triclinic structure with P-1 space group. Its absorption spectrum was found by UV-Vis spectrum. Hardness study was also carried out for applying different loads and its found that the material belongs to soft material.

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